

Para-Xylene Production from Bio-renewable Feedstock

LCGPM



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Executive Summary- Wyatt Keller

The objective of this process is to manufacture para-xylene via reaction pathways utilizing fructose as a feedstock with chemical grade purity (99.8 weight percent), at a minimum of 250 million pounds per year. The process was designed and modeled using Aspen Plus, with customized physical property estimations to accommodate chemicals not present in the Aspen Plus databanks. This process utilizes three key reactions: the conversion of fructose to 5-hydroxymethylfurfural (HMF), HMF to 2,5-dimethylfuran (DMF), and DMF to para-xylene. Reaction pathways and conditions were developed using literature research, and making several key assumptions, which will be discussed in detail throughout this report.

The process simulation produces 262 million pounds of para-xylene per year at 99.8% weight purity. An installed Fixed Capital Investment (FCI) totaling \$63 million was found to build the plant from the ground up. A net present value of -\$350 million was found at a 10% discount factor, with an NPV of -\$650 million at 0%. This results in no IRR because there is no payback period. These values are heavily affected by risk factors such as para-xylene, byproduct, catalyst, solvent, and feedstock prices.

Based on the results of this process design and simulation, it is our recommendation that more research be conducted to verify the assumptions (no solvent feasibility, possible side reactions, etc.) made in this design before any commitment to building a facility. Because the economics of this process are highly sensitive to small changes in sales prices of para-xylene and byproducts, a more-detailed analysis of all the economic variables and assumptions should be conducted. Additionally, more information regarding an ion exchange column used for separation in Section 1 must be obtained, in order to examine its impact of the process feasibility.

Scope of Work- Zach Witters

Project Definition

The overall goal of this project is to produce 250 MMlb/year of Para-Xylene in an efficient, renewable, and economically feasible manner.

Para-xylene (PX) is an aromatic hydrocarbon that is heavily used in the plastics industry as a reactant for dimethyl terephthalate (DMT) and terephthalic acid (PTA). DMT is a diester commonly used to make plastic bottles and PTA is an acid used in the production of cigarettes. PX has historically been produced from petroleum products where roughly 0.5-1% of crude oil consists of PX [1]. Although oil reserves are not in a severe and immediate shortage, these petroleum sources will eventually run out. PX is a promising source, for the plastics industry, that can be derived from many simple sugars that can be obtained from organic waste such as corn stover or sugar canes. Currently the market for PX-derived plastics is growing quickly. The market for PX is robust and generally sees a steady year-on-year demand growth in the range of 6-8% per year [2]. Due to this market growth increase, the amount of processes needed for manufacturing PX also increases, this is further developed through concern that shortages may rise due to finite oil reserves. Fortunately, glucose and other simple sugars can be used as a viable feedstock for this process while maintaining efficiency, avoiding high costs of separation of PX from other petroleum products, providing a sustainable resource for PX production.

This report outlines the process of converting fructose into para-xylene at a rate of 262 million pounds of para-xylene (PX) per year at 99.8% mass purity. This process has not been industrially proven; however, the company Virent out of Madison, Wisconsin has developed novel technologies in this industry to form historically petroleum-based products from sustainable resources. [3] While the process of converting fructose to PX does not have a well-defined industrial method, we have scaled research and developed assumptions that would be represented in an industrial size plant. For

simplification and better understanding, our report is split into three sections, each containing a major reaction. The first section is fructose to 5-hydroxymethylfurfural (HMF), the second section is HMF to 2,5-dimethylfuran (DMF), and the third section is DMF to PX. Each section has its own difficulties and constraints.

Constraints

Global para-xylene market demand was estimated at 36.83 million tons (81196 million pounds) in 2014. [4] The demand for para-xylene is robust and generally sees a steady year-on-year growth in the range of 6-8% per year [2]. Thus using 6% to estimate the demand increase per year in pounds of PX, we see an increase of about 4870 million pounds per year. While there is ample room for growth, our process is only 5.4% of the global growth per year; it is difficult to scale our process up. Capital costs of our process dramatically increase when the production rate is increased.

Section one, the process of converting fructose to HMF, has large capital costs due to long reaction times (12 hours) resulting in very large reactor volumes needed for the reaction. These large reactors are required due to solvent concentrations up to 90% by mass. The solvents are required to decrease byproducts of reactions, thus decreasing solvent concentrations, while decreasing capital cost, will ultimately decrease the profitability of our process due to lower yields and more separations processes required. Major constraints in this project are reactor volumes, currently in the order of 1,000,000 gallons, where 3 tanks are run in series in order to our process continuously. To reduce capital costs associated with catalysts, solvents, reactors, and separations a smaller plant will have to be designed, while more research must be conducted to reduce solvent concentrations and in turn decrease capital costs. This will allow for economically friendly payback periods and larger incentives to produce PX from renewable sources such as fructose or glucose.

Section two, the process of converting HMF to DMF, uses a Platinum and Cobalt catalyst. The current cost of Platinum is around \$34/gram [5]. To decrease the cost of section 2's catalyst a bimetallic catalyst is used which uses only 3 percent by mass of platinum. It should be noted that the larger the production the more catalyst will be required for this process and the higher capital costs will rise. Further research will have to be done to decrease the amount of catalyst used in the reaction or develop catalysts that still has a high yield and conversion of HMF to DMF. This will ultimately allow for further increase in the production rate of our plant.

Section three, the process of converting DMF to PX, also contains a solvent that is concentrated at 90% by mass. The solvent in this section also contributes to large reactors and large recycles. Hexane which is priced at 44 cents per pound is extremely expensive, especially when our product is priced at 70 cents per pound. Thus, it is essential to recycle as much hexane as possible in section three's process to reduce production costs. The volume of the reactor required for section three is 132,000 cubic feet where two will be in parallel to allow for continuous operation. The catalyst for this reactor is 12724 lb, greatly increasing the size of the reactor needed for this section. The combination of catalyst and solvent requirements to keep high PX yields and DMF conversions also require a smaller process.

Our production is kept low to keep capital costs manageable and in turn allow for an implementable plant that produces profitable PX derived from renewable process. The specifications of our plant are as follows.

Introduction- Zach Witters

Background

PX has historically been produced from petroleum products due to the large production and low costs of hydrocarbons. Although oil reserves are not in a severe and immediate shortage, these petroleum sources will eventually run out. To reduce the amount of oil consumption, many ideas have been created to decrease the amount of oil consumption and create a sustainable energy infrastructure by producing biodiesel. One of these innovations has been to convert fructose to PX. The earliest pilot plant developed for this process is Virent, which was built in 2010. This plant was originally developed to produce pure hydrogen for fuel cell vehicles, however the market did not take off. Thus they have switched their R&D to focus on the production of PX that they sell for both automotive and jet fuel purposes. Their pilot plant is capable of producing 10,000 gallons of bio gasoline per year. “2011 was a year of firsts. Virent produced the first bio gasoline from corn stover and pine harvest forest residuals as a recipient of the DOE’s grant to the National Advanced Biofuels Consortium. Virent produced PX from plant sugars, becoming the first company to produce the missing 70% needed to create the first 100% renewable PET packaging. Virent also received its largest federal award to date, up to \$13.4M from the DOE to convert the corn stover to jet fuel. Finally, Virent also welcomed its first chemical customer, The Coca-Cola Company, to its list of world-class partner companies.” [3] These past accomplishments show the how promising the development of PX from fructose and other simple sugars can be.

