Suggested Design Projects – 2021-2022

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

Background

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:

$2H_3BO_3 + 3 CON_2H_4 \implies 1 BN + 3 CO_2 + 4 NH_3$

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 CO₂ pricing will be needed as part of the analysis. At this point assume that the CO₂ 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 CO₂ 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 CO₂ 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.

References

- 1) CEP, January 2020, p 4-5
- Fan, M., et al., "Atomic Ru Immobilized on Porous h-BN through Simple Vacuum Filtration for Highly Active and Selective CO₂ Methanation," ACS Catalysis, 9, pp 10077-10086, doi:10.1021/acscatal.9b02197.
- 3) Supporting Information for above article: "Atomic Ru Immobilized on Porous h BN through Simple Vacuum Filtration for Highly Active and Selective CO₂ 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, Fanshu Yuan, Robert Vajtai, Jieshu Qian, Jiazhi Yang, Boris I. Yakobson, James M. Tour, Jochen Lauterbach*, Dongping Sun*, Pulickel M. Ajayan*

- Chakrabartty, S. and Kumar, S, "Preparation of Hexagonal Boron Nitride from Boric Acid and Characterization of the Materials", Transactions of the Indian Ceramic Society, 1995, 54:2, p 48-51. DOI: 10.1080/0371750X.1995.10804678.
- 5) Durkin et al, Synthesis of Green Hydrocarbons Using the AIR TO FUELS[™] Technology, University of Pennsylvania CBE Senior Project Report, 2019.
- 6) McPhy, "Augmented McLyzer." McPhy. https://mcphy.com/en/ourproducts-and-solutions/electrolyzers/augmented-mclyzer/.
- Schmidt, O., A. Gambhir, and I. Staffell. "Future Cost and Performance of Water Electrolysis: An Expert Elicitation Study." ScienceDirect. December 28, 2017. <u>https://www.sciencedirect.com/science/article/pii/S0360319917339435</u>
- 8) <u>https://www.hydrocarbonprocessing.com/news/2020/08/german-oil-refinery-to-build-30-mw-hydrogen-electrolysis-plant?id=52975357</u>
- 9) <u>https://www.eia.gov/outlooks/steo/data/browser/#/?v=21&f=A&s=0&maptype=0&ctype=linecha</u> <u>rt</u>
- 10) <u>https://www.eia.gov/outlooks/steo/data/browser/#/?v=16&f=A&s=0&maptype=0&ctype=linecha</u> <u>Ort</u>

2. Production of Acetaminophen (Paracetamol / APAP) by Batch and Continuous Processes (Recommended by Alex Marchut, Esperion and Art Etchells, Consultant – retired from DuPont)

Background

Acetaminophen is an API (active pharmaceutical ingredient) in Tylenol® and other over the counter pain relief drugs. The current production rate globally is 80,000 metric tons per year. It is a typical small molecule chemical produced by a non-biological / synthetic process. The current global market value is \$350 million dollars. A typical price in the US is \$8 per kilogram but the project should include a sensitivity study to determine if it could be sold at a lower cost.

The current batch process consists of starting with phenol, a commodity chemical, then turning that into nitro-phenol. There are two isomers which must be separated by distillation. Then the para isomer is converted into amino-phenol by hydrogenation. All are liquid phase reactions. The nitration requires two liquid phases and the hydrogenation is a gas liquid reaction with a solid catalyst. The last step is to add acetic anhydride which precipitates the final product. This crystal product is then recrystallized for purity and then converted into tablets with the addition of excipient which enhance digestibility. The solids handling steps to produce the tablets are outside of the scope of this project – it ends with the purified and dried acetaminophen crystals.

Project Statement

The product is an article of commerce and it has been suggested that one way to enhance profits is to reduce production costs by changing the process to a continuous process. The plant design is to be 30,000 metric tons / year batch or continuous, this large production rate may make continuous attractive. Batch and continuous designs should be completed to do a thorough comparison, i.e., two manufacturing process trains will need to be designed: one batch and one continuous. There are several synthetic possibilities to make this API but it is recommended to focus on starting with p-nitro phenol, undergoing a hydrogenation, to p-amino phenol and then adding acetic anhydride to yield the API. Please consider the regulatory constraints mentioned in the appendix when defining which steps will be run under Good Manufacturing Practices (GMP). It might be more economic to buy the nitro-phenol rather than making it unless the continuous hydrogenation process is very economic under GMP constraints.

The solvent for the early steps is often given as benzene. This is an unpopular solvent because of health reasons. Other solvents should be considered such as toluene. For the crystallization, combinations of alcohols and water seem to work as solvents at elevated temperatures.

The current prime manufacturer is Mallinckrodt with a large plant in Raleigh NC Research Triangle Park. They have an extensive patent position as do several other companies.

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 and 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 & solvents, no waste is released to the environment, and any risks of dust and / or solvent explosions are accounted for in the design (also note the flammability

hazards related with hydrogen). The final design should compare a batch and a continuous process, ultimately making a recommendation as to which is a wiser investment.

