Suggested Design Projects – 2022-2023

1.   Bio-MEG, Monoethylene Glycol
(Recommended by Leonard Fabiano, Adjunct Professor, Penn)

Background

A recent AIChE SMART BRIEF, April 2022, described a renewed interest in commercialization plans and projects to produce MEG via a bio-based source.

"Petrochemical company Braskem and Japanese trading company Sojitz say they'll work together to produce bio-monoethylene glycol, which is largely used in packaging, and bio-monopropylene glycol, commonly used in polymer resins and cosmetics. The partnership will include the construction of three industrial plants, with the first potentially starting production in 2025." The details of their process were not disclosed.

Companies such as Nestlé, PepsiCo, Unilever, and Coca-Cola that use PET for packaging materials that are derived from terephthalic acid and MEG that essentially depend on petroleum-based feedstocks see the need to transition to renewable feedstocks. However, the only currently operating biobased MEG plant in India does not produce the product at a competitive cost with conventional processes.

For background information the chart below describes the alternatives that have been used to produce MEG:
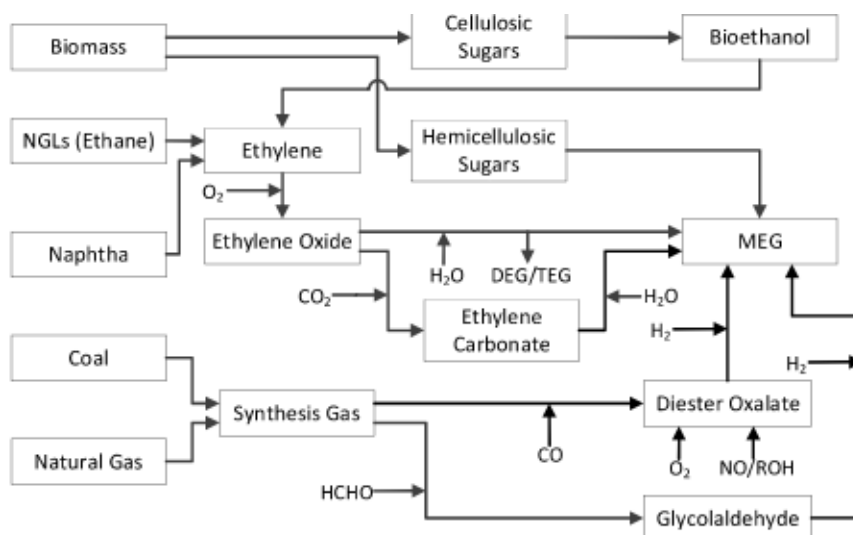
Several generations of process development using bio-based concepts have been proposed over many years dating back to the 1970s. The "fourth generation" process proposed by Aventium appears to have made progress towards cost justification to compete with other bio-based and other conventional processes. This organization was formed in 2000 by Shell Oil Corporation after their development efforts and many granted patents. The aim by Shell was to form an organization that can concentrate on the further development and commercialization of this technology.

The patents are:
Aventium patents US 10,131,600 and US 10,294,180 and US 11,059,768, and Shell's patent US 10,654,782 all address catalysts.

Reduction of byproduct patent US 10,233,138
US 9,656,933 and US 10,450,249 from Shell addresses fouling in reactor piping
Continuous loop reactor concept and run information US 10,294,181
Continuous process concept US 11,008,269
Patents that provide information on separations of difficult to separate close boiling side products US 10,294,180, US 8,906,205
Improving selectivity US 9,440,897

Your management of "Sustainable Technology, Inc." needs your team to evaluate the Aventium technology for consideration for future capital investment. Your evaluation will consider a 400 Kta MEG production capacity that seeks the 15 % minimum IRR over 15 years. What licensing fee can your company afford and still meet our capital recovery and profit margins?

Your feedstock is glucose syrup which is produced on a large scale by several US firms and overseas companies. There are five manufacturers in the U.S.: Archer Daniels Midland Inc., Corn Products International, Cargill, Roquette America, and Tate & Lyle.

2. Biomethane by Green Sourcing
(Recommended by Rick Bockrath, Consultant – retired from DuPont)

Background

It is clear from recent geopolitical events in the Ukraine, electrical shortages in Europe and Texas due to inconsistent winds, dramatic price increases for lithium for batteries, etc. that the transition to a sustainable future will be complicated and lengthy. No one technology has emerged as the dominant energy source for the future. It will likely take a large mixture of solutions to satisfy all of the world's power needs. Solutions that can make use of existing infrastructure such as pipelines, electrical grids, etc. will play a key role over the next 30 years.

Problem Statement

You are a Senior Vice-President at a major green electrical energy provider. Your energy supply is sourced from hydropower, solar cells and wind turbines. You have been chartered by the Company's Board to develop a plan to ensure full utilization of the power being generated by your sources. You know only too well that each of these sources has problems with seasonality, high variability in output and daytime versus night-time issues. As a result, you sell far less electricity than you are capable of generating in the course of a day or a year.

You have created a Scientific Advisory Board to propose various technology options. Your organization will perform technical and economic analyses on the most promising candidates. The only boundary condition that you have given the Board is that the final product must enter a large supply chain so that there is constant high demand for the product. The concept is that your electricity is converted via some technology into an easily sold product. The easily sold product will be sold as a green energy source at a premium. One concept that the Board has proposed is based on scouting work at the University of South Carolina (ref. 1, 2 and 3).

The basic product chemistry is the methanation of CO_2 by hydrogen to methane. What is interesting about the article is:

    a) Much lower Ru metal loadings on the novel catalyst
    b) High catalyst productivity
    c) Very high selectivity to product.
    d) Limited catalyst stability testing which shows the catalyst to be stable.

The biggest negative to the article is that the catalyst manufacturing process requires excessive amounts of guanidine carbonate. Therefore, while there is a very large savings in Ru cost for the catalyst, those savings are lost by the high cost for the guanidine carbonate. One of the Board members, who is a catalyst expert, has suggested that the analysis be done using the recipe in ref. 4. In this reference, the guanidine carbonate is replaced by far less expensive urea. This of course is a major assumption. If the analysis looks promising, then this assumption would need to be explored in much more detail. At this point in time, your analysis team is to accept this critical assumption. The Board member suggests the following chemistry for forming the catalyst:

$$2H_3BO_3 + 3CON_2H_4 \implies 1BN + 3CO_2 + 4NH_3$$
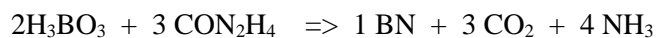
You will quickly realize that this is not a fully balanced equation. There are far fewer hydrogen and oxygen atoms in the proposed products than in the feedstocks. The Board member believes these ions remain in the initially formed catalyst precursor and are driven off during the annealing process. The equation is adequate for determining the kilograms of boric acid and urea feedstocks needed to make a

kilogram of catalytic support, BN. If the analysis is positive; then, upper management may want to approach the owner of the technology to discuss a joint development R&D partnership.

To provide consistency across the various technical and economic analyses that your group will perform, the following assumptions are recommended by the Scientific Advisory Board:

- Electricity should be costed at industrial sales price in the Midwest USA.   Ref. 9 is a good source of information.
- A sensitivity analysis for CO_2 pricing will be needed as part of the analysis. At this point assume that the CO_2 is coming from an ethanol plant in the Midwest and can be acquired at a cost that ranges from $0/ton to a credit of $50/ton (assumes future CO_2 tax).
- The hydrogen will be generated by an electrolyzer.   Ref 5, 6, 7 and 8 provide guidance on costing.
- Your plant is located adjacent to a 100 million gallon ethanol plant.
- Your CO_2 supply will be 25% of the output from the typical 100 million gallon ethanol plant or 75,000 metric tons/yr.
- The BN/Ru catalyst should be costed using the following tool. The tool includes Ru recovery.

https://catcost.chemcatbio.org/

- The methane generated will go directly into an adjacent pipeline. You will need to pressurize the methane to 500 psig.
- Assume that waste hydrogen and carbon monoxide is used as boiler feedstock.
- Assume a catalyst life of 1 year.

The key output of the analysis will be the price of the methane generated. This will need to be compared to the price of commercial methane to see how large a premium in pricing is required to achieve a reasonable return on the investment. Commercial methane pricing can be found in ref 10.

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 20% should be sufficient.

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. You will need to make many assumptions and these need to be fully documented in your analysis.