Business Opportunity

Para-xylene is an aromatic compound used as a solvent in the printing, rubber, leather, plastics, biofuels, and medical industries [6]. It is most often used as a feedstock material for the production of dimethyl terephthalate (DMT), purified terephthalic acid (PTA), or dimethyl-terephthalate (PET)-saturated polyester fibers. In fact, 98% of the annual consumption of PX is for creating PET fibers [7]. These

polyester fibers can be used in a wide variety of ways such as producing plastics for water and soda bottles, chemical and food containers, and fabrics used by the textile industry to produce clothing, bedding, upholstery, as well as other products [8]. As PTA is used predominately for plastic bottles in the U.S., it scales during warming seasons and usually sees around 75 c/lb and 65 c/lb depending on the season [7]. In addition to the plastic and fibers industry, PX can be used as a biofuel for the future and in turn reduce greenhouse gas emissions.

The Asia Pacific region dominated the global para-xylene market and accounted for 79.2% of the overall demand in 2014. Asia Pacific was followed by North America and accounted for 11.7% of the global demand in 2014. [4] Developing renewable means of producing hydrocarbons in the U.S. could help integrate renewable fuels into our energy infrastructure in the future. It could be promising to develop an infrastructure of producing biofuels for other applications (such as the plastic or fiber industry), then when fuel prices get high enough, renewable fuels can be integrated into energy infrastructures. This could help to reduce the U.S.'s dependency on fuels in the future.

It is extremely important to note that, in order for PX to be used for other processes, it must be produced in high purity to avoid decreasing the efficiency in future processes and impurities in consumer goods. For example, to create polyethylene terephthalate (PET), PX is first converted into terephthalic acid using a cobalt-manganese-bromide catalyst. To avoid catalyst poisoning, the PX must be very pure when it is used to generate the terephthalic acid. Safety concerns are introduced when using impure feedstocks to produce consumer goods. These impurities, which could dissolve in water from plastic bottles, could have serious health concerns for the public. In addition to purity, para-xylene is not a prominent component in crude oil and producing PX from petroleum sources is a very energy-intensive process involving many separation and distillation processes. Producing PX from a sustainable resource where the reactions (depending on the feedstock and catalysts) can be manipulated and

optimized through research will allow for a more pure PX product through a less energy-intensive process, thus producing PX in a more economically promising way.

Broader Impacts & Contemporary Issues

As it was stated in the Business Opportunity section, PX is normally derived from petroleum sources. In recent years, the US has consumed about 2.5 times more crude oil than has been produced, thus requiring imported oils [9]. With the fluctuating oil market (especially in more recent times), this causes the PX market to fluctuate as well. Moving to renewable resources would remove the instability of the para-xylene market. Also, as stated in the Business Opportunity section, PX must be made with high purity to create terephthalic acid without poisoning the catalyst used in this process. Figure 1 depicts the fluctuations in oil and PX prices over time.

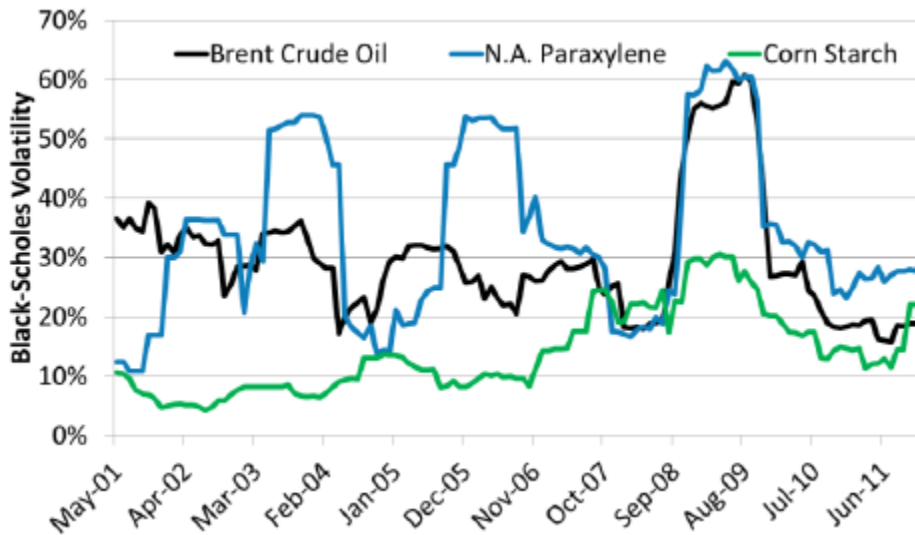


Figure 1. Fluctuation of PX price and oil prices, where corn starch is a much more stable feedstock price than crude oil [7].

Alternative Approaches

There are many companies that are currently producing PX for plastics and are considering selling them as hydrocarbons developed from renewable means. Three of these companies are: Gevo, Virent, and Avantium [10].

Gevo, a fermentation facility in Luverne, Minnesota, produces isobuanol, ethanol and protein-rich animal feed. They use renewable process to develop hydrocarbons that are sold as either solvents, reactants, or sold as biofuels. These biofuels allow for neutral greenhouse gas emissions. Isobuanol has broad market applications as a solvent and a gasoline blend-stock that can help refiners meet their renewable fuel and clean air obligations. Crude oil is increasingly being mixed with renewable biofuels to decrease our overall greenhouse gas production. While this is a promising way to produce biofuels, our process allows for a more energy dense fuel that can be sold to a much larger market when the prices of fuel increases and when research on the process makes the process efficient enough where it is economical to sell as biofuels. Biofuels still have a long ways to compete with the low cost of crude oil, and much more work is needed to be done. However, if the cost is decreased to the cost of fuels, the market will greatly increase.

Avantium and Virent both are focused on deriving hydrocarbon aromatics from simple sugars. This is exactly our process, however since this is such a new field their actual process is not well defined in industry and it is an extremely competitive market. "Avantium was founded in February 2000 as a spin-off from Shell. The objective was to accelerate and exploit the application of high-throughput R&D, initially developed by Shell for catalysis research, across a range of industries." [11] Research seems to be a large part of both Virent and Avantiums business plan, this is due to the high solvent concentrations and unknowns present in published research. However due to the high cost of levulinic acid (2.25\$/lb) (a byproduct commonly found in our reaction scheme) these processes can produce small amounts of PTA

that will fund research to further decrease the capital costs, solvent concentration, catalyst costs, and unknowns associated with this process.