Appendix: Some Regulatory Constraints

In the pharmaceutical industry, for regulatory purposes production is governed by US Food and Drug Administration Good Manufacturing Practices. The starting materials must be defined, and they must be commercially available (there must be at least 3 suppliers that make them). Whatever is done to make those raw materials (known as Regulatory Starting Materials or RSM's) is not subject to Good Manufacturing Practice. GMP facilities are extremely well regulated and subject to a variety of audits and therefore generally more expensive (for this work assume that materials made under GMP have a 50 percent increased cost added).

References

1. "Manufacturing & Effluent Treatment Process" Adroit Pharmaceuticals Pvt.Ltd. Amadi (V), Nagpur (D).

2. "Continuous Crystallization of Paracetamol (Acetaminophen) Form II: Selective Access to a Metastable Solid Form" L. R. Agnew et al., Cryst. Growth Des. 2017, 17, 5, 2418–2427

There is a video on YouTube of the final precipitation crystallization step

3. A Communal Waste Treatment Facility for Dairy Farms (Recommended by R. J. Gorte, UPenn)

Dairy farming has become largely industrial and most farms now have 5,000 to 10,000 cows. With farms this size, disposing of the manure is a major issue. Much like a municipal waste treatment facility, the manure is first pumped into a large tank. In the past, when farms were smaller, the gases evolving from the tank would be allowed to escape and the tank would simply be emptied periodically by spreading the contents over the fields as fertilizer. However, venting the gases from these large systems is not allowed and spreading the unprocessed liquids and solids can be disturbing to neighbors and a source of pollution for local streams. As an alternative to flaring, the gases emitted from the tank (the digester) can be collected for use as a fuel. The remaining product (the digestate) can be further processed to yield fiber as bedding for the cows, a soil amendment product, and a liquid fertilizer that can be injected directly into the soil. A number of such systems have been built across the country for particularly large farms, with most converting the methane to electricity onsite. BC Organics has proposed a *community* manure digester designed to process manure from a number of neighboring farms near Wrightstown, WI. A description of the system is given in the minutes of a planning meeting for the facility, which can be found at: https://townofwrightstown.org/wp-content/uploads/2019/08/Board-Meeting-Packet-of-8-5-19-04552291.pdf. The system is anticipated to produce 1,800 MMBTU/day of natural gas of sufficient purity to add to the pipeline and to return the other products back to the farms. For reference, one cow produces roughly 40,000 BTU/day.

You have been asked to design a similar system for a group of 5 farms (10,000 cows each) 30 miles to the Southeast of Wrightstown. The farms are all reasonably close to a natural-gas pipeline, where there is a sufficient amount of land available to build the plant (You may assume that the farms are 0.5, 1.0, 2.0, 3.0, and 5.0 miles from the proposed plant site, respectively.). You have the option of sending the liquid manure to the site by pipeline, which would need to be built from each farm to the site, or by tanker truck. As in the BC Organics system, methane will be the main product that you have to sell, but you have been asked to determine whether the CO_2 might also have value. (You should determine what effective CO_2 price is required, net of all taxes and credits, in order to earn a 10% IRR on the incremental investment to recover the CO_2 as a separate co-product.) The solids and liquid fertilizer will be returned to the farms, but you will need to charge each farm for having their waste processed. This will establish a price for the bedding and the fertilizer.

References

https://www.youtube.com/watch?v=K6wtsgW9klo

https://www.youtube.com/watch?v=Nc9LhbW6Q_Q

http://www.ethanolproducer.com/articles/18396/carbonconnector#:~:text=The%20Summit%20Carbon%20Solutions'%20pipeline,their%20Cl%20scores %20in%20half.





4. PFAS Removal from Water Supply (Recommended by Ryan Lam and Isabel Gutierrez, UPenn)

PFAS Overview

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic chemicals associated with a host of human health and environmental concerns. PFAS are manufactured internationally across many different industries, including the production of coated paper food packages, non-stick cookware, fire-fighting foams, personal care products, and household cleaning products. The carbon-fluorine backbone (C-F) of these molecules is extremely strong, with a bond dissociation energy of up to 130 kcal/mol. Due to this property, PFAS have an extremely long environmental half-life and have been dubbed "forever chemicals."¹

Because PFAS are water-soluble and are particularly mobile in the aqueous phase, the central environmental concern regarding PFAS is stormwater runoff into surface bodies of water and infiltration into groundwater. As the primary pathway for pollution, the rainwater transport of PFAS and subsequent migration into drinking water supplies poses a major environmental issue for fish, other animals, and humans. While bioaccumulation of PFAS in wildlife has a directly detrimental effect on global ecosystems, biomagnification of PFAS in humans, either through the consumption of plants and animals in which PFAS has accumulated or through direct consumption of polluted water, poses an even more serious health concern.



Molecular structure of PFOA and PFOS, the first two PFAS chemicals to be regulated in the US.

In terms of human health, PFAS has been identified as a probable link to hypercholerolemia, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension and preeclampsia.² As such, the US EPA has established the health advisory levels of PFOA and PFOS (two major PFAS chemicals) at 70 parts per trillion for drinking water.³ Worryingly, PFAS levels have been regularly reported to be on the parts per billion level across the United States.