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3) Supporting Information for above article: "Atomic Ru Immobilized on Porous h BN through Simple Vacuum Filtration for Highly Active and Selective CO_2 Methanation", Mengmeng Fan, Juan D. Jimenez, Sharmila N. Shirodkar, Jingjie Wu*, Shuang ming Chen, Li Song, Michael M. Royko, Junjie Zhang, Hua Guo, Jiewu Cui, Kuichang Zuo, Weipeng Wang, Chenhao Zhang,

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10) https://www.eia.gov/outlooks/steo/data/browser/#/?v=16&f=A&s=0&maptype=0&ctype=linechart

3. Drug Product Production for a Highly Variable Supply Chain (Recommended by Alex Marchut, Wellstat Therapeutics)

Background

Albatol is an oral solid drug product (a tablet) used to treat high blood pressure with a very low side effect profile. It has recently been approved by the FDA (and will soon be approved in the EU and UK as well as several important countries in Southeast Asia) due to this benefit of almost no side effects. However, a number of other medicines for this indication already have a substantial foothold in this market. For this reason, it is very difficult to forecast the demand for this drug product. The current estimate of the global production rate is between 160 million tablets to 1.6 billion tablets per year.

The product is a typical small molecule formulated into tablets in a process that consists of first a high shear granulation of the Active Pharmaceutical Ingredient (API) and excipients, further blending with an additional excipient (magnesium stearate), compression into tablets, and coating of the tablets. The tablets are each 100 mg comprised of 10 mg API and 90 mg of various excipients. The plant you will be designing will be a profit center for a pharmaceutical company. The parent company has assigned your plant a transfer (selling) price of \$0.03/tablet, excluding the cost of the API and excipients. You will estimate the cost of manufacture, NPV and IRR of your plant based on free raw materials, a selling price of \$0.03/tablet, and considering the investment needed to install the facility and the variable and fixed costs to run it. You should calculate these economics over the full range of possible production, so management understands how attractive the plant is at each production rate. The project should include a sensitivity study to determine an appropriate (lower if possible) price per tablet.

Problem Statement

As you have no doubt witnessed in recent years, supply chain shocks can have dramatic effects both when there is too little and when there is too much supply of a consumable good. In order to avoid these effects in the supply chain of Albatol, you have been asked to design a small molecule drug product formulation facility that is capable of producing both 1.6 billion tablets per year and 160 million tablets per year, to run making a decent profit for the investors in both cases (and in any case in between). Batch and continuous operations should be evaluated for every unit operation (except tablet compression which is continuous in all cases) and a recommendation should be made for each unit operation including a rationale for why batch or continuous was selected. Although it may be advantageous to make the facility fully batch or fully continuous, there is no requirement to do this – a hybrid approach with some unit operations continuous and others batch is an acceptable solution. Also note that many sub-batches of granulation may be blended together and compressed to make one batch and that coating of the batch may be carried out either in one large batch or in many smaller sub-batches. Testing including in-process controls, final release testing, and evaluation of traditional methods as compared to Process Analytical Technology (PAT) are considered out of the scope of this project.

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. 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. The facility should be designed so that the operators are safe from hazards like inhaling dust from the powders or explosions from the powders and no waste is released to the environment.

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3. Burcham et al. "Continuous Manufacturing in Pharmaceutical Process Development and Manufacturing," Annual Review of Chemical and Biomolecular Engineering, Volume 9, 2018

4.   Production of Bispecific Antibodies by Functional Arm Exchange
(Recommended by Jeffrey D. Cohen, Janssen R&D)

A bispecific antibody (BsAb) is an artificial antibody that contains two different antigen binding sites and consequently binds to two different antigens [1,2]. BsAbs can bind tumor cell receptors and cytotoxic immune cells at the same time, stimulating an Antibody-dependent cellular cytotoxicity (ADCC) immune response [3].

BsAbs are different from normal monoclonal antibodies (mAb) given the fact that they have dual functionalities. Therefore, BsAbs are in theory superior to conventional mAbs because they offer the benefit of combining two drugs in one molecule. Clinical development of BsAb is currently focusing on cancer therapy, inflammatory and autoimmune diseases, such as rheumatoid arthritis, systemic lupus erythematosus, and psoriasis. The goal of these efforts is to simultaneously target various multiple targets involved in disease pathways and thereby increase therapeutic efficacy.
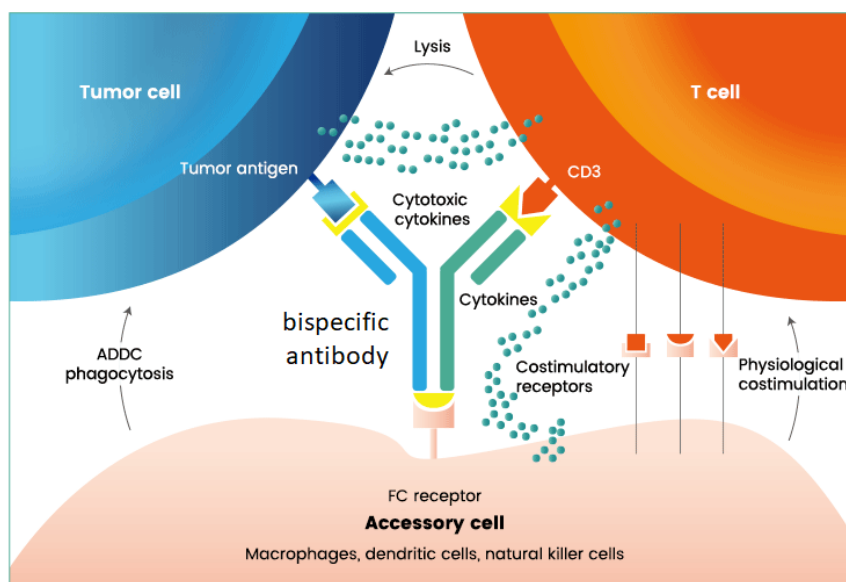

Figure 1. Bispecific antibody mechanism of action
https://www.sinobiological.com/resource/antibody-technical/bispecific-antibody

One method of producing BsAbs is to employ Functional Arm Exchange (FAE) [4] within a solution of two species of parental mAbs, e.g., a solution of mAb-A + mAb-B. FAE is performed by:
1. combining mAb-A + mAb-B in solution
2. chemically lysing the disulfide bonds that link the heavy chains of mAbs in solution by adding a chemical agent [5,6]
3. allowing time for half-mAb-A and half-mAb-B to complex, i.e., associate in close-proximity, assembled thermodynamically
4. gradual removal of the disulfide lysing agent to allow disulfide bond formation, resulting BsAb production

The project objective is to:
- design a process to produce 100 Kgs of BsAb annually
- generate an unsteady-state, i.e., dynamic, kinetic simulation of the FAE chemistry that enables estimating the time periods needed to complete the sequential:

- o parental mAb reduction, i.e., lysis of disulfide bonds to produce half-mAbs-A and half-mAbs-B, and
- o concurrent removal of disulfide bond lysing agent and oxidative-formation of BsAb product with disulfide linkage
- perform a technoeconomic analysis of the process quantifying capital investment, operating cost, and profitability estimate.

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5. Bioremediation of Heavy Metals with Waste Lignocellulosic Biomass
   (Recommended by Gabriel Gonsalves Bertho, Penn)

Background

Heavy metal pollution is a worldwide environmental concern. Once an environment is contaminated with heavy metals, they will persist in the system for a long time due to their low environmental mobility. Heavy metal ions are highly toxic, non-degradable, and tend to bioaccumulate and biomagnify, affecting wildlife and contaminating all organisms in the food chain, including humans [1]. High concentrations of heavy metals in the human body are related to adverse effects on the nervous, blood-forming, cardiovascular, renal, and reproductive systems [2]. Furthermore, crops growing in areas with heavy metal pollution show reduced growth and yield, which could eventually lead to food insecurity [1].

TABLE 1. The MCL (maximum contaminant level) standards for the most hazardous heavy metals [3].

Heavy metal	Harmful health effect	MCL, mg/L
As	Skin and vascular diseases, visceral cancer	0.05
Cd	Kidney damages, renal disorders, carcinogenicity	0.01
Cr	Headache, diarrhea, nausea, vomitation, carcinogenicity	0.05
Cu	Liver damage, Wilson disease, insomnia	0.25
Hg	Rheumatoid arthritis, kidney, circulatory system and nervous system diseases	3.0×10^{-5}
Ni	Dermatitis, nausea, chronic asthma, coughing, carcinogenicity	0.20
Pb	Fetal brain damage, kidney, circulatory system and nervous system diseases	6.0×10^{-3}
Zn	Depression, lethargy, neurological signs, increased thirst	0.80

. The byproducts of mining, smelting, and electroplating operations are the most prominent sources of heavy metal pollution to the environment. However, most toxic heavy metals including lead, thallium, cadmium, and antimony, are common in industrial operations, increasing the cost and technical challenges of wastewater reuse [4]. In the US, particularly, coal ash leaks from thermoelectric power plants have been related to the contamination of groundwater with heavy metals [5].

Chemical precipitation with hydroxides is one of the most widely used methods for heavy metals removal but has been losing popularity due to its generation of a toxic sludge that is hard to manage and poses an environmental risk [6]. As a result, membrane processes and ion exchange have been used as effective methods for heavy metal remediation with lower sludge generation. However, the high costs associated with the operation and the maintenance of membranes and ion-exchange resins are not attractive to the industry, especially at sites with relatively lower generation of metal-contaminated wastewaters [7]. Biosorption of heavy metals with microbes and waste lignocellulosic biomass offers a low-cost alternative. The functional groups in cellulose have the capability of complex formation with metals, thus allowing a variety of agricultural waste materials to be applicable for metal removal [8]. Advancing the use of the

biosorption properties of lignocellulosic biomass can decrease the costs of heavy metal remediation and consequently incentivize industries to reuse wastewater.