One alternative that we considered entailed producing PX from glucose. Glucose is isomerized to fructose and then further reacted to HMF. While this process allows for the byproduct of levulinic acid, it has additional concerns related to capital costs. The Hydrochloric acid catalyst and salt in this reaction are known to overreact fructose to additional byproducts. To solve this problem a biphasic reactor is used. As stated earlier, the first section of the process converts glucose to 5-Hydroxymethylfurfural (HMF). In the aqueous phase, glucose is isomerized to fructose and then dehydrated to HMF. By doing so, the yield of HMF is increased compared to direct conversion of glucose to HMF. The reaction uses a Lewis acid, Aluminum Chloride (AlCl_3), to isomerize glucose to fructose. Following the isomerization, Hydrochloric Acid (HCl) catalyzes the dehydration reaction of fructose to HMF. The feed conditions of the reactor are 5% weight glucose in water that has been saturated with salt (NaCl). The Lewis acid catalyst is fed at a molar ratio to the organic phase of 1 to 67 with glucose to maintain the proper reaction conditions [9]. This resulted in a reactor volume of upwards of 64 million cubic feet. This is simply impractical and other alternatives have been looked into this semester.

Reasons Behind our Approach – William Duncan

Our approach presents a practical means of synthesizing para-xylene from fructose at a total conversion of 75%, presenting a promising way of producing para-xylene that could be further used to produce PTA, DMT, or PET. The current design provides a good initial design that uses bio derived feedstocks to achieve products that are normally achieved from crude oil. The ability to create commodity chemicals at high purity is desirable especially using alternative reproducible energy sources. Also, the choice to redesign section one was driven by trying to reduce the dilution in our process.

Accordingly, the approach that was taken reduces equipment sizes and equipment costs. The new chemistry applied to the first section conveniently uses products that are more environmentally friendly and are not toxic or flammable. Accordingly, safety has been improved for the process. Similarly, our proposed process also allows for a high purity product (99.8%) that can be used as a reactant without poisoning other process reactions. This allows for a very promising and marketable product.

Description of Base Case

Process Description – Zach Witters

Our process produces 262 MMlbs/yr of PX. This is done through 3 reaction schemes that dehydrogenate fructose to an aromatic ring. Figure 2 shows a basic process flow diagram for this process which includes all three reactions, the appropriate purges, decants, and recycle streams.

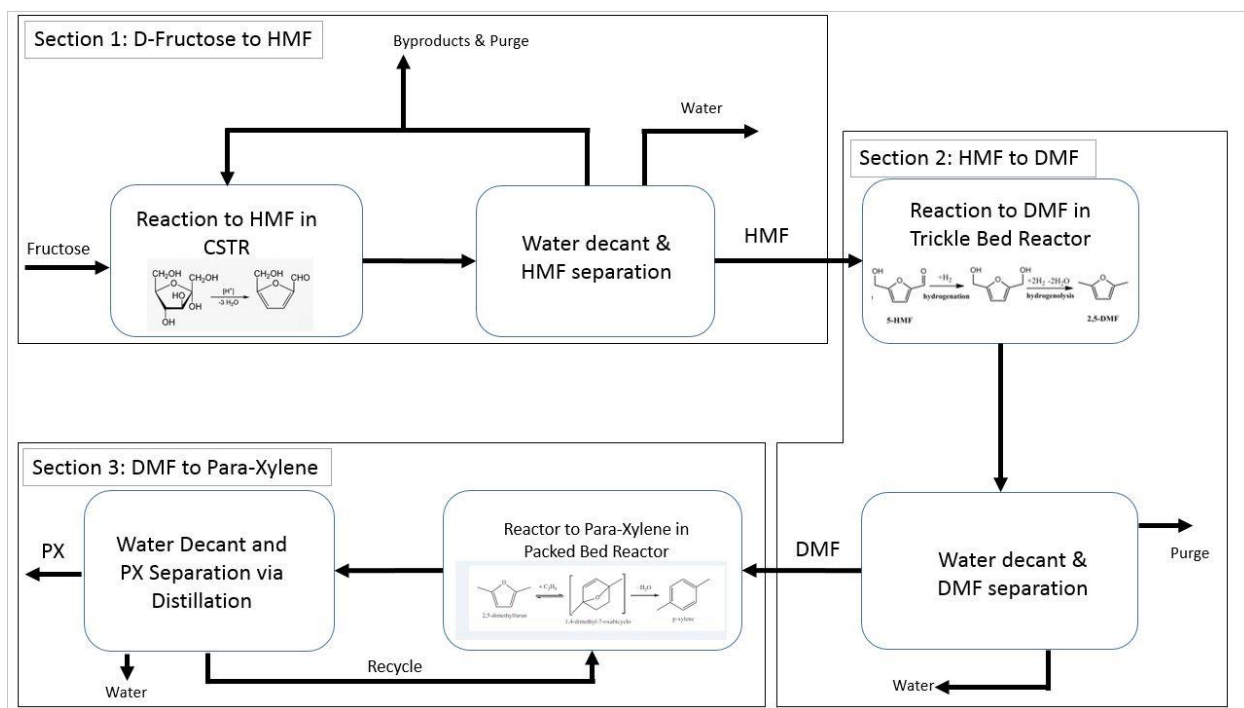


Figure 2. Shows a block flow diagram of our entire process. It also highlights what each section is meant to accomplish.

This process has been split up into three sections: one for each of the reactions. Section 1 is for the reaction of fructose to HMF, Section 2 is for the reaction of HMF to DMF, and Section 3 is the reaction of DMF to PX. Each of the flow sheets pertaining to each section are given as well as the feeds, products, byproducts, reaction conditions, and conversions. Figure 2 shows the respective sections and how each section correlates to the other. Further explanation of each section is presented in the associated Section part of Process Description.

Overall Flow Sheet

See Appendix #2 for a complete flow sheet.

Overall Mass and Energy Balance

See Appendix #3 for the overall energy and mass balance.

Description of Physical Properties – William Duncan

For this simulation, some of the components we needed were not in the Aspen Databanks. Accordingly, we were required to do lots of properties estimations. To start, our total components list can be seen on the next page in Table 1:

Table 1. Components list for all simulations.

Component ID	Component name	Alias
D-GLUCOS	.ALPHA.-D-GLUCOSE,-MONOHYDRATE	C6H14O7
MALTOSE	MALTOSE	C12H22O11-N2
FRUCTOSE	D-FRUCTOSE	C6H12O6-N1
ISOPROP	ISOPROPYL-ALCOHOL	C3H8O-2
NH4CL	AMMONIUM-CHLORIDE	NH4CL
HMF	5-HYDROXYMETHYLFURFURAL	C6H6O3-N5
IMF		
1-BUT	N-BUTANOL	C4H10O-1
DMF	2,5-DIMETHYLOXOLE	C6H8O-N1
DMTF	CIS-2,5-DIMETHYLTETRAHYDROFURAN	C6H12O-N22
2MF	2-METHYLFURAN	C5H6O-N1
CH4	METHANE	CH4
H2O	WATER	H2O
HEXANE	N-HEXANE	C6H14-1
ETHYLENE	ETHYLENE	C2H4
PX	P-XYLENE	C8H10-3
MPB	1-METHYL-4-N-PROPYLBENZENE	C10H14-E10
H2	HYDROGEN	H2
HEXDIO	2,5-HEXANEDIONE	C6H10O2
CO2	CARBON-DIOXIDE	CO2
CO	CARBON-MONOXIDE	CO
HEXANOL	1-HEXANOL	C6H14O-1
PROPANE	PROPANE	C3H8

Some of the components in our simulation file are not currently being used. Some of the components were introduced for alternative designs or separation methods but were not implemented in the final design. Components in Table 1 that are not used in the final design are 1-butanol and 2,5-hexanedione. Glucose and Maltose are not found in the simulation either but are present because an ion exchange column is used to reach a fructose purity of 99%, but is not modeled. This will be discussed in detail in the description of Section 1.