¹ https://cen.acs.org/sections/pfas.html

² http://www.c8sciencepanel.org/index.html

³ https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

Effective methods for the separation of PFAS from drinking water have been established industry wide. Namely, adsorption onto granular activated carbon (GAC) and reverse osmosis (RO) membrane filtration have been shown to remove >90% of PFAS in water. However, handling the waste byproduct of these processes, that is, the spent carbon or membranes, has been challenging. Currently, incineration of PFAS contaminated waste at temperatures of at least 1000°C is believed to break down PFAS, but these claims are disputed as some PFAS may remain in incinerator ash due to incomplete combustion.⁴

Problem Statement

Novel methods of PFAS management include improved filtration methods with materials more specific to PFAS, ultrasonic degradation, electrochemical oxidation, application of ultraviolet radiation, application of high heat and pressure, and plasma reactors.⁵ In particular, field demonstrations of pilot scale, enhanced contact plasma reactors have already been shown to produce promising results, achieving purification of PFAS contaminated water to EPA advisory levels within three reactor cycles.⁶ Enhanced contact plasma reactors function by utilizing a gas diffuser to generate bubbles that concentrate surfactant-like contaminants and enhance contact between dissolved contaminants and plasma, which itself generates oxidative species such as hydroxyl radicals that attack and break down organics.



Diagram of example batch reactor used for removal of PFAS.

The objective of this project is to compare the commercial viability of a commercial-scale plasma reactor to a traditional water treatment plant using GAC/RO. To that end, a process design should be completed in a similar level of detail for both the plasma system and the traditional system - so that a meaningful comparison can be drawn. This should include a complete examination of the end-to-end process, including for example the cost of thermal GAC regeneration and the disposal of the RO reject stream. Special attention will need to be paid to the electrical equipment needed for the plasma reactor, rather than relying on typical electrical factors in estimating the capital cost to build the plant. Both designs should utilize a "pump-and-treat" approach and be sized to handle the PFAS in the four public

⁴ https://www.sciencedirect.com/science/article/abs/pii/S0045653520318543

⁵ https://cen.acs.org/environment/persistent-pollutants/Forever-chemicals-technologies-aim-destroy/97/i12

⁶ https://pubs.acs.org/doi/10.1021/acsestwater.0c00170#

wells located in New Castle, Delaware, with total well capacity approximately 2.33 million gallons per day.⁷ Proximity to the New Castle County Airport and adjacent Delaware Air National Guard, which have historically used PFAS-containing firefighting foams, has resulted in contamination ranging from 630 parts per trillion to 4,500 parts per trillion.⁸

⁷ https://documents.dnrec.delaware.gov/fab/Documents/DE-DWR-Needs-Assessment-1-24-20.pdf

⁸ https://apnews.com/article/business-health-environment-and-nature-956fa8e2d60f3e5b2f92fb520ea2ac53

5. 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 $1-2 \mu$ m, Macherey-Nagel, Germany) to remove larger particles and impurities. The composition and pH of the used hemicellulose fraction are depicted in Table 1 below.

components	$(mol L^{-1})$
glucose	0.024
D-xylose	0.245
arabinose	0.017
xylooligosaccharide"	0.221
5-HMF	0.006
furfural	0.002
acetic acid	0.115
ethanol	0.087
рН	1.6
^a D-Xylose equivalent.	

Table 1. Organosolv Hemicellulose Composition Used for Hydrothermal Furfural Production

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 the 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, some place 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 last year's project 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

6. CO₂ and CH₄ to Liquids Via Plasma Excited Catalyst (Recommended by Leonard Fabiano, Adjunct Professor)

Background

A major breakthrough has been made in the direct conversion of methane and carbon dioxide into liquid fuels and chemicals. Researchers claim that the new process could help industry reduce greenhouse gas emissions while producing vital chemical feedstocks. The researchers from the University of Liverpool have developed a plasma synthesis process for a direct, one-step activation of carbon dioxide and methane into higher value liquid fuels and chemicals such as acetic acid, methanol, ethanol and formaldehyde. Their findings have been published in the journal Angewandte Chemie.

Converting carbon dioxide and methane into liquid fuels and chemicals using single step processes such as catalysis has proven a significant challenge because they are both inert molecules. Typically, the conversion will require high temperature, energy intensive syngas production process and high pressure syngas processing for chemical synthesis. The University of Liverpool scientists' one-step roomtemperature production of liquid fuels was achieved by using a unique atmospheric pressure, non-thermal plasma reactor with a water electrode and a low energy input.

"These results clearly show that non-thermal plasmas offer a promising solution to overcome the thermodynamic barrier for the direct transformation of CH_4 and CO_2 into a range of strategically important platform chemicals and synthetic fuels at ambient conditions," said Dr. Xin Tu, from the University of Liverpool's department of electrical engineering. "Introducing a catalyst into the plasma chemical process, known as plasma-catalysis, could tune the selectivity of target chemicals." "This is a major breakthrough technology that has great potential to deliver a step-change in future methane activation, CO_2 conversion and utilization and chemical energy storage, which is also of huge relevance to the energy & chemical industry and could help to tackle the challenges of global warming and greenhouse gas effect."

According to a statement from the University, plasma systems have the flexibility to be scaled up and down. In addition, high reaction rate and fast attainment of steady state in a plasma process allows rapid start up and shut down compared to other thermal processes, significantly reducing the overall cost and offering a route for the plasma process powered by renewable energy to act as an efficient chemical energy storage localized or distributed system. The process could also prove a solution to the problem of gas flaring from oil and gas wells by converting flared methane into valuable liquid fuels and chemicals which can be easily stored and transported.