Problem Statement

Among lignocellulosic biosorbents, coconut coir (or fiber) is a particularly useful candidate for heavy metal removal due to its abundance as waste in tropical areas and to its high metal biosorption capacities [9] Moreover, coconut coir fibers are highly porous, serving as a site for biofilm formation. The complex microbial consortiums and morphologies present in biofilms have empirically enhanced the efficiency of microbial processes applicable to wastewater treatment [10]. Finally, research has shown that metals sorbed in coconut coir have high recovery rates compared to other biosorbents, which can be an economic advantage for the mining industry [9].

Coconut coir can be used as a packing material in bioreactors, taking advantage of both its biosorption and biofilm-forming capacities [11]. The goal of this project is to design a coconut coir packed bioreactor for the removal of heavy metals (lead, cadmium, and arsenic) from wastewaters of a commercial scale facility and determine if it is economically advantageous.

An industrial facility produces 1 MGD (millions of gallons per day) of wastewater. Metal analyses showed that the waste contains an average of 0.25 mg/L of lead, 0.50 mg/L of arsenic, and 0.012 mg/L of cadmium. Based on that, the existing plant needs to add on a heavy metals removal process in order to remain in the good public graces and stay in operation. A contractor has proposed installing their ion exchange process to remove the heavy metals and would charge the plant $0.02/lb of wastewater treated. Estimate the capital and operating costs of the coconut bioremediation technology, estimate the NPV compared to the ion exchange proposal, and make a recommendation to the company management.

The operation of a coconut coir packed bioreactor would involve adding a fresh batch of coconut fibers to the reactor tanks, inoculating the fibers with bacteria consortia, letting them rest for a specific period so that biofilms can be formed, running the bioreactor until the fibers/biofilms get saturated, then removing the fibers and restarting the cycle. In order to allow for continuous operation, the plant would have to add a minimum of 3 bioreaction tanks with heating jackets, reflux pumps, a mechanism to input fresh coconut fibers with bacteria growth media, and a system to remove saturated fibers from the tanks and move them to the appropriate final destination. Your team must determine the arrangement possibilities of the packing material, the optimum outlet and reflux rates of the bioreactor, the options for further processing of saturated coconut fibers (production of activated carbon and biochar are possibilities), the microbial strain/biofilm formation method to be used based on the literature, the necessity of an aeration system depending on the microbes, and whether pretreatment of the coconut fibers is cost-effective for this case.

Details

The commercial facility has the following data about their wastewater:

Wastewater load: 0.8 – 1.2 MGD; avg: 1.0 MGD
[Pb]: 0.20 – 0.33 mg/L, avg: 0.25 mg/L
[As]: 0.20 – 0.80 mg/L, avg: 0.50 mg/L

[Cd]: 0.008 – 0.020 mg/L, avg: 0.012 mg/L

Packed-bed bioreactors using coconut coir as the packing material in the literature have used the following specifications [11];[12]; [13]; [14]:

Microbial strains: *Acinetobacter* sp. 158; *Pseudomonas Putida*; Biofilm formation by dipping fibers in sludge for 12hrs.

Inoculation time: 6 – 48 hrs.

Hydraulic retention time: 4.34 hr. – 5 days

Packing bed height: 13.3" - 70"

Packing Bed diameter: 1.52" - 2.36"

Working Volume: 0.26 – 5.28 gal

Operation temperature: 37°C

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6.   Production of "Green" Furfural from Hemicellulose
       (Recommended by P. C. Gopalratnam, Consultant – retired from DuPont, INVISTA)

Background

Furfural is considered as one of the most interesting and versatile bio-based chemicals. It can be used as a precursor for several non-fossil-based compounds such as furfuryl alcohol, 2-methyltetrahydrofuran (2-MTHF), or furan and in conversion to diesel or jet fuel, blending component for gasoline, or the development of biopolymers. In our constant search for commercial products made from waste byproducts, black liquor from the paper industry converted to furfural is intended as feedstock for biofuels for the aviation market.

Agricultural raw materials rich in hemicellulose, like corncobs, oat hulls, or bagasse, are used as feedstock for pulp and paper production. Annually over 300 million tons of wood are required. However, less than 50% is converted to chemical pulp. The rest, consisting of hemicellulose and lignin, is utilized for energy recovery of the pulping process. In contrast to lignin, hemicellulose has a low calorific value. Therefore, waste liquors from pulp and paper industry are promising feedstocks for furfural production with tremendous environmental benefits, due to the large quantities of unused hemicellulose. By adding large quantities of mineral acid and hot water/steam, only the hemicellulose fraction is dehydrated to furfural.

Pilot Study

Samples of hemicellulose fraction were provided from a "lignocellulose biorefinery" for the pilot plant study. Spent liquors were produced by fractionation of industrial debarked beech wood (Fagus sylvatica) chips by ethanol−water pulping using a batch process. In each batch, 70 kg (oven dry) of wood chips was pulped in a 540 L batch reactor with forced circulation at 170 °C for 100 min using 150 kg of an ethanol/water mixture (mass ratio 1:1) and 0.8 wt % of sulfuric acid (based on oven-dried wood) as a catalyst. The hemicellulose fraction was obtained by dilution precipitation of the dissolved lignin. Therefore, the organosolv spent liquor was diluted 1:2 with water. Subsequently, the precipitated lignin was filtered out from hemicellulose solution and residual ethanol was removed by rectification. To increase the sugar concentration, water was removed in a falling film evaporator at reduced pressure. Finally, the hemicellulose solution was filtered by vacuum filtration using a paper filter (MN 619 DE, retention capacity 1−2 μm, Macherey-Nagel, Germany) to remove larger particles and impurities. The composition and pH of the used hemicellulose fraction are depicted in Table 1 below.

Table 1. Organosolv Hemicellulose Composition Used for Hydrothermal Furfural Production

components	(mol L^{-1})
glucose	0.024
D-xylose	0.245
arabinose	0.017
xylooligosaccharide[a]	0.221
5-HMF	0.006
furfural	0.002
acetic acid	0.115
ethanol	0.087
pH	1.6

[a] D-Xylose equivalent.

Hydrothermal conversion of organosolv hemicellulose as well as furfural degradation in a temperature range of 160−200 °C was studied. Results were modeled on the basis of three different reaction mechanisms. Overall, regarding furfural formation, model 3 has shown the best performance and should be used for the plant design.
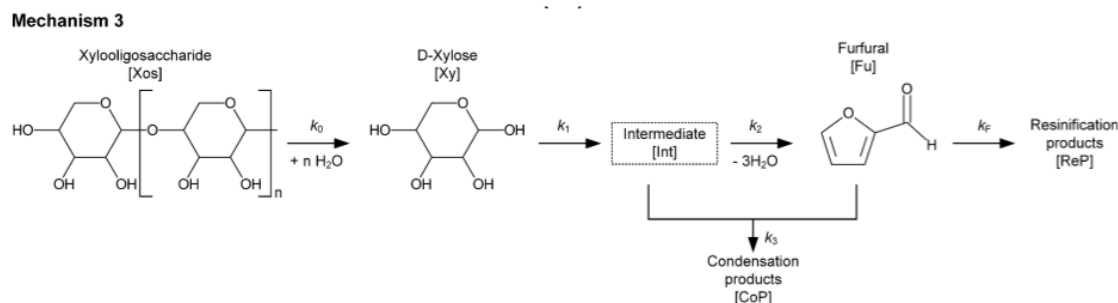
Process description

Based on the experimental method hydrothermal conversion experiments with organosolv hemicellulose (Table 1) were carried out at different temperatures (160, 180, and 200 °C). On the basis of these results, experiments with D-xylose (0.37 mol L−1), and furfural (0.1 mol L−1) were conducted additionally. The residence time was varied at four stages between 150 and 1400 s. D-Xylose and furfural solutions were acidified with 1.5 mL of concentrated sulfuric acid (96%), resulting in a pH value of 1.6.

For the experiments, a coiled tube reactor was used (see link attached). The reactor, made of stainless steel (AISI 316Ti), has a total length of 6.8 m (dotted line, Figure S.1) with an internal diameter of 7 mm. This results in a reaction volume of 263 mL. The aqueous reaction solutions were provided through the reactor by a membrane pump and first heated up by an electrically driven preheater. Afterward, the reactants pass the reaction zone (dotted line, Figure S.1). The reactor tube is coiled around a heating cartridge over a length of 800 mm and isolated from environment. The reaction temperature was kept constant by a temperature controller. After leaving the reactor, the processed liquor was cooled to ambient by a water-cooled heat exchanger. To avoid a transfer of the aqueous reaction solutions to the vapor phase, the back pressure regulator was set at 50 bar, to ensure complete liquid operation.