Property estimation was done for most components followed by the letter "N" in the alias name. These components tended to not have complete property parameters but are present in the

databanks. However the component isoproxymethylfurfural (IMF) did not exist in the databank. Accordingly, the molecule was drawn under the mole structure in the properties window of AspenPlus. Once the molecule was drawn, the bonds were calculated. This allows AspenPlus to determine the general structure of the molecule and start to estimate some parameters of the molecule.

Next, pure component data was estimated. First, boiling points (TB), critical temperatures (TC), critical pressures (PC), standard enthalpies of formations (DHFORM), ideal gas heat capacities (CPIG), vapor pressures (PL) and enthalpies (DHVL) were estimated for HMF and IMF. The other components had enough pure component data to do binary data estimation. After pure component data was finished, the values were compared to values provided by our mentor John Myers. The values were estimated using the same method but through ENRTL which is the electrolyte NRTL property method. The values that were provided were quite close to the estimated values for our project. This was important and valuable to us because it verified the methods that were used for other components as well. We used the values that were provided by John Myers to get the best accuracy and is attached in the appendix.

Then, binary properties were estimated. This was done using the NRTL for the property set. UNIFAC groups were also estimated to get better results as well. To estimate the UNIFAC groups, a table was found in the AspenPlus Help menu that provides a numerical code that corresponds to the functional group in the molecule that is being estimated. We used the table in conjunction with the control panel to assign UNIFAC groups to components that needed to be estimated. Following that, we estimated the binary interaction parameters for all the components except for values that already existed in databanks. This ensured that only missing binary parameters were estimated and existing values were not overwritten. Data for the pure component and binary properties can be found in the

review tab and NRTL tab respectively under the parameters tab in the Methods section of the properties environment within AspenPlus.

Lastly, we had all other missing parameters estimated because some of the needed parameters to compute tower sizing were missing. It is noted that when the simulation is run it asks if the existing parameter values want to be replaced with the estimated value. It is important that the selection “No to All” is chosen to ensure that no existing databank parameters or previously estimated parameters are replaced. The properties file was then used for the simulation of our project.

Each section of this process is discussed on the pages below.

Section 1-William Duncan

Fructose to HMF

Figure 3 below shows the simulation flow sheet for this section of the process (Fructose to HMF). It should be noted that some pieces of equipment were not modeled. Accordingly, each block and its function as well as conditions will be explained in detail.

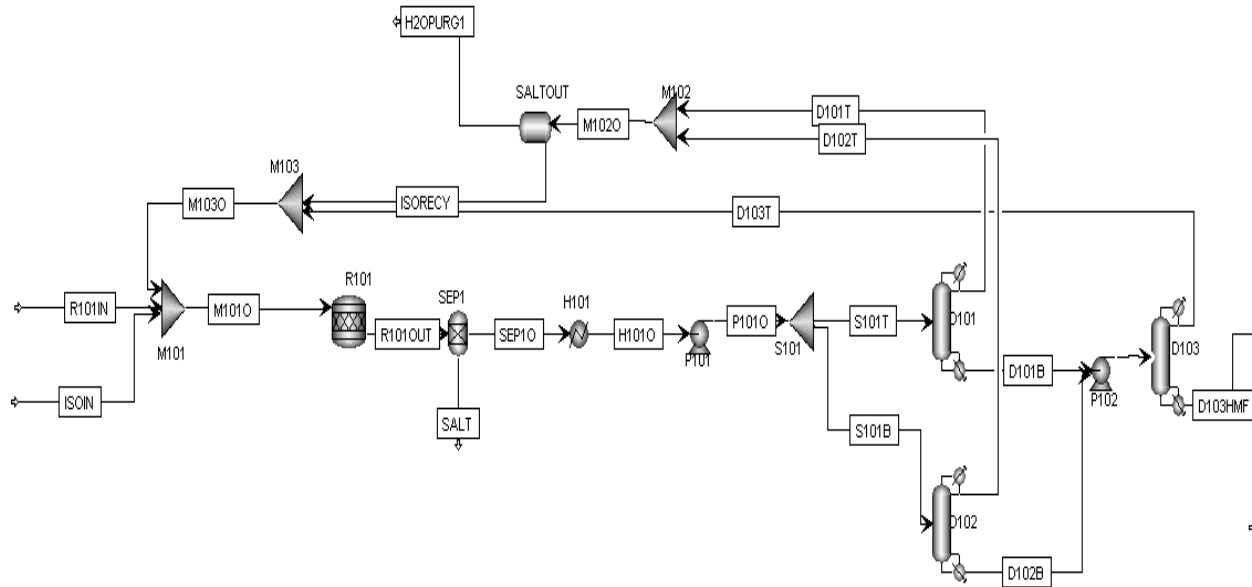
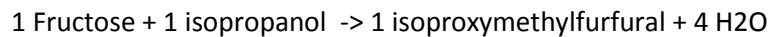
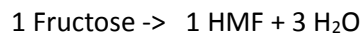


Figure 3. The Aspen Plus simulation flow sheet of fructose to HMF.

Reactions:



The first reaction is the primary reaction and the second reaction is the side reaction to byproducts.

Feeds:

Fructose

Isopropanol (organic solvent)

Catalyst:

Ammonium Chloride (Salt Catalyst)

Products:

HMF

Byproducts:

Isopropoxymethylfurfural (IMF)

Water

Reaction conditions:

Feed = 10 wt% Fructose in isopropanol

2 L of Isopropanol per mole of fructose (approximately 88.4 wt%)

Salt ratio to fructose is 0.5 (approximately 1.6 wt%)

Temperature = 248°F

Pressure = 14.7 psi

Conversions:

Theoretical: 100% conversion of fructose in a batch system. The literature provides reaction data that produces a 96/4 ratio of HMF to IMF. The total yield is 71% where 65% of that is HMF and the remaining 6% is the byproduct IMF. The other 29% is the production of water in the dehydration of fructose [12].