Your project team is to develop a design for a commercial scale facility and via your economic analysis determine if it is economically viable. The typical rate of return of 15 % internal rate of return over a 15-year period is normally expected. However, in this case the reduction of greenhouse gases is high on the list of the government's plans to reduce CO_2 in our atmosphere, so there may be an opportunity for government incentives. If needed to meet economic viability, what government incentives would be required? This concept is likely a more attractive alternative to storing CO_2 in underground caverns for which there is no economic return.

The reference by Tu and Whitehead provides CH_4 conversion and selectivities to H_2 , CO, acetylene, ethylene, propene and propane. The selectivities shown change modestly with discharge power. Management has asked you to decide on the most economic overall application of this technology, so you have freedom to adjust the process to produce, purify and sell any combination of these products that maximizes the NPV of the plant. However, you are limited to a natural gas feed rate of 5,000 SCFM for the first commercial plant. Ideally your group would run preliminary process and economic calculations incorporating discharge power and its impact on conversion and selectivity to decide the optimum process conditions and thus the product mix.

Mixtures of H_2 and CO are generally referred to as "syngas" that has value to produce other valuable products. Note that there is an excess of H_2 and CO in the product mix. Obviously, it is the building block mix to produce the products listed. Recovering this mixture may be another valuable product for sale. Is there any opportunity to use this mixture as a recycle stream?

Your team must determine:

- 1. Source of CO_2 available. Can less than 100% CO_2 be employed?
- 2. Source and compatible amount of methane available.

3. How to address the impurities in the methane as the information available on the reactions do not include components other than methane.

- 4. Can renewable solar energy be employed?
- 5. Total products produced.

References: (PDF copies available upon request)

Plasma Catalysis, Xin Tu J. Christopher Whitehead Tomohiro Nozaki Editors. Chapters 1 and 9 in particular. (Available via Franklin)

Plasma-Catalytic Dry Reforming of Methane in an Atmospheric Dielectric Barrier Discharge: Understanding the Synergistic Effect at Low Temperature by X. Tu and J.C. Whitehead, Applied Catalysis B: Environmental 125 (2012) 439-448

One-Step Reforming of CO₂ and CH₄ into High-Value Liquid Chemicals and Fuels at Room Temperature by Plasma-Driven Catalysis by Dr. Li Wang, Dr. Yanhui Yi, Dr. Chunfei Wu, Prof. Hongchen Guo, and Dr. Xin Tu, Angewandte Chemie <u>https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201707131</u>

Plasma Chemistry by Alexander Fridman, Drexel University, Cambridge University Press, 2009 (available in Van Pelt)

Other electronic references will be provided that will be most useful to your efforts.

7. Cellular Agriculture (Recommended by Jeffrey D. Cohen, Janssen R&D)

Cellular agriculture is an emerging biotechnology aimed at producing cultured meat by accumulating animal cells grown in-vitro [1]. It may have the potential to slow the rate of climate change, nourish an increasing human population, repurpose farmland, and reduce the slaughter of animals.

The first cultured meat burger in 2013 reportedly cost \$332,000 in research funds to produce. More recently, a strip of steak and chicken nuggets were both reported to cost \$50 each to produce in 2019, and in 2020 a chicken burger cost \$35 to produce. These were produced in research facilities, rather than production facilities, and are not accurate indicators of cultured meat's future price when produced for sale [2].

Startups are working to make cultured meat, i.e., synthetic- or clean-meat, employing a cultured meat process (CMP), the same price as conventional meat. As production efficiency increases, the price of cultured meat could become equivalent to or less than conventional meat. This could increase food security for a greater number of people across the globe.

Global production and consumption of meat continue to surge as demand is driven upward by population growth, individual economic gain, and urbanization [3]. In 2012, the Food and Agriculture Organization (FAO) of the United Nations projected the global demand for meat would reach 455 M metric tons by 2050, a 76% increase from 2005. Likewise, the global demand for fish is projected to reach 140 M metric tons by 2050. The majority of this increase is attributed to middle-income countries.

Muscle, fat, collagen, and other cells may be collected from living animals and subsequently cultured, i.e., grown to accumulate in laboratory and production facilities to manufacture cultured meat, with additional downstream processing [4,5,6].

The objective of this project is to design and estimate the economics of a manufacturing process to produce a cultured meat product consistent with the details listed below. The upstream process, to produce the cultured meat mass, may employ accumulation of animal cells, e.g., muscle, fat, collagen, etc. in production-scale bioreactors [7], biomass harvest, i.e., solid-separation, and a downstream process to form a composite into an edible product, final packaging, and cold-storage.

Details

- Product is for human consumption
- Annual Production: 35,000,000 lbs. per facility
- CMP type: choice of the project team, e.g., substitute for beef, chicken, pork, fish, other
- Genetically-modified animal cell technology permissible albeit not required
 - Assume animal cell-bank(s) exists and available to your enterprise
- Cell doubling time: TBD according to cell species, typically 24 (+/- 10) hours, cite literature values
- Aerobic upstream process
- Upstream growth media components: predominantly plant based, e.g.:
 - o grain, soybean, as carbon and amino acids source
 - may purchase these preprocessed or install unit operations to make these bioavailable to animal cells
 - Synthetic growth factors, e.g., insulin, vitamins, etc. may be needed
- Product form: composite of CMP, choice of project team
 - o most-straightforward may be an extrusion process for burger, nugget, links, etc. [8].