Furfural Destruction. Under the given reaction conditions, in addition to the formation, furfural is degraded by two loss reactions: (i) furfural resinification (furfural reacts with itself, self-polymerization) and (ii) furfural condensation (furfural reacts with D-xylose or D-xylose intermediates, cross-polymerization). The details of kinetics and other parameters from the pilot study along with useful references may be found in the reference.

Problem Statement

Design a single site manufacturing plant to make 300 kT of furfural annually in the U. S. Midwest, someplace close to the availability of agricultural raw material with black liquor as the starting material. Evaluate alternate designs using various reactor arrangements and using zeolite or other forms of aluminosilicate minerals as catalyst to propose an ideal process train based on overall economics.

Under the given reaction conditions, in addition to the formation, furfural is degraded as described above. Since furfural synthesis appears as an intermediate step in the "A to B to C" scheme as described, the desired product must be removed judiciously in order to optimize its yield. Note yield optimization would require a large "fly-wheel" of recycle stream with low conversion back to the reactors following product separation towards maximizing the overall economics.

The market price for furfural may be obtained from trade journals and other means or it may be assumed as $4 per lb as quoted in some geographical market space. Furfural price may also be calculated from suggested cost of jet fuel and its conversion cost found in the recent senior design report titled "Biofuels for Aviation".

In arriving at the final proposal, describe all design alternatives with details of options that were considered/ discarded for optimal energy consumption. Include details of on-site raw materials as well as product storage requirements with detailed discussions on safety and environmental considerations relating to the use of sulfuric acid and other waste streams. The plant design must also be controllable and safe to operate.

Reference

https://pubs.acs.org/doi/10.1021/acs.iecr.8b03402

7. Green Hydrogen Liquefaction
(Recommended by Adam Brostow, Sr. Process Engineer, Cryo Technologies - Chart)

Background

As global climate change is progressing, hydrogen is becoming an important clean fuel. Blue hydrogen is produced by steam methane reforming with CO_2 capture. It is subject to the volatile natural gas (NG) market (the EU gets 40% of NG from Russia). Green hydrogen is typically produced by electrolysis of water. Electricity comes from renewable sources such as the sun or wind. Hydrogen can then be liquefied for transport or storage. The first liquid hydrogen (LH2) ship completed its voyage in 2021.
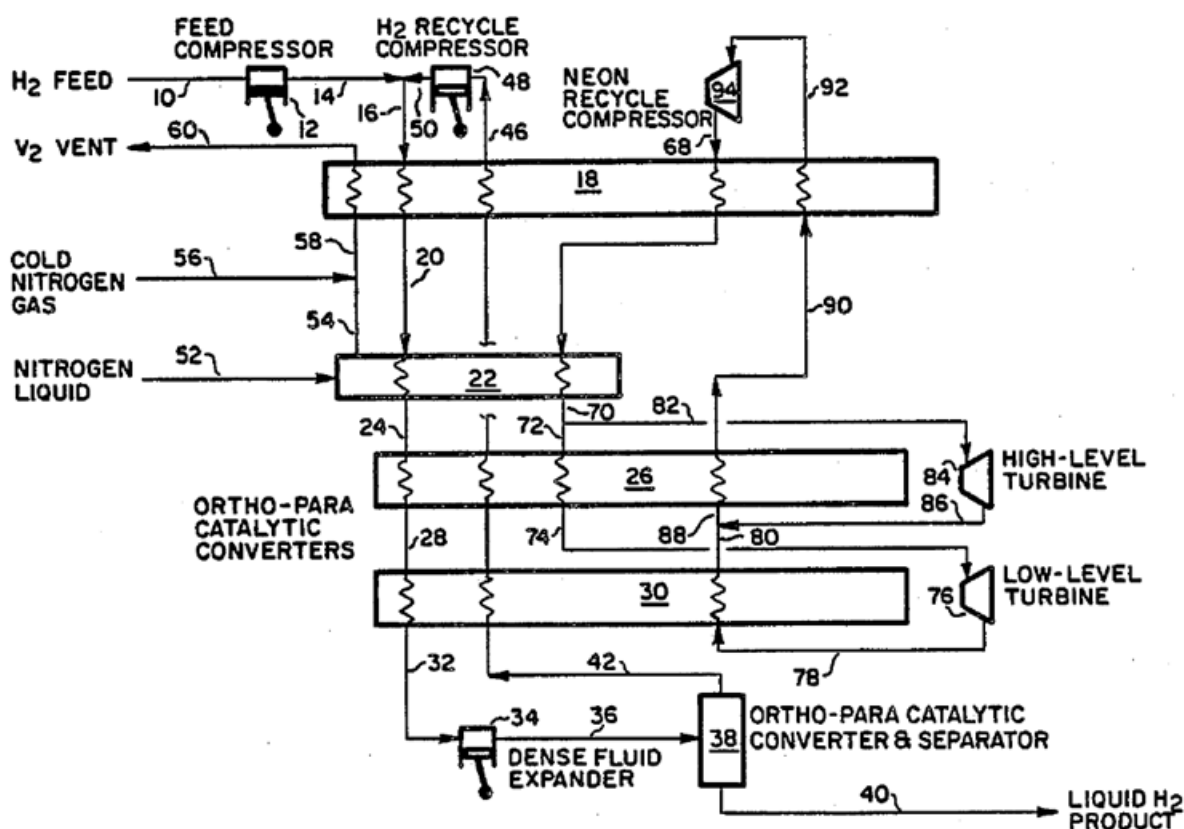
Fig. 1

Fig. 1 shows a typical hydrogen liquefaction process. The H_2 is optionally compressed and liquefied. Normal hydrogen contains 75% ortho-hydrogen and 25% para-hydrogen, spin isomers. Liquid hydrogen contains at least 95% of para-hydrogen. The ortho-para (O-P) conversion is catalytic and exothermic. Compared to natural gas or nitrogen liquefaction, O-P conversion and temperature of about 20 K pose additional challenges in designing the liquefaction process. The heat exchangers used are brazed aluminum plate-and-fin (BAHXs).

Problem Statement

The group is to design a plant producing 15 MTD (metric tons per day) of LH2. The feed is precooled with liquid nitrogen (LIN). Most of the refrigeration is supplied by the so-called reverse-Brayton cycle,

isentropic expansion of gas in two turboexpanders. The working fluid may be neon, helium, hydrogen, or the mixture of the above suggested in a recent paper (Cardella et al.).

The PFD follows Fig. 1. This is the NBA (next best alternative), coming from a relatively old patent. Students are encouraged to suggest improvements based on the newest developments mentioned in literature and their own new ideas. The problem is open-ended.

Basis of Design

Normal H_2 feed is at 100 deg. F, 265 psia. LH2 product is flashed to 52 psia and is to contain more than 95% para-hydrogen. The feed and refrigerant recycle compressors can be modeled in Aspen Plus as a 3-stage MCompr, with cooling water available at 90 deg. F, approach on inter/after-coolers of 10 deg. F, the pressure drop of inter/after-coolers of 5 psi, adiabatic (isentropic) efficiency of 85%. The turboexpanders have adiabatic efficiency of 85%. The dense fluid expander's adiabatic efficiency is 70%. A simple Joule-Thompson valve is to be considered in case the dense fluid expander is not operational. CAPEX-OPEX tradeoff is to be documented. There is no O-P conversion in the product phase separator. Precooling LIN is supplied saturated at 20 psia. It is throttled to atmospheric pressure (plus HX pressure drop) to provide refrigeration at about 77 K. Pressures such as feed booster compressor and recycle compressor discharge are to be optimized for minimal power consumption. The BAHX minimum approach is 3 deg. F, maximum 50 deg. F (due to thermal stresses). The cryogenic equipment is inside a vacuum cold box.

The group should perform techno-economic analysis of the base case (NBA) using pure neon and to consider using pure hydrogen and, time permitting, helium, neon-hydrogen, or neon-helium (nelium) mixture. They must consider ortho-para conversion (there is more than one way to do it). There is currently a shortage of neon due to war in Ukraine.

The group is to consider the power required to make LIN for pre-cooling, part of the life-cycle analysis. This information can come from literature, not a simulation. Green technologies require correct life cycle analysis as the benefits are often quoted out of context. What does the carbon footprint of green hydrogen look like if the liquefaction power comes from the grid (e.g., NG combined cycle)?

The group is encouraged to use SQP (sequential quadratic programming) optimization in Aspen Plus, but this is not required (instructions will follow). This is a useful skill.