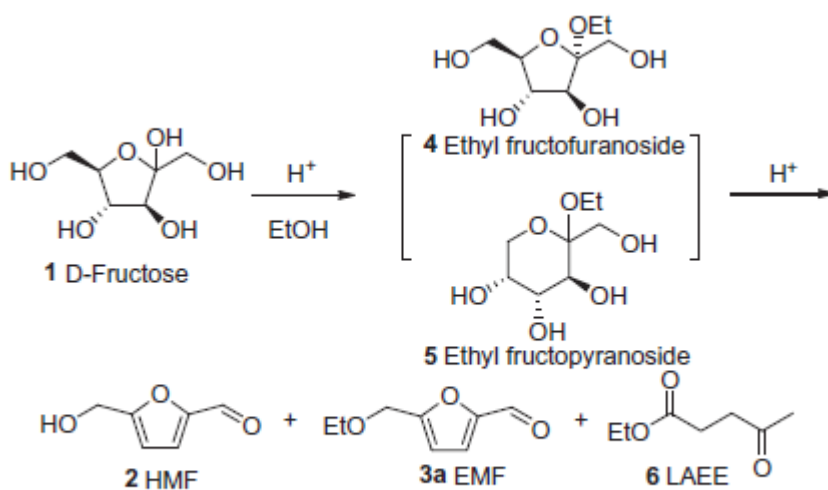
Actual: In the simulation, the fructose is about 100% with the yield of HMF around 64%. The simulation modeled the literature conversion values accurately. However, separation results in some lost materials and lower yields.

Description:

Reactor Conditions and Theory:

As stated earlier, the first section of the process converts fructose to 5-Hydroxymethylfurfural (HMF), which occurs in a group of batch reactors in parallel. The reaction involves a strong Lewis Acid to force the dehydration of the multistep reaction. The first step dehydrates fructose to Isopropyl fructofuranoside and Isopropyl fructopyranoside and one water molecule. The second step dehydrates these intermediates further to HMF and two more water molecules. This second step requires a strong

acid because weak Lewis Acids such as NaCl do not produce desirable reaction conversions. Literature compares different salts and the yields that are produced. Ammonium chloride was chosen because it produced the highest yield of HMF and EMF (5-Ethoxymethylfurfural) [12].



Scheme 1. Conversion of D-fructose (1) into HMF (2) and EMF (3a).

Figure 4: Reaction Scheme for D-Fructose to HMF

Isopropanol was used for the solvent because it obtains high yields and reaction conversions. The solvent is also desirable because it is less reactive in the system compared to other solvents such as methanol.

The components of the reaction are also important for many reasons. Mainly, the products do not have azeotropic behavior with HMF, which allow for the isolation of the product easier. Also, the components are more environmentally friendly compared to other methods that produce HMF such as ionic liquids [12]. However, isopropanol has an azeotrope with water, which requires further treatment to separate isopropanol that is recycled back to the reactor. This separation will be discussed in detail later along with an alternative design that was analyzed as well.

The reaction runs in a group of parallel batch reactors at a temperature of 248 degrees Fahrenheit and atmospheric pressure. The feed conditions to the reactor are 10% fructose by weight, 1.6% NH_4Cl by weight and 88.4% isopropanol by weight. Multiple reaction conditions were tested, but these conditions matched with the selection of isopropanol as the solvent produce the best ratio of HMF to byproducts with the highest conversion. The reactor is made from stainless steel so that the salt will not corrode the tank environment. The reactors are batch reactors and require a 12-hour residence time to ensure complete conversion [12]. The reactors are designed using literature for the reaction conditions to ensure appropriate conversions and yields are used in the simulation. Accordingly, there will be three reactors in parallel that will all be started and emptied at different times. The system will be similar to fermentation plants where long residence times are handled. There will be a tank that all the reactor material will be fed to after the reactors are emptied. This is not modeled in AspenPlus because it would be a large storage tank. This tank would then provide constant flow to the rest of the process. The control system for the tank would need to make sure that the tanks do not overflow or run empty while the reactors are running so that pumps and other equipment will not run dry and become ruined.

Another important aspect of the catalyst and solvent that are utilized in the design is the ability to be recycled in the process. Literature has tested the recycle ability of the catalyst and provided that after through 4 cycles of reactions with only rinsing the catalyst with isopropanol the conversion was still 99%. After 5 cycles the conversion reduced to 90%, which was attributed to catalyst loss in separation and humin formation [12]. Currently, catalyst recovery is not simulated or priced but has been looked into. In our process, the catalyst is not soluble in isopropanol so the salt will remain in the aqueous phase. Accordingly, a decanter is used to siphon off the water and catalyst. Afterwards, there are two methods of capturing the salt. One was is through an ion exchange column and the other is through

evaporation because the solution is concentrated enough that reverse osmosis cannot be used.

Evaporation is the most likely method because an ion exchange column may clean the water but may cause issues in recapturing the salt after it has been absorbed into the column. It should be noted an analysis of catalyst recovery and economic impacts of the added equipment and utilities should be conducted in future work. This system will be used for the SEP1 block and SALTOUT blocks to recover the needed materials for recycle.

Finally, the literature also tested the scalability of the reaction and ran it with 10 grams of fructose while maintaining the same conditions and weight fractions. They determined that the process is scalable and provides consistent data and similar data to that of the smaller scale reaction [12].

Key Assumptions:

A few assumptions were made in this project to simplify the process. First, we are assuming that scaling up the process to the level that we need would still work and provide similar yields and conversions. Also, we are assuming that the catalyst regeneration would go smoothly and not a substantial amount of mass would be lost in regenerating the catalyst. These assumptions would need to be simulated in AspenPlus and verified for final designs.

Overall Section 1 Process Description:

To start the process, high fructose corn syrup (HFCS) can be obtained easily and relatively cheap at 42% by weight. In a general HFCS plant, 42% HFCS is passed through an ion exchange column to obtain greater than 90% HFCS [13]. Then the 90% HFCS is mixed with the 42% HFCS to make 55% HFCS, which is used widely in soft drinks and as artificial sweeteners.

However, our process has an ion exchange column so that we can obtain purities of greater than 99% fructose. This is possible by choosing the correct ion exchange column and will reduce the cost of

raw materials to by a lower purity of HFCS. Also, it is possible that we could sell the impurities of maltose and glucose back to the HFCS plant to optimize our cost of raw materials. Accordingly, our process starts by increasing the purity of fructose through an ion exchange. A fractionation ion exchange resin will be used to separate fructose from other sugars via chromatographic separation. Literature from Purolite verifies that with the correct resin structure that creates more sites for hydrogen bonding and the correct calcium ion concentration, 42% HFCS can reach purities exceeding 99% fructose [13]. Purolite also has different resins that have life expectancies that can last up to 10 years [13]. The column is not simulated and has not been priced yet, but will be looked into for future work.

After the ion exchange column, the catalyst salt is added to a mixer M101. M101 also has streams ISOIN and M1030 entering it. M1030 is the solvent recycle that sends isopropanol back to the reactor. ISOIN is the makeup for the solvent to ensure the correct reactor conditions. These streams are mixed into stream M1010. This stream enters the reactor at atmospheric pressure and 110°F. The reactor operates at 248°F and atmospheric pressure. The reactor (R101) conditions and yields have been described above in greater detail. After the reactor, the components enter a separator block that removes the catalyst. This separator block (SEP1) is what was used to simulate a decanter and evaporator system. SEP1 was sized as a decanter and included in the economic analysis. However, an evaporator or ion exchange column should be analyzed and incorporated into the final design. The decanter will run at the same conditions as the reactor. The catalyst recovery system was described above and can be seen in greater detail.