- Plant-based binders may be used [9], or
- o alternatively, 3D printing has been proposed in this application [10]

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8. Polyhydroxyalkanoate (PHA) – A Biodegradable Polymer (Recommended by W. D. Seider, UPenn and Geetanjali Yadav, NREL)

Traditionally, plastics are derived from petroleum feedstocks. About 6% of the world fossil fuel consumption is used to make polymers (equivalent to the global aviation sector)¹ and it is projected to increase to 20% global fossil consumption by 2050. In 2016, the US generated the most plastic waste globally (about 42 million metric tons)². Polyhydroxyalkanoates (PHAs), biodegradable biopolymers from blue-green algae (cyanobacteria) cells and bacteria, are gaining popularity as substitutes for conventional fossil-derived polymers. In recent years, several hundred products have appeared for an array of applications, including extrusion coatings, extrusion lamination materials, film resins, and injection molding resins. Over the past decade, worldwide companies (e.g., Danimer and Mango Materials in the U.S.) have positioned themselves to provide an important alternative to upcycling of conventional plastic products.

Production costs for PHAs are still very high, largely due to the cost of carbon feedstocks for the bacteria that produce the polymers, and the cost of extracting the polymers after production. The goal of this design project is to synthesize a process to produce PHAs from green microalgal biomass. Researchers (Garcia et al., 2021)³ have reported the production of PHAs from *Scenedesmus* sp. for the first time after careful evaluation of critical nutritional parameters that result in increased PHA accumulation within the algae cells³. Although PHA accumulation occurs naturally in photosynthetic organisms, such as microalgae, their yield can be improved in response to nutrient deficiency conditions in the presence of a carbon source.

As seen in Figure 1, the synthesis of PHA in photosynthetic microorganisms starts with the consumption of acetyl-CoA, grown in a glycolysis fermentation of glucose. Two acetyl-CoA molecules are joined together to form one acetoacetyl-CoA molecule in a \beta-ketothiolase (PhaA) catalyzed condensation reaction. This molecule is then reduced to R-3-hydroxybutyryl-CoA by nicotinamide adenine dinucleotide phosphate (NADPH)dependent acetoacetyl-CoA reductase (PhaB). Finally, PHB synthase (PhaC) catalyzes the binding of R-3-hydroxybutyryl to an existing polyhydroxybutyrate (PHB) molecule through an ester bond, releasing HSCoA. The chemical composition of the resulting PHA polymers can be manipulated by varying the substrates fed to the Scenedesmus sp. algae. Since the synthesis of PHA is regulated at the enzymatic level, the intracellular concentration of acetyl-CoA and free CoA plays a central role in the synthesis of the polymer. The enzymatic activity and the availability of the PHA precursors are dependent on the presence of different compounds (such as glucose, glycerol, and the like) in the growth medium³.



Figure 1. PHA/PHB synthesis pathway from acetyl-CoA in microalgae.

The process to be designed should use their laboratory data to scale-up an industrial process that utilizes closed airlift photobioreactors, light and nutrients (especially glucose) for the cultivation of algae biomass and simultaneous accumulation of PHA within the cells. *Scenedesmus* sp. do not require supplementation with large amounts of exogenous carbon to produce PHA, an economical advantage over the use of higher accumulating bacteria. Also, its tolerance to salinity stress makes its cultivation possible using seawater/wastewater, instead of freshwater. Further, it also produces other valuable metabolites such as lipids and carbohydrates – macromolecules of interest for the production of biofuel and bioethanol, thereby improving the spectrum of utilizing co-product credits.

Next, the microalgal biomass must be harvested using one of the several dewatering techniques such as dissolved air flotation, froth-flotation, etc. The dewatered biomass should undergo downstream processing to disrupt the cells for recovering a mixture of metabolites including PHAs, lipids and carbohydrates. Finally, this mixture should be separated from the residual slurry employing appropriate techniques and/or solvents to recover high purity PHAs ready to be packaged after drying⁴. The remaining culture medium should be recycled to the cultivation step.

The objective will be to demonstrate PHA production (\$/kg of PHA) through microalgae growth achieving an economically favorable internal rate of return (IRR) of the PHA plant, with a minimum of 15% IRR. The design project must incorporate an adequate consideration of each one of the processing stages, their yields, and the market value of the obtained copolymers that have desired polymer properties (e.g., average molecular weight, glass transition and melting temperatures⁵) during economic evaluation.