References

LH2 patent (source of Fig. 1), Gaumer at al.:
https://patents.google.com/patent/US4765813A/en

LIN production patent, Brostow et al.:
https://patents.google.com/patent/US6298688B1/en

Economically viable large-scale hydrogen liquefaction, Cardella et al., 2017
https://doi.org/10.1088/1757-899X/171/1/012013

On green H_2:
https://www.cowi.com/insights/green-hydrogen-the-oldest-element-is-creating-a-new-world

Catalyst information:
https://www.molecularproducts.com/wp-content/uploads/2017/03/166_Rev-C_Technical-Datasheet_OP-Catalyst.pdf

The heat of O-P Conversion:
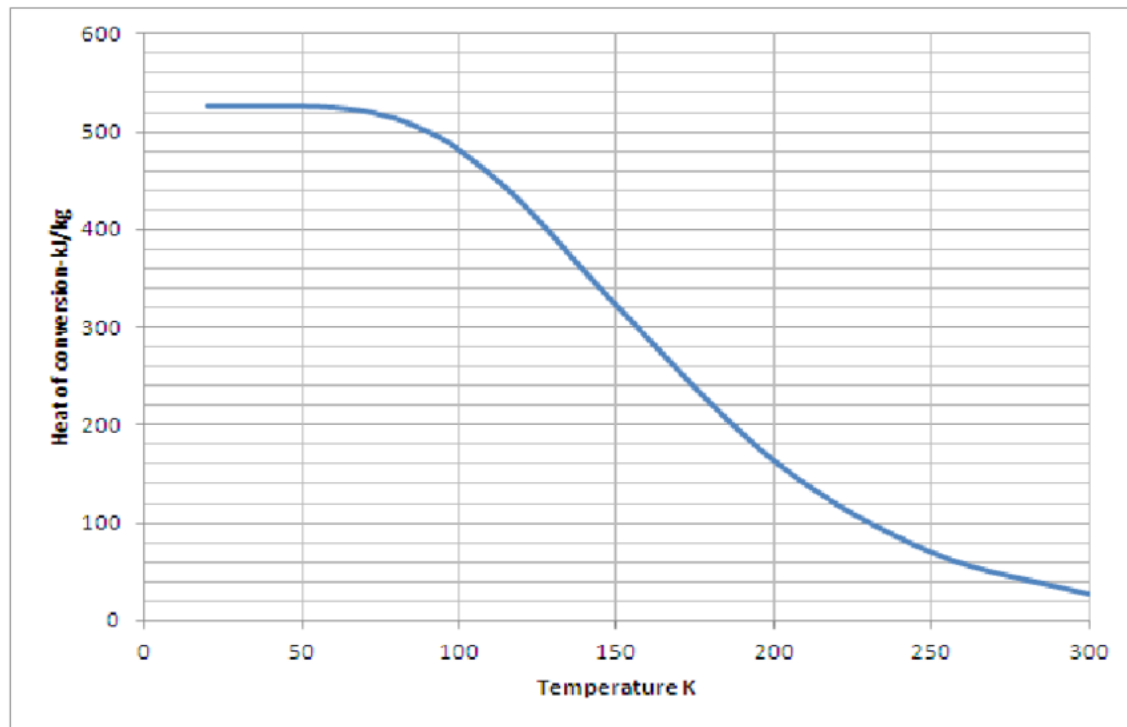
8. Toluene Diamine (TDA) and Polyol from Polyurethane Foam
   (Recommended by Stephen M. Tieri, DuPont)

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 communications. 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.

Through research, discovery, and innovation, your company has developed hydrolysis technology to depolymerize polyurethane to toluene diamine (TDA) and polyol. After converting the TDA to Toluene Diisocyanate (TDI), it can be re-polymerized with the polyols to generate new polyurethanes, saving energy and minimizing the use of additional fossil based raw materials. In the past, hydrolysis routes to polyurethane's starting monomers have required high temperatures to achieve reasonable processing rates, which resulted in higher than economically viable energy requirements. The company's new technology & catalyst achieves desired rates at mild process conditions, significantly reducing the energy burden for the depolymerization reaction. The company believes consumer interest in recovered and recycled materials as the main input for "new" materials, and economic conditions are aligned for implementation of this technology to be economically successful. As a major polyurethane producer, this technology also provides opportunities for the company to mitigate impacts from fossil raw material cost and supply issues and diversify future feedstock options.

While executives and business management are eager to commercialize a new line of circular polyurethanes, produced with monomers regenerated using this technology; they recognize that specific choices about how best to implement the new technology are critical to environmental and economic sustainability, and overall success. It is expected that successful startup and operation of this facility will be followed by both strategic investments for additional internal company capacity and licensing agreements to provide global recycling capability for production of circular polyurethanes. To this end, the company established agreements with a network of mattress retailers and wholesalers to provide in-region reverse logistics (collection, short term storage, transportation, etc.) for post-consumer polyurethane foams as feed to the new facility.

Your team has been assembled to design a commercial scale facility to implement the company's new, innovative, and lower energy depolymerization technology to generate TDA and polyols for new circular polyurethanes. While the company's previous economic forecasts indicate significant economic potential from this program/project, based on preliminary investment, cost, and revenue estimates, the results and recommendations from your team's economic analysis of the final design will be used for project approval.

The project's business objective is to design a commercial scale facility to convert 100,000 MT/yr (dry basis) post-consumer polyurethane foam to TDA and polyol. The post-consumer polyurethane material is expected to be reasonably dry and clean, with minimal environmental moisture, dirt, and other extraneous materials. The recovered polyurethane material is expected to be supplied in standard sized bales. The toluene diamine (TDA) and polyol products, and any additional monomer co-products, must meet or exceed current commercial requirements for purity and quality for polymer grade material, to be

acceptable to customers. Current market pricing is to be expected for products (ex. TDA), raw materials (including recovered polyurethane waste), and utilities.

In addition to detailed process equipment and unit operation designs, the completed project is expected to include estimates of facility investment, expected operating costs, revenue, and overall business profits. 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. The design and investment estimates should include appropriate raw materials feed and monomer product storage capacity to reasonably segregate product material for quality testing and decouple the new independent depolymerization and purification process from an existing polyurethanes polymer process. Any downstream polyurethane production capacity, potential expansion requirements, and/or additional supporting monomer storage facilities are outside the scope of this project. Business management identified and narrowed the potential initial location options to the US Gulf Coast, US Pacific Northwest, US East Coast, and central Europe. However, selection of the final location will be based your team's analysis, results and recommendation.

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 provided above and listed in the references below. Cite any literature data used. If and when required, make reasonable assumptions, state them, and identify to what extent your design or economics are sensitive to the assumptions you have made.

References

•"Evonik Develops New Chemical Recycling Process for Polyurethane Foam"; Bailey, mary Page; November 11, 20211; https://chemengonline.com/evonik-develops-new-chemical-recycling-process-for-polyurethane-foam/
•"The Dream of Foam"; Giesler, Johannes; https://elements.evonik.com/wp-content/uploads/2022/06/EVMAG_0122_EN_2631_PU-Recycling.pdf
•WO2022042909A1; Depolymerization of Polyurethanes Under Mild Conditions; Hildebrand, Jens et al.; March 3, 2022; https://patents.google.com/patent/WO2022042909A1/en?oq=WO2022042909A1
•WO2022042910A1; New Depolymerization Method for Polyurethanes; Hildebrand, Jens et al.; March 3, 2022; https://patents.google.com/patent/WO2022042909A1/en?oq=WO2022042910A1
•Efficient Method of Recycling Mattresses; https://corporate.evonik.com/en/sleep-well-168405.html
•Chemical Process for Recycling PU Foam Mattresses / Partnership with Vita Group / Plasticiser Portfolio Extended; November 19, 2021; https://www.plasteurope.com/news/Chemical_process_for_recycling_PU_foam_Partnership_with_Vita_Group_t249016/
•Life Cycle Assessment of Polyurethane Foams from Polyols Obtained through Chemical Recycling; Marson, Alessandro et al.; January 7, 2021; https://pubs.acs.org/doi/10.1021/acsomega.0c05844
•http://www.eia.gov/forecasts/steo/
•Conceptual Design of Chemical Processes; Douglas, J.M.; McGraw-Hill; 1988
•Flow of Fluids Through Valves, Fittings, and Pipe – Technical Paper No. 410; Crane Co.; 1988
•http://www.plasticseurope.org

9. Integrated Melamine and Urea Production
   (Recommended by Stephen M. Tieri, DuPont)

Melamine is a useful functional valuable material with numerous industrial and consumer applications. Melamine resins enable materials with high temperature stability, moisture resistance, hardness, and chemical resistance. The majority of current global melamine consumption is by the construction industry, for laminates and wood adhesives.

Your company is a major urea, methanol, ammonia, and melamine producer with numerous technology licensing partnerships with global melamine producers. In addition to its role as a major technology provider, it also provides basic design, engineering, equipment, and construction services to the melamine industry. Through research, innovation, and optimization, your company has developed the leading energy efficient technology for melamine production, providing the lowest greenhouse gas footprint, and without the need for catalyst, additional chemicals, or effluent waste treatment. This technology integrates urea and melamine production at the same manufacturing site. One advantage of this integrated technology is that it recycles ammonia and carbon dioxide produced in the melamine process to make additional urea, avoiding release of that carbon dioxide to the atmosphere, as is done in the conventional melamine process.