Next the stream SEP10 will have all the reaction products and will be free of catalyst. This stream enters a cooler (H101) that operates at atmospheric pressure and condenses the stream to its bubble point. The outlet temperature of H101 is 180°F and the cooler removes 2.02×10^8 BTU/hr of heat. This heater is a concurrent double-sided heat exchanger that is priced with stainless steel to ensure that

corrosion from salt is reduced. The total area of the heat transfer is approximately 9605 square feet and uses cooling water to condense the process fluid so that the pressure can be increased in pump P101.

The pump P101 is used to increase the inlet pressure to the distillation towers D101 and D102. P101 is a centrifugal pump that has a discharge pressure of 75 psia. The pump is large enough to handle an inlet flow rate of 1610 gpm. Due to the flow size, the pump requires 52.5 kW of power. The pump is an API610 cast steel pump that is rated up to 150 psia with an in-line vertical motor. This pump feeds a splitter (S101) that splits the flow evenly to two identical distillation columns.

The two distillation towers D101 and D102 are identical towers and are in parallel to reduce the diameter needed for separation. Each tower is has 17 sieve trays operating at 80% efficiency with 2 foot spacing. The towers are both 54 feet tall and have diameters of 17 feet. D101 and D102 have total condensers that operate at 55 psia with a 0.1 psia pressure drop per stage as well as reboilers. The condenser uses cooling water for heat exchange and the reboilers use condensing steam at 265 psia. The feed to the towers are above stage 3 and enter at a pressure of 75 psia and 180°F. Each tower has a reflux ratio of one and a distillate rate of 5215 lbmol/hr. To obtain the desired separation a design specification was set for each tower that varied the distillate rate to achieve a 99.999% mass recovery of water to the distillate stream (D101T and D102T). The design specification was used to recover our solvent to be separated from water to be recycled. The distillates of D101 and D102 go to mixer M102 for solvent recovery. The bottoms from the towers are sent to pump P102.

The pump P102 has a discharge pressure of 60 psia to increase the pressure that feeds tower D103. The pump is an API-610 cast steel centrifugal pump that can handle pressures up to 150 psia. The inlet flow is 465 gpm and requires 0.113 kW of power.

Pump P102 feeds the distillation column D103 which separates the remaining solvent and water from the reaction products HMF and IMF. The column has 10 sieve trays that are 80% efficient and have a spacing of 2 feet. The feed stream P102O enters on stage 2. The tower is 40 feet tall and has a diameter of just over 2 feet. D103 has a total condenser that operates at 55 psia with a 0.1 psia pressure drop per stage and a reboiler that is fueled by a furnace to reach temperatures of 520°F. The tower has a distillate rate of 15 lbmol/hr and a reflux ratio of 13. The tops from the tower recycle back to mixer M101 and the bottoms are sent to section two to be reacted further to DMF.

In the recycle stream, there is a decanter SALTOUT which removes water from isopropanol using a salting method. Water forms an azeotrope with the solvent isopropanol that restricts extraction of isopropanol. The Figure below shows the azeotrope that is present in the recycle streams. Accordingly, we needed another method to capture as much of our solvent as possible.

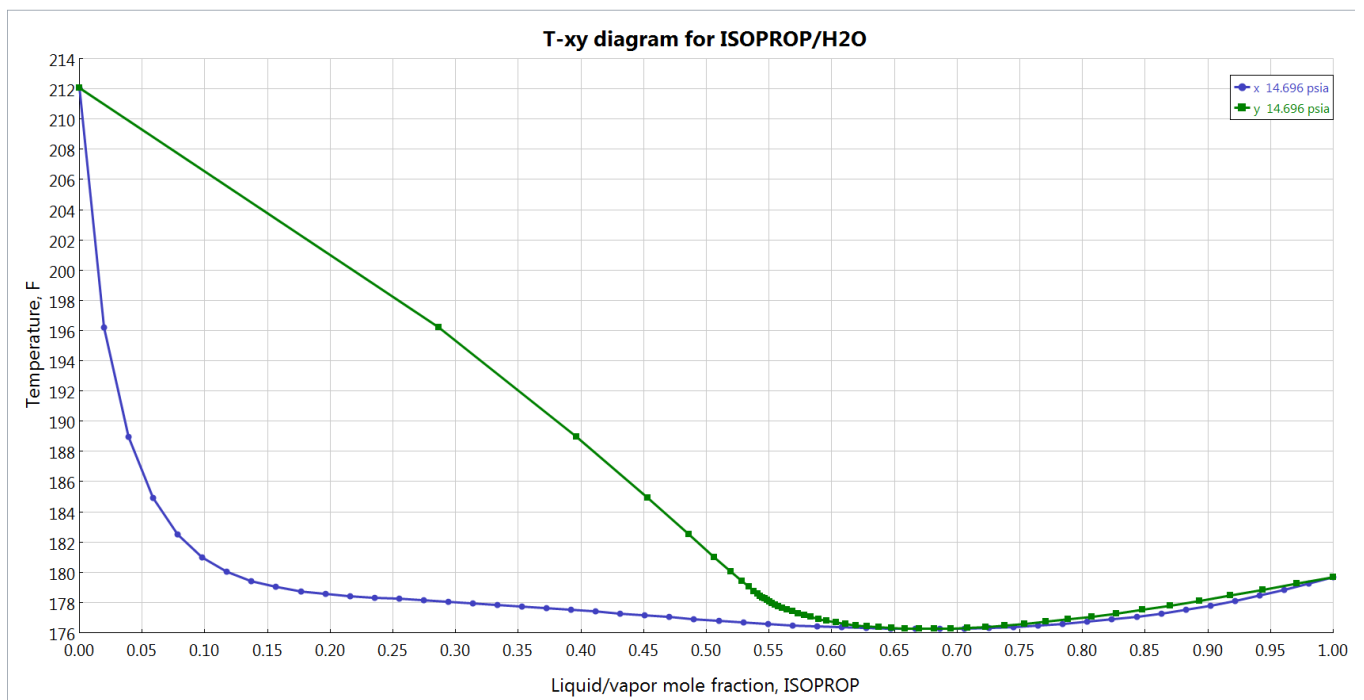


Figure 5. Azeotrope between Isopropanol and Water.

One way to do that is by adding sodium chloride to the solution [14]. NaCl dissolves in water but not nearly as well in isopropanol. This changes the pH of the aqueous phase and allows for isopropanol recovery greater than 99% [14]. This method is used to obtain the highest recovery of isopropanol possible. To recover the salt, a similar evaporative method that was described for the catalyst recovery in SEP1 will be used. An alternative design to separate isopropanol using extractive distillation was analyzed and modeled in AspenPlus and will be discussed in greater detail in the Alternative Designs section. The decanter used for isopropanol recovery operates at 55 psia and is about 10 feet in diameter and 20 feet tall. The decanter sends a stream of isopropanol with small amounts of water back to M101 to be recycled to the reactor and the other stream is sent to an evaporator to recover the salt and purge water.

Recycles and Outlet Flows:

An overview of the material balance for Section 1 can be seen on the next page in Table 2.