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9. Mixed PET Plastics Waste to Dimethyl Terephthalate & Ethylene Glycol (Recommended by Stephen M. Tieri, DuPont)

Plastics and polymers are integral to the modern world and global economy; enabling innovations in transportation and construction efficiency, personal and food safety, electronics, and communication. The inherent durability and potential to adjust physical and mechanical properties with recipe adjustments provides for a fabulous range of applications, but adds significant difficulty and complexity to the question of how to handle the material once the products have satisfied their intended purpose. Traditional plastic/polymer recycling technologies are largely optimized for "clean" uncontaminated material scrap from primary manufacturing of 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 technology to depolymerize polyethylene terephthalate (PET) into dimethyl terephthalate (DMT) and ethylene glycol (EG). This will then enable resin produced with the recycled monomer content to have a significantly lower (up to 30% less) greenhouse gas burden. The company believes consumer interest in more sustainably produced materials, customer demand for products with significant recycled content, and economic conditions are now aligned for implementation of their technologies to be economically successful. While executives and business management are eager to commercialize the new PET waste-to-monomer 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 circular plastics.

Your team has been assembled to design a commercial scale facility to implement the company's new innovative and most robust waste PET depolymerization technologies. While the company's previous economic forecasts indicate significant economic potential from this program/project, based on preliminary investment, cost, and revenue estimates; 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) mixed PET waste to dimethyl terephthalate and ethylene glycol. The mixed post-consumer PET material is expected to contain items from packaging and carpet fiber. This material is expected to be both wet and "dirty"; including moisture, oils, organic/food residue, and with pigment solids (TiO₂ and other pigments). The mixed PET plastic feed is expected to be supplied in standard sized bales. The dimethyl terephthalate (DMT) and ethylene glycol (EG) 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. DMT and EG), raw materials (including mixed PET/plastic 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. Downstream PET polymer production capacity, any potential expansion requirements, and/or additional supporting monomer storage facilities are outside the scope of this project; the design and investment estimates should include appropriate 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 PET polymer processes. Business management identified and narrowed the potential location options to the US Gulf Coast, US Pacific Northwest, and US East Coast; 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.

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- 10. Natural Gas Conversion into Clean Hydrogen and Carbon for Li-ion Battery Electrodes Using Renewable Energy (Recommended by Dr. Matthew Targett, SpruceWorks LLC)

Overview

Decarbonization of the power sector is already underway - big strides are being made in terms of renewable energy availability and cost affordability from wind and solar power. These solutions are scalable now and expected to make significant contributions to decarbonizing the electric power grid. Promising new grid decarbonization technologies, such as advanced nuclear and CCUS, are expected to further contribute to grid decarbonization in next 10~20 years.

Additionally, the increasing availability of inexpensive renewable electricity provides an opportunity to decarbonize energy intensive processes, such as in the commodity chemical industry due to large energy requirements and greenhouse gas emissions⁹. A new potential paradigm for electrification involves replacing fossil fuel-heated systems with renewable electricity to produce commodity chemicals, two examples are hydrogen and carbon black.

- Hydrogen produced conventionally from methane in a high temperature endothermic steam reforming process with a greenhouse gas footprint of roughly 10 kg carbon dioxide emissions per kg hydrogen produced.
- Carbon Black produced conventionally from methane and refinery residual fractions in a high temperature endothermic cracking process with a greenhouse gas footprint of roughly 3 kg carbon dioxide emissions per kg carbon black produced.

Commodity Product	Conventional Process	Emissions kg CO ₂ /kg	Market Size
Hydrogen	Steam Methane Reforming (SMR)	9 [~] 10	130
Carbon Black	Natural Gas Fired Furnace	2~3	18

The general market overview for these two products is shown in Table 1.

Table 1: General Market Overview and Emissions Profiles for Hydrogen and Carbon Black

Decarbonizing chemical processes leverages developments in renewable electrification. Both hydrogen and carbon black can also assist in downstream decarbonization initiatives, in the case of hydrogen providing a means of replacing coal and coke feedstocks in steel making, and in the case of specialty conductive carbon blacks providing materials required for Li-ion batteries used in electric vehicles. The conceptual process design for such a process is shown below in Figure 1.

⁹ Schiffer, Zachary J. and Karthish Manthiram. "Electrification and Decarbonization of the Chemical Industry." Joule 1, 1 (September 2017): 10-14



Figure 1: Using Renewable Energy to Convert Natural Gas into Useful Products – Conceptual Process Design

SOURCE: Transform Materials

Powered by renewable electricity, this process creates sustainable hydrogen for clean energy, and locksin the carbon from the methane source by chemically converting it into durable high-value conductive carbon products.

Electric Arc Plasma

Electrical systems can provide heat to chemical systems via simple electrical resistive or Joule heating. Another means is generation of plasma in volumetric space in which chemical reactants can be directly converted to useful products. According to Dr. Bruce Locke¹⁰ at FSU, plasma, often considered the 4th state of matter, can be defined as a system of highly ionized species which are on average electrically neutral. Plasma systems are used in industry. Some examples include reactors for ozone production for use in water treatment and pollution control, plasma displays in televisions, and lightning. Plasmas are typically made when an electric field is formed in a gas leading to ionization and subsequent electrical breakdown. A plasma contains free electrons and positive and negative ions. These highly energetic electrons and ions can be used for a number of purposes, with particular interest here in initiating desirable chemical reactions in gases, liquids, and on the surfaces of solids. For example, gas phase electrical discharges can be used to either reduce or oxidize (depending upon the chemical environment) hazardous and toxic gases such as nitrogen oxides, sulfur dioxide, and many volatile organic compounds. Gas phase

¹⁰ https://www.eng.famu.fsu.edu/cbe/research/plasma-reaction-engineering

electrical discharges have also been used commercially to produce ozone for many years. Liquid phase discharges have recently been used to oxidize small aromatic organic species, destroy microorganisms, and for use as tools in surgery. Surface discharges are commercially used for the plasma coating of polymers.