Within the last few months, the company secured contracts to provide the technology and design for three (3) new facilities, expanding its licensed melamine production to >1 MM tonnes/yr once complete and operational. Safe and successful startup and operation of these facilities is expected, in line with the company's past performance, corporate and customer core values, and industry reputation for robust and safe operation.

Your team has been assembled to design the first commercial scale facility to implement the company's new "next generation" melamine production technology. Although the company's initial economic forecasts identified preliminary investment, manufacturing cost, and licensing fee/royalty targets, the results and recommendations from your team's economic analysis of the final design will be used for customer approval and final license cost structure. Your team will determine the licensing fee/charges to maximize company revenue and optimize customer/licensee margins.

The project's business objective is to design a commercial scale integrated melamine and urea facility to produce 120,000 MT/yr of melamine. While the customer is open to opportunity for additional urea co-product sales, this additional urea capacity and investment must be economically justified. The melamine, and any additional urea co-product, must meet or exceed current commercial requirements for purity and quality (ex. 99.8 wt %, moisture, and low APHA color) to be acceptable to the customer/licensee. Current market pricing is to be expected for products, raw materials, and utilities.

In addition to detailed process equipment and unit operation designs, the completed project is expected to include estimates of facility investment, expected operating costs, revenue, overall customer business profits, and company licensing/royalty fees. 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. The design and investment estimates should include appropriate equipment and systems for raw materials feed and product storage capacity. The customer identified the new facility will be in located in South Korea.

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 and when required, make reasonable assumptions, state them, and identify to what extent your design or economics are sensitive to the assumptions you have made.

References

•"Eurotecnica To Provide Process Technology for World's Largest Melamine Plant"; Bailey, Mary Page; August 15, 2022; https://www.chemengonline.com/eurotecnica-to-provide-process-technology-for-worlds-largest-melamine-plant/

•"Eurotecnica Wins Two Melamine Plant Contracts"; Bailey, Mary Page; September 2, 2022; https://www.chemengonline.com/eurotecnica-wins-two-melamine-plant-contracts/

•"Integrated Process for the Production of Melamine and Urea"; De Amicis, Alberto et al.; January 6, 2022; https://patentimages.storage.googleapis.com/76/c2/fa/89883659bd49d3/EP4006011A1.pdf

•"Low-Energy consumption Process with Reduced Ammonia Consumption, for the Production of High-Purity Melamine through the Pyrolysis of Urea, and Relative Plant"; Santucci, Roberto; January 22, 2020; https://patentimages.storage.googleapis.com/94/72/ab/e1caf77959f80d/EP3597641A1.pdf

•Euromel® Melamine Technology"; Proman.org; January 23, 2020; https://www.proman.org/wp-content/uploads/2020/05/Proman-Eurotecnica-brochure-2020-01-23-FINAL-.pdf

•http://www.eia.gov/forecasts/steo/

•Conceptual Design of Chemical Processes; Douglas, J.M.; McGraw-Hill; 1988

•Flow of Fluids Through Valves, Fittings, and Pipe – Technical Paper No. 410; Crane Co.; 1988

•http://www.plasticseurope.org

10. A Greener Route to Hydrogen Peroxide
   (Recommended by Gary Sawyer, Process Evaluations LLC)

Aqueous hydrogen peroxide has applications from household antiseptic to paper bleaching to chemical intermediates such as in the production of propylene oxide.

The legacy process to make hydrogen peroxide is the anthraquinone (AQ) process, which feeds hydrogen and oxygen to an organic "working solution", from which the hydrogen peroxide is extracted into water.[1] Large scale hydrogen production by steam methane reforming (SMR) is widely commercialized but is a significant contributor to greenhouse gas emissions.[2]

Both hydrogen and oxygen can be made from electrolysis of water, but either excess hydrogen is generated, or supplemental oxygen is needed, since H2O → H2 + ½ O2, and we need equimolar hydrogen and oxygen. **Part 1 of your project** is to calculate the electricity consumption per pound of hydrogen peroxide, assuming water electrolysis with excess hydrogen generation. Your group is responsible for researching electricity consumption for water electrolysis. Calculate the cost of electricity used for this process, using historical pricing data from www.eia.gov. However, no process design, capital or operating costs are required for the AQ or electrolysis processes.

A review of direct synthesis routes for hydrogen peroxide is found in reference 1 below. **Part 2 of your project** focuses on a novel electrochemical route by Murray, et. al. [3], as shown below.
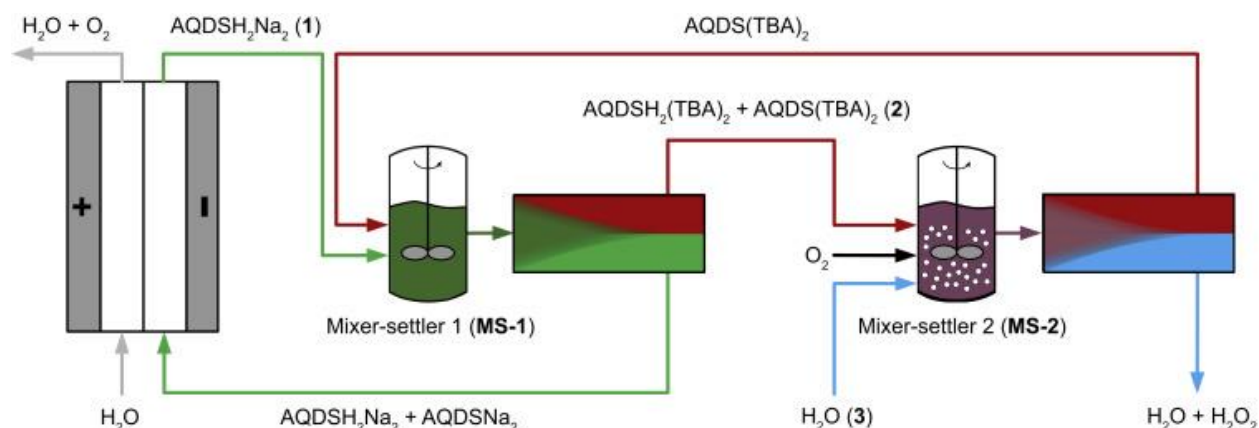
The reference article has performance data on faradic efficiency (how many electrons – or current needed) and voltage to produce hydrogen peroxide. Power consumption is calculated from P=I x V, where P is power in Watts, I is amperage, and V is volts. Note that there are now two loops of "working solution". Your project is to prepare a more detailed material balance and process flow diagram, and calculate equipment sizes, needed to produce 100,000 metric tonnes per year of H2O2 contained in as a 35 wt% solution in water, a commercially common concentration. The bulk of your effort and report will

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[1]

https://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=0CAQQw7AJahc KEwiY5e_c4f35AhUAAAAAHQAAAAAQAg&url=https%3A%2F%2Fwww.mdpi.com%2F2073- 4344%2F8%2F9%2F379%2Fpdf&psig=AOvVaw2IB0ygXoyV4HzV46yVppk5&ust=1662470989574872

[2] 9 kg CO2 / kg H2, per Argonne GREET Publication : Updates of Hydrogen Production from SMR Process in GREET® 2019 (anl.gov)

[3] Electrosynthesis of Hydrogen Peroxide by Phase-Transfer Catalysis: Joule (cell.com)

be on this process. Full capital and operating costs and profitability analysis should be included, to determine the economic viability of this process.

Part 3 of your project is to compare greenhouse gas emissions of the three routes to determine whether there are societal benefits, independent of the economics, to the electrosynthesis of hydrogen peroxide –

- Conventional AQ using hydrogen from SMR
- Conventional AQ using hydrogen from electrolysis
- Electrosynthesis of hydrogen peroxide in Part 2 of your project.

If needed, you will be given references for greenhouse gas emission rates for electricity from various sources as well as that of pure oxygen, required for the AQ process.

**11. Conversion of Wood Waste Biomass into Biochar and Green Hydrogen – a carbon dioxide removal (CDR) technology
(Recommended by Dr. Matthew Targett, SpruceWorks LLC)**

<u>Overview</u>

Biochar is a product of heating biomass residues such as wood chips, compost, and green waste, in an oxygen-starved environment – a process known as pyrolysis. The result is a stable biochar which cuts greenhouse emissions, while boosting soil fertility.

Entrepreneurial and climate change mitigation interests in biochar have grown dramatically in the last 10 years. In 2018, the International Panel on Climate Change officially listed biochar[1] as a negative emissions technology (NET), signaling its promise as a carbon dioxide removal (CDR) solution. New production capacity is being incentivized with new carbon removal credit markets[2], and carbon removal credits purchasers such as Microsoft[3]. Biochar markets are expected to grow in the coming years. New policy requirements and new biochar quality standards are further incentivizing biochar investments in Europe and North America.