Table 2. Material balance of in and out streams for section 1.

	R101IN	ISOIN	H2OPURG1	D103HMF
Temperature F	248	100	100	519.5
Pressure psia	14.7	14	14	55.9
Mole Flow lbmol/hr	525	14	1064	350
Mass Flow lb/hr	72416.15	841.354	19168.257	44728.28
Volume Flow cuft/hr	2703.989	17.336	309.168	448.851
Enthalpy MMBtu/hr	-174.268	-1.901	-130.309	-58.646
Mass Flow lb/hr				
D-GLUCOS				
MALTOSE				
FRUCTOSE	63055.19			
ISOPROP		841.354		0.009
NH4CL	9360.961			
HMF				42373.58
IMF				2354.695
1-BUT				
DMF				
DMTF				
2MF				
CH4				
H2O			19168.257	trace
HEXANE				
ETHYLENE				
PX				
MPB				
H2				
HEXDIO				
CO2				

Table 3 on the next page shows the heat duty utility for the unit operations in Section 1. The operations are separated by the type of unit and a description is provided to show where in the process the unit is located.

Table 3: Heat Duty Requirement for Section One

Heat Duty Utilities		
Heat Exchanger ID	Description	Duty, BTU/hr
H101	D101 Reboiler	-202027012
H102	D101 Condenser	181492709
H103	D102 Reboiler	-162849661
H104	D102 Condenser	181492709
H107	D103 Condenser	-5997362
Vessel ID	Description	Duty, BTU/hr
SALTOUT	Water and salt decanter	-69400474
SEP1	Cat. and Water Decanter	N/A
Reactor ID	Description	Duty, BTU/hr
R101	HMF Reactor Batch	192931248

Section 1 also has pumps that increase pressure for the streams that feed the tower. The energy requirement for the pumps can be seen in Table 4 below.

Table 4: Pump Utility for Section One

Pump ID	Description	Utility (kW)
P101	S101 Feed Pump	52.53
P102	D103 Feed Pump	0.11

Section 1 required a furnace as well to reach desired temperatures in the reboiler of a distillation column. The process duty and amount of natural gas used for the furnace can be seen in Table 5 below.

Table 5: Furnace Utilities for Section One

Furnace	Description	Process Duty MMBTU/hr	Nat Gas Used, MMBTU/hr
F101	D103 Reboiler	6.06	6.730

The outlet flow to Section 2 is at 520°F, 60 psia and is about 94.7% HMF. There is about 5.3% IMF, and trace components of water and isopropanol. The overall mass flow to Section 2 is 44,700 lb/hr. D103HMF is the only outlet stream that is sent to another section of the process.

There is one major recycle that has been modeled in Section 1. The recycle stream M103O replenishes the reactor with isopropanol. The stream is almost completely isopropanol with small amounts of HMF and water. The total mass flow is 556,300 lb/hr. There are also two more recycles that are not modeled that would recover the salts used in the process. One of these would regenerate the salt catalyst NH_4Cl to the reactor and the other would recover NaCl that is used to extract isopropanol from water in the solvent recycle.

Section 2 is described starting on the next page.

Section 2 – Zach Witters

HMF to DMF

Figure 6 below shows an Aspen file of the blocks associated with section 2 of this process.

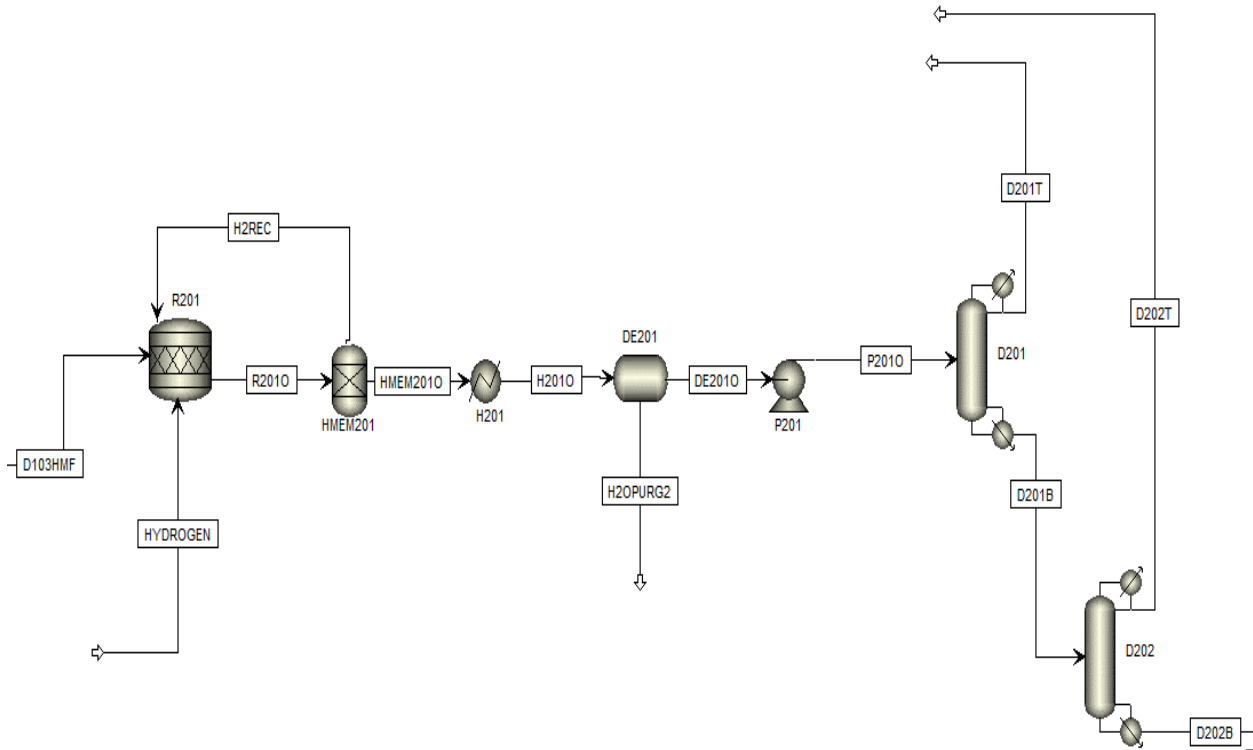
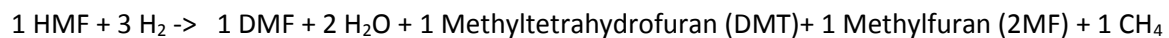


Figure 6. Shows the process flow diagram of section 2, the reaction from HMF to DMF takes place in this section.