The advent of the plasma arc in the chemical process industry dates to the 1940's in Germany with the Chemische Werke Hüls GmbH¹¹ development of an 8 MW torch for the synthesis of acetylene¹² in a hydrogen plasma. The Hüls process shown in Figure 2 is configured to convert methane and mixtures of light hydrocarbon gases into acetylene¹³.

Other thermal arc processes for acetylene production have been developed and operated with success, including the DuPont thermal arc process in the 1960s and most recently a handful of start-up companies have reportedly developed new technologies¹⁴.

Figure 2 : Hüls Arc Process of the 1940s - Arc Arrangement for Acetylene Process

Microwave Plasma

US-based start-up, Transform Materials, has emerged as a new producer¹⁵ of acetylene using a different methane pyrolysis technology based on microwave plasma to split the methane molecule into hydrogen and acetylene. Following the microwave plasma reactor, the Transform Materials process uses

¹¹ https://history.evonik.com/en/predecessor-companies/huels

¹² Boulos M.I., Fauchais P., Pfender E. (2016) Handbook of Thermal Plasmas. Springer.

¹³ Vladimir Haensel and Ernest Cotton; Plant of Chemische Werke Hüls, U.S. Technical Industrial

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¹⁴ <u>Stephen Harrison, Microwave Plasma for Natural Gas Transformation to Acetylene and Hydrogen;</u> Petro-online, 2021

¹⁵ ibid

Temperature Swing Adsorption (TSA) to remove heavier hydrocarbon impurities from the product gas stream. Then, the lighter hydrogen and acetylene leaving the TSA are separated to capture the acetylene¹⁶. Finally, the hydrogen is purified using a Pressure Swing Adsorption (PSA) system, which is a common final stage hydrogen purification technology.

Reaction Pathway – Methane to Acetylene

The overall conversion of methane to acetylene consists of the following.

 $2CH_4 \rightarrow C_2H_2 + 3H_2, \ \Delta H^0 = 377 \text{ kJ mol}^{-1}$

Plasma can achieve similarly high temperatures (>2000 K) as typical burners, or heaters, and can produce chemically active species such as radicals, ions, and high-energy electrons, which promote the initial activation of methane *via* the formation of a methyl radical. The methyl radical is highly reactive recombining to form ethane and subsequent steps shown below, terminating at the formation of elemental hydrogen and carbon solids. The first step is considered the rate limiting step¹⁷.

 $CH_4 \rightarrow CH_3^* \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C+H_2$

At sufficiently high temperatures, fast quenching of the reaction is required to prevent the successive thermal pyrolysis of C_2H_2 . Given this, it is essential to immediately lower the reaction temperature after the formation of acetylene to fix the product in the acetylene state. According to experimental research at SINTEF¹⁸ in the 1970s, at a reaction temperature of 1800 K or higher, the reaction time should be limited to approximately 4 ms in order to guarantee a C_2H_2 yield greater than 70%, as shown in Figure 3. Similar kinetic studies have been reported by Finke¹⁹ of the Idaho National Lab and by Miller^{20,21} of British Oxygen Company.

Chemistry Process Design and Development, 1976 15 (3), 439-444

¹⁹ Fincke etal; Thermal Conversion of Methane to Acetylene Final Report, Idaho National Engineering and

Environmental Laboratory, 2000

¹⁶ ibid

¹⁷ Louis Kassel; The Thermal Decomposition of Methane, Journal of the American Chemical Society, 1932, 54 (10), 3949-3961

¹⁸ Holmen etal; High-Temperature Pyrolysis of Hydrocarbons. 1. Methane to Acetylene, Industrial & Engineering

²⁰ Miller SA (1965) History of Acetylene Industry. British Oxygen Co., Guildford, UK.

²¹ Miller SA (1965) Acetylene: Its Properties, Manufacture, and Uses (11th ed.). Academic Press, New York, NY, USA.



Figure 3: Effect of residence time (reaction time) on the product yield, calculated based on a simplified reaction

Project Statement

For the purposes of this project, the objective will be to determine the optimal commercial microwave process configuration for converting methane to acetylene, purification of acetylene, and converting acetylene into acetylene black. The overall plant design will be comprised of two main processing blocks: Step 1 - natural gas to acetylene, and Step 2 - acetylene to acetylene black, as shown below in Figure 4.



Figure 4: Overall Process Block Flow Diagram

The Step I conversion of methane to acetylene will be based on the Transform Materials process as described in their granted patent²² specification. Their system is modular and comprised of multiplexed microwave generators which consume nominally 100KW each with a conversion efficiency of approximately 86% (electrical power to microwave power). Heat losses on the reactor system is specified as nominally 10%.