One of the main biochar benefits is as an effective means of removing carbon dioxide from the atmosphere via storing organic carbon as a stable and beneficial additive to soils. Biochar provides "recalcitrant" soil carbon that resists decomposition for hundreds of years. Research indicates that biochar can sequester carbon, reduce soil methane emissions and nitrous oxide emissions, increase soil water holding capacity, adsorb and stabilize other soil organic carbon, improve crop yields on marginal land, and enhance reforestation in degraded areas.

Biochar can be produced at scales ranging from large industrial facilities down to the individual farm, and even at the domestic level, making it applicable to a variety of socioeconomic situations[4]. Various pyrolysis technologies are commercially available that yield different proportions of biochar and bioenergy products, such as bio-oil and pyrolysis gas, as shown below in Figure 1.

The gaseous bioenergy products are typically used to generate electricity; and the bio-oil may be used directly for low-grade heating applications and, potentially, as a diesel substitute after suitable treatment, or as biogenic feedstock for producing low carbon intensity hydrogen, itself a useful feedstock for the downstream production of renewable diesel, renewable aviation fuels and renewable LPG.

Pyrolysis processes are classified into two major types, fast and slow, which refer to the speed at which the biomass is altered. Fast pyrolysis, with biomass residence times of a few seconds generates more bio-oil and less biochar than slow pyrolysis, for which biomass residence times can range from minutes to hours.

<u>Problem Statement</u>

For the purposes of this project, the objective will be to determine an optimal commercial process configuration for converting biomass into biochar, bio-electricity and hydrogen. The author envisions two potential configurations, each of which can be optimized with pyrolysis temperature as shown below in Table 1 below.

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[1] 2018 IPCC Special Report - Global Warming of 1.5C - Chapter 3
[2] https://puro.earth/CORC-co2-removal-certificate/
[3] Link to Microsoft carbon dioxide removal (CDR) program website
[4] Woolf, D., Amonette, J., Street-Perrott, F. et al. Sustainable biochar to mitigate global climate change. Nat Commun 1, 56 (2010)
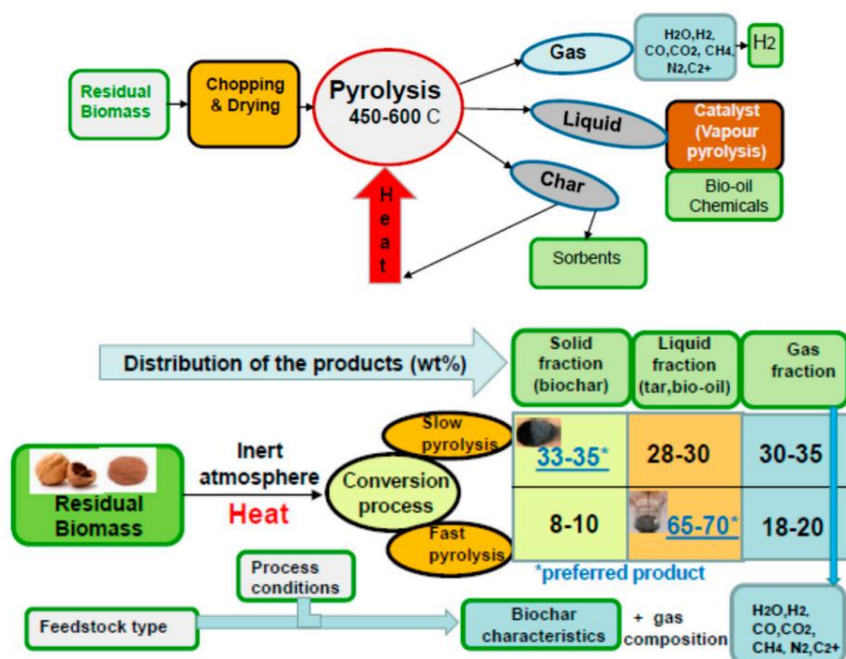
FIGURE 1 : Generalized Pyrolysis Schematic of the three main coproduct streams from biomass pyrolysis – biochar, bioliquids and pyrolysis gas from (David, 2020)[5]

Case		Biochar	Bioliquids	Hydrogen from Pyrolysis gas
1	Base Case (no H_2 recovery)	Recovered	Combusted as fuel for power generation	H_2 not recovered – pyrolysis gas stream combusted as fuel for power generation
2	Optimized Case (with H_2 recovery)	Recovered	Combusted as fuel for power generation	Recover H_2 from raw Pygas stream, H_2-depleted pyrolysis gas combusted as fuel for power generation

TABLE 1 : Potential Biochar-Hydrogen coproduction cases

It is recognized that other hydrogen coproduction scenarios exist, and these could also be considered as substitutes for those shown in Table 1 if warranted at the outset of the project. One example is adding a steam reforming step to recover additional hydrogen from the hydrocarbons (CH_4) in the pyrolysis gas stream.

It is also recognized that pyrolysis product distributions are not well characterized in the literature with detailed reaction kinetic or equilibrium product distribution models. The team will therefore rely on best available correlation data from the literature. One reasonably good resource, as a starting point, is the work of Neves etal (2011)[6].

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[5] Elena David, *Evaluation of Hydrogen Yield Evolution in Gaseous Fraction and Biochar Structure Resulting from Walnut Shells Pyrolysis*; Energies 2020, 13, 6359; doi:10.3390/en13236359

[6] 2011, Neves etal.; *Characterization and Prediction of Biomass Pyrolysis Products*; Progress in Energy and Combustion Science 37 (2011) 611e630

In terms of production scale, it is recommended that the facility is large enough to process about 100,000 metric tonnes (dry basis) per year of waste wood biomass. In terms of 'fast pyrolysis' processing versus 'slow pyrolysis' processing, it is recommended that 'slow pyrolysis' is chosen because it produces more biochar and biogas than 'fast pyrolysis'. In terms of temperature selection there is a wide range of known processing conditions. However, rather than attempting to map the entire range in pyrolysis temperatures, it may be more expeditious to choose a low, mid and high temperature scenario for each of the two cases in Table 1 above, creating an array of six techno economic scenarios for modelling.

Project Statement – defined criteria

Overall
- o Process Inputs: Woody Waste Biomass (thinnings, slash, mill residues, saw dust, bark, hog fuel, etc)
- o Synergistic siting: Ideally in heavily forested areas in Northwest, and Southeast US.

Feedstock
- o As part of the location decision making also take into consideration wood types available, select what is typically available and search for relevant characterization data, such as elemental composition, heating value, as-delivered moisture content, etc
- o 100,000 metric tonnes (dry basis) per year of woody biomass feed

Main Production – Unit Operations
- o Biomass Prep – Size Reduction, Grinding
- o Biomass Dryer – Heated with waste heat is a plus
- o Pyrolyzer – there are several designs from which to choose, rotary kiln, heated auger, etc.
- o Bioelectricity – burn fuels in reciprocating engine directly or burn fuels to make steam in a turbine generator cycle
- o Hydrogen Recovery – cyclic sorbent-based gas separations or membrane-based gas separations
- o For pyrolyzer product yield data as a function of temperature, utilize cited references

Biochar Product
- o Refer to product standard from Verra[7] or equivalent from International Biochar Institute (IBI), or European Biochar Certification (EBC)

Key Input Variables – to be varied for the purposes of defining each of the six cases
- • pyrolysis converter designs (temperature)
- • heat integration designs

Key Output Variables – to be determined by modelling
- • OPEX costs
- • Capex investment costs
- • IRR/NPV
- • Financial projections should also take into account biochar carbon removal credits offered on the voluntary markets. See PURO[8] as an example of CDR marketplace with posted prices for carbon removal credits.

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[7] https://verra.org/wp-content/uploads/2022/08/VM0044_v1.0_Methodology_for_Biochar.pdf

[8] https://puro.earth/CORC-co2-removal-certificate/

12. Fermentation Route to HMD
   ## (Recommended by Bruce M. Vrana, Penn)

Hexamethylene diamine (HMD or HMDA, both acronyms used interchangeably) is one of two monomers, along with adipic acid, required to make nylon 6,6. Nylon 6,6 was invented by Carothers at DuPont, with initial applications in fashion ("nylons"). World War II saw the use of nylon in parachutes. Since then, the nylon market has grown to include fashion (again), carpeting, engineering polymers (with various applications including light-weighting cars), etc., with total annual sales of nylon exceeding $20 billion.

About 2 million (metric) tons of HMD is made annually, almost exclusively by hydrogenation of adiponitrile (ADN). ADN in turn is made via two primary routes from fossil sources. Most ADN is made from butadiene and hydrogen cyanide. Besides the obvious hazards of cyanide, its carbon footprint is significant as it is made from natural gas and ammonia. The other route to ADN is by the electro-hydrodimerization of acrylonitrile. Acrylonitrile is made from propylene and ammonia, again with significant carbon footprint. Hydrogen to produce HMD is generally made by steam reforming of natural gas, with its own carbon footprint. HMD is also used in coatings and adhesives, but its major use is in nylon.

To develop a more sustainable route to nylon, Geno (formerly Genomatica) and Covestro (formerly Bayer Material Science division of Bayer) have developed a route to HMD by fermentation of plant-based material. Covestro reportedly has an option to license the GENO™ HMD technology from Geno.

Geno can reportedly produce HMD from glucose, with 88% of the glucose converted to HMD. The final reaction titer is 116 g/L HMD. Production rate is believed to be 3.3 g/L/hr. All of these metrics seem reasonable for the fermentation route to compete economically with the fossil route.

As a fossil-based nylon 6,6 producer, your company executives saw the recent publication listed in the references and have panicked about the existential threat to the company, endangering their significant long-term stock compensation. Your leadership needs to understand the Geno technology and the potential advantage it might bring to your competitors. Your group has been charged with developing a plant design to make 100,000 (metric) tons of HMD per year and the predicted economics, using published data from Geno, before possible discussions with Geno to license the technology. Because these negotiations can be sensitive, your management has forbidden any form of contact with anyone at Geno or anyone else (other than industrial consultants and faculty at Penn). Your group must use only published patents or applications, papers, web sites and other public sources. The objective is to obtain a license at the lowest possible price, if the technology warrants, so you do not want to tip off your company's interest in the process until your engineering analysis is complete.

The main Geno patent referenced below describes various options for recovering the HMD from the fermentation broth. HMD exists in the di- or mono-protonated form or as free base in aqueous solution, depending on the pH. CO_2 formed in fermentation or added to the broth obviously plays a role in pH. Recovery options include solvent extraction with hexane and water evaporation or steam stripping. There are numerous other patents and some publications – you must search for and decide which ones to use.

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

You may locate the plant anywhere in the United States. Consider logistics costs, both of feedstock glucose and product HMD, as well as construction and labor costs. One possible location would be near a corn wet mill to reduce the shipping cost of glucose syrup feedstock. Another would be near polymerization plants largely located in the Southeast, to reduce the shipping cost of your product. A third possible location would be on the U.S. Gulf Coast, where construction, energy and labor costs are relatively low due to the large chemical industry infrastructure there. There may be other logical locations to consider.

The plant design should be as environmentally friendly as possible, at a minimum meeting Federal and state emissions regulations. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that if the negotiations are successful, you will be there for the plant start-up and will have to live with whatever design decisions you have made.

References

https://www.globenewswire.com/news-release/2022/01/19/2369255/17500/en/Covestro-and-Genomatica-produce-important-chemical-raw-material-using-biotechnology.html

"Method of producing & processing diamines", World Patent application assigned to Genomatica, WO 2016/106367A1

13. Stranded Natural Gas to Liquid Products
   ## (Recommended by Bruce M. Vrana, Penn)

Natural gas is often co-produced when crude oil is extracted from the ground. If this crude oil is located in sufficiently remote regions or the natural gas is produced in relatively small quantities, the gas is sometimes flared, releasing carbon dioxide to the atmosphere. While this greenhouse gas emission is not desirable, it is far superior to releasing the natural gas. However, it is often not economical, logistically possible, or environmentally or societally acceptable to compress and pipe so-called "stranded gas" in much of the U.S. and elsewhere around the world.

One possible solution is to turn that natural gas into a more dense liquid product that can be economically shipped, as the crude oil is. All manner of liquid products have been proposed, but capital costs are often too high to justify at the scale of a typical oil field. Many liquid products have been impossible to produce because there has not been an efficient process to convert methane to ethane or ethylene.

Researchers at Iowa State and coworkers at Purdue and elsewhere have reportedly solved that roadblock. They have developed a coke-resistant, non-oxidative catalyst that converts methane to C_2 products with greater than 98% selectivity. Unfortunately, C_2 is not routinely transported as liquid, so the C_2 must be further oligomerized to make C_8 products, which is well known technology. The overall proposed process (from the first reference) is shown below. The first reference and its supplemental material contain information on the selectivity and kinetics of different reactions over different catalysts, as well as data over 72 hours of reaction time. Data on the dehydrogenation and oligomerization steps is readily available, for example in the references cited in the first reference below.
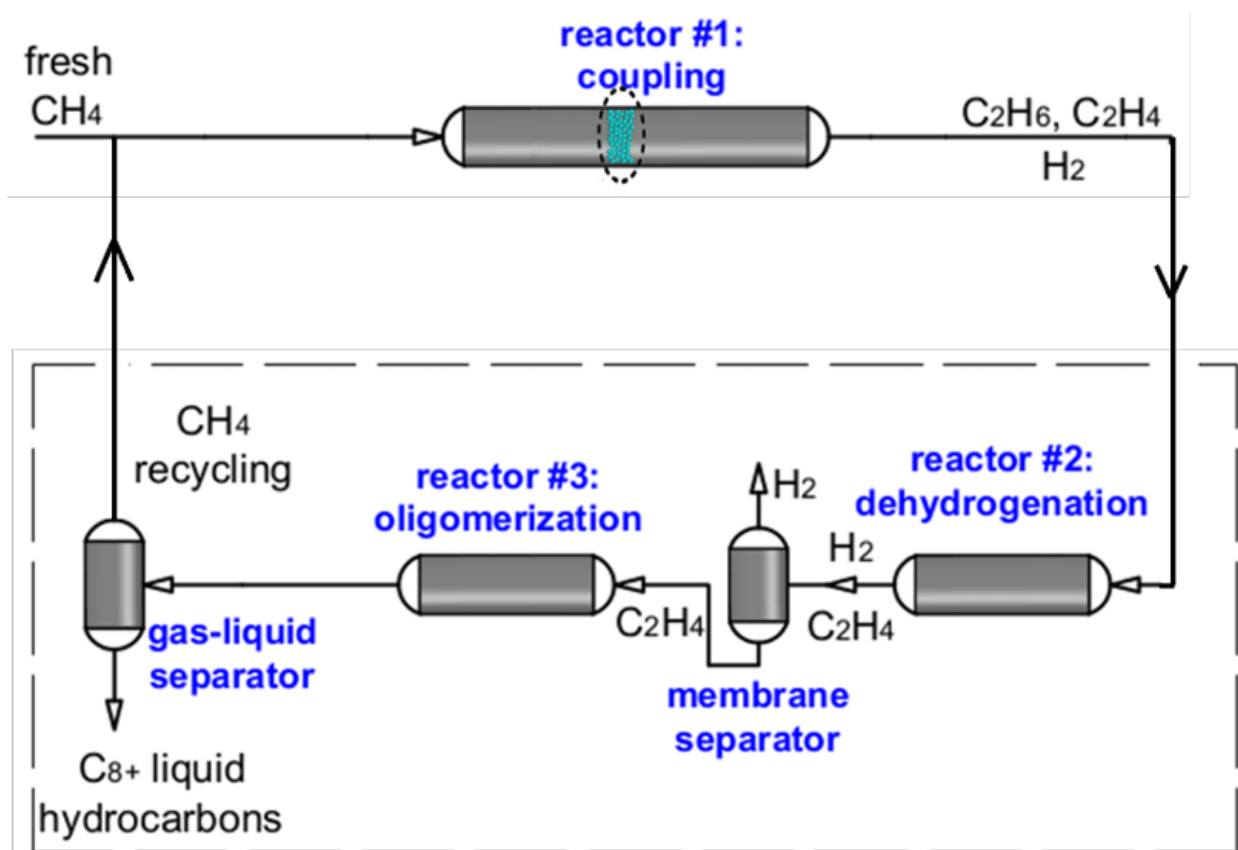
The energy company you work for has commissioned your group to determine the attractiveness of this technology for its operations. Your company currently flares 1 billion cubic feet per year of natural gas from one of its operations in the Permian Basin. All of that flared gas is located close enough to be viably used in one facility. Your group has been asked to design a facility to convert that gas to liquid hydrocarbons using this technology and estimate the economics.

Hydrogen will be a co-product from this process. You will need to decide what to do with it – transport and sell it (see problem statement 7 above), use it to make something else, burn it for fuel value, flare it, or any other idea you have.

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. Test your economics to reasonable ranges of your assumptions. If there are any possible "show-stoppers" (i.e., possible fatal flaws, if one assumption is incorrect that would make the design either technically infeasible or uneconomical), these need to be clearly communicated and understood before proceeding.

The plant design should be as environmentally friendly as possible, at a minimum meeting Federal and state emissions regulations. Recover and recycle process materials to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate. Remember that if your company builds this facility, you will be there for the plant start-up and will have to live with whatever design decisions you have made.

References

Li, Z., Xiao, Y., Chowdhury, P.R. et al. Direct methane activation by atomically thin platinum nanolayers on two-dimensional metal carbides. Nat Catal 4, 882–891 (2021). https://doi.org/10.1038/s41929-021-00686-y

https://www.futurity.org/methane-greenhouse-gas-catalyst-2671132/