²² U.S. Patent 10,676,353



Figure 5: Step 1 - Conversion and Purification of Acetylene from Natural Gas SOURCE: Transform Materials

The Step II conversion of acetylene to acetylene black will be based on Pentacarbon process²³. Acetylene black is a high purity carbon black produced in closed reactors obtained from the thermal decomposition of acetylene. Due to its production process, acetylene black differs from other carbon black grades. Owing to the high crystalline carbon structure of acetylene black it exhibits higher thermal conductivity and higher electrical conductivity than carbon blacks made in other processing configurations. Acetylene blacks are available in powder form, difficult to densify and impossible to pelletize. Due to their high conductivity, acetylene blacks are primarily used as conductive blacks in electric cells, batteries, antistatic rubber and plastic applications and cable manufacturing. Shown below in Figure 6 is a simplified schematic process for producing carbon black. Other process descriptions would indicate that the use of air is limited to initial start-up conditions to sufficiently heat the system up to standard operation temperature. In the patent literature²⁴, Denka Corporation specifies a reactor temperature range of 1800°C – 2200°C and residence time of approximately 10 seconds, and Shawinigan²⁵ provides reactor sizes and flow rates. Additional kinetic information can be found in Miller's acetylene compendium²⁶.



²³ https://pentacarbon.de/en/wiki/

²⁴ U.S. Patent 4,340,577

²⁵ U.S. Patent 2,453,440

²⁶ Miller SA (1965) Acetylene: Its Properties, Manufacture, and Uses (11th ed.). Academic Press, New York, NY, USA.

Figure 6: Acetylene Black Process SOURCE: Pentacarbon

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, natural gas pretreatment, acetylene production, quench design, gas handling, purification and recycle, acetylene black production and purification.

For reference, shown below in Figure 7, is the main processing equipment for a furnace black plant. A portion of these unit operations will overlap with typical acetylene black process.



a) Furnace black reactor; b) Heat exchanger; c) Collecting or agglomerating cyclone; d) Bag filter; e) Carbon black outlet to
pneumatic conveying system; f) Tail gas blower; g) Collector; h) Exhaust air filter; i) Blower for the pneumatic conveying air;
j) Fluffy storage tank; k) Pelletiser; I) Dryer drum; m) Conveying belt; n) Storage tank for carbon black pellets

Figure 7: Furnace Black Production Plant

Project Statement – defined criteria

Overall

- Capacity: 10 TPD H₂ production, based on an array of 100KW individual-sized microwave generators
- Process Inputs: Natural Gas, Renewable Electrical Power
- Synergistic siting: Ideally near utility-scale solar or wind farm, with close proximity to natural gas pipeline, and close proximity to a hydrogen consumer or hydrogen pipeline

Step I – Acetylene Production

- Identify potential needs to purify the natural gas feed with pre-treatment steps to remove potentially incompatible impurities CO₂, H₂S, N₂, H₂O as deemed necessary
- Determine the amounts of recycle hydrogen
- Decide on the amounts of unconverted methane, and coproduct light hydrocarbons that can be recycled back to the conversion step. Decide whether fuel gas will be sold as an article of commerce or fully recycled back to the converter

- T, P, res time : as indicated in cited reports *NOTE patent specification indicates vacuum pressure operations, increasing pressure may improve economics
- Utilize reaction kinetics available in cited references, to size the individual reactors, and maximize to acetylene production
- *NOTE the bulk average temperature of the reaction zone will be lower than the observed kinetics would indicate due to high excitation and activation of electron species in the microwave plasma, which will require some special heuristic treatment to be determined as a portion of the project scope
- Calculate the overall specific energy requirement to produce acetylene, i.e., kW-hr electrical / kg $C_{2}H_{2}$
- Decide on method of quench
- If water/steam quench is used, then determine needs for feed water, and fate of spent water in terms of treatment, potentially requiring another unit operation such as a biological wastewater treatment plant (WWTP) or other equivalent
- Decide on method of gas purification

Step II – Acetylene Black Production

- T, P, res time : as indicated in cited reports²⁷
- Utilize reaction kinetics as available in cited references to size the reactor
- Decide on temperature control for the reactor, given the exothermic nature of acetylene decomposition, special attention given to avoidance of runaway reaction.
- Decide on cooling of the product gas and product solids streams and whether or not any of this heat can be utilized in an efficient manner to preheat feed streams to Step I converter or used in other energy efficient ways
- Produce hydrogen at pipeline grade purity.
- Price the acetylene black according to its market value as a thermally and electrically conductive specialty material

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

- converter designs (temperature, volume)
- heat integration designs

Key Output Variables – to be determined by modelling

- OPEX cost, \$ per ton of solid and gaseous products; kW-hr_{el}/kg H₂, kW-hr_{el}/kg C₂H₂
- Capex investment, \$ per ton of annual CH₄ consumption
- IRR/NPV

²⁷ Zádor etal; Initiation Reactions in Acetylene Pyrolysis, Submitted to the Journal of Physical Chemistry A (2017)

• Financial projections must take into account tax credits for CO₂ utilization as indicated in section 45Q of US tax code.²⁸

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EOR			500		ŝ	100		100		-	35
Utilization			25			25		25			35
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Credit Value (\$/tCO ₂) 0 07 09 09	-										-
Credit Value (\$/tCO ₂) 0 07 07 09	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026

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

²⁸ https://www.energy.gov/sites/prod/files/2019/10/f67/Internal%20Revenue%20Code%20Tax%20Fact%20Sheet.pdf