Process Description:

Reactions:



The first reaction is the primary reaction and the second reaction is the reaction of byproducts from the first section

Feeds:

HMF

Isopropanol (organic solvent)

IMF

H₂

Catalyst:

Platinum Cobalt Carbon Nano-spheres

Products:

DMF

Byproducts:

Methyltetrahydrofuran (DMT)

Methylfuran (2MF)

Water

Methane

Propane

Reaction conditions:

Feed= 94.7% mass HMF, 5.3% IMF and 202 PPB of Isopropanol

Temperature = 356°F

Pressure = 145 psi

Overall Process Description of Section 2

This process involves the conversion of HMF to DMF through hydrogenation. While there has been little research done on the conversion of HMF to DMF via a trickle bed reactor, given the catalyst reactivity, low amount of byproducts, and purity of feed we are recommending that research be done to show to feasibility of this reaction. Special attention was paid the catalyst and possible byproducts, however it must be noted that this process has not been experimentally proven and that much more research and development needs to be done before we recommend industrialization.

The reaction parameters presented in this section are for a trickle bed hydrogenation reaction of HMF to DMF. HMF with a byproduct of IMF will be trickled into reactor R201 with a small remaining amount of isopropanol. Hydrogen will be flowed through the R210 at a pressure of 10 bar, or 145 psi.

The hydrogen will then be collected out the top of the reactor and be separated from liquid organics through a prism membrane. This will then allow for the combustion of propane for fuel and the separation of the remaining components in the reactor. Due to the high Carbon and oxygen bond selectivity presented by the hollow Pt/Co carbon nano-sphere we postulate very few byproducts, further information on the catalyst and the reaction byproducts will be presented below. It should be noted that the Pt/Co carbon nano-sphere catalyst has only been tested in a batch reactor with very high concentrations of solvent. The solvent is known to have azeotropes with some of the byproducts of the reaction. To alleviate these problems a trickle bed reactor with no solvent is purposed for the remainder of this project.

Inlet flows to the reactor, unit R201, include Isopropanol, HMF, IMF, hydrogen, and small amounts of water. The HMF reacts with water to produce 2MF, methane, propane, DMTF, water, and the desired product, DMF. Since the paper describing the catalyst has a conversion of 100% of HMF it is also assumed that the overall conversion here is 100% as well. The additional impurity sent into the reactor, IMF, is also assumed to have a 100% conversion as it is very similar to HMF. The reactor is operated at 145 psia and a temperature of 356° F. This has also been shown to be the optimum parameters used when doing a batch reaction, further tests will have to be done to conclude the optimum reaction parameters for a trickle bed reactor.

To reduce costs and minimize reactants required for purchase a hydrogen recycle will be used. The byproduct propane and hydrogen are taken out of the top of the reactor and sent through a prism membrane. The flow rate of the recycle steam called H2REC, is 40.318 lb/hr and contains pure hydrogen. It is assumed for this process that all hydrogen is separated and sent through the recycle. This may not be true as research will have to be done on our specific process to determine the separation. Hydrogen prisms are known to only recover up to 85% to 95% of hydrogen, however any

remaining hydrogen will go out the distillate in tower D201 where it will then be combusted. The cost of this membrane is \$100,000. The membrane in our process operates at 145 psia and 356 degrees F. Prism membranes are very robust and are known to be stable for roughly 2,000 years. The block in section 2 that contains the prism membrane is called HMEM201. The liquid outlet from this block will then be sent to a heater for further separation (heater H201). [15]

After hydrogen separation the main byproduct of the reaction, water, is separated via a decanter (DE201). The outlet of the reactor stream is first cooled in a heat exchanger to 150° F and 140 psia via heater H201. The heater reduces any remaining vapor products to liquid so that only two liquid phases will be present in the decanter. This allows the decanter to separate water from the remaining organics. The decanter, block DE201 in the flowsheet, itself operates at a temperature of 100 F and a pressure of 135 psia. The decanter allows for the separation of about 98.92% of the water out of the system. The remaining solution is then sent to a pump (P201) to prepare for distillation.

Once the water has separated from the system the solution is then pumped to a pressure of 240 psia in pump P201. This is meant to really condense a lot of the material going into the preceding distillation column D201. Tower D201T separates methane, propane, and the remaining water using a distillation column with 25 stages and a tray efficiency of 80%. The pressure of the distillation column is 235 psia with a stage pressure drop of 0.1 psi. To ensure most of the heavy hydrocarbons go to the bottoms the inlet stream is fed at stage 4. The distillate stream is then combusted and used for its heating values further reducing to CO₂ and H₂O. The bottoms of tower D201 are then sent to an additional tower to vent one of the byproducts in the reaction done in reactor 201.

Tower D202T is used to separate 2MF from the product stream. This is done with a condenser pressure 15 psia, while each stage has a pressure drop of 0.1 psi. The tower is 63 stages due to the difficulty of 2MF and DMF separation. The feed stage for this tower is 40 to reduce the amount of DMF

in the distillate. A very high reflux ratio of 51.4 is also used to help reduce the amount of DMF in the distillate. This tower is able to remove 99.999% of 2MF from the product stream, reducing 2MF buildup in the hexane recycle stream. DMF, and DMTF are then sent to the final section to react into para-xylene. The 2MF and DMF that are obtained in the distillate of D202 are then combusted and reduced to CO₂ and H₂O and used for heating purposes.

For preliminary designs the catalyst will then be sent through a furnace where the excess product and byproduct will be burnt off and then washed with fresh 1-butanol before being sent back into the reactor. The catalyst recycle and furnace have not been incorporated into the simulation yet due to the research required on the catalyst's durability. This will determine how the catalyst is recycled and how often it is required to resynthesize the catalyst. This is a key aspect of the longevity of this project and it is very important that durability results and a recycling procedure be researched before implementation. The known results of the catalysts durability are explained in the Catalyst Durability section.

The conversion of HMF and IMF in this section is 96.1%. It is unfortunate that some of the DMF is separated when removing the 2MF and further studies might look into the economics of potentially using pressure shift distillation recycle between a new tower and tower D202 to prevent such a large loss of DMF. However for preliminary results the second process shows a very promising outcome. Further research will have to be done to conclude the feasibility of this design.

Key Assumptions

There are multiple assumptions that were made in this sections. The research paper that presents the PtCo@HCS uses a batch reactor with butanol as its solvent. This however introduces multiple azeotropes including one with DMF and butanol, butanol and water, and butanol and 2MF.

Thus it is assumed that the reaction, without any solvent, will have the same conversion and byproducts. The trickle bed reactor presented in this paper will require a great deal of research before implementation. [16] It is likely that 100% conversion of HMF and IMF may not occur and an additional recycle or second pass in the reactor may need to happen. Further research will have to be done on the proposed reactor scheme.

It is also assumed that 100% of hydrogen will be recycled. This is not a huge assumption and could be modeled but was left out for simplicity. Prism membranes recover roughly 85-95% of hydrogen and the hydrogen is around 92% pure. The unrecovered hydrogen would just be in the distillate of column D201 where propane, water, and methane are purged.

The catalyst is also assumed to have constant reactivity, this is not practical as it will likely poison and deactivate. This would decrease the conversion and increase the byproducts. However, few catalyst durability tests were done and future research will need to be done.

Hydrogenation reaction

The hydrogenation/hydrogenolysis of HMF to DMF is a fragile reaction in the sense that the reaction must hydrogenate C=O, but not the C=C double bonds on the furan ring of HMF. A schematic of the two main reaction is shown in Figure 8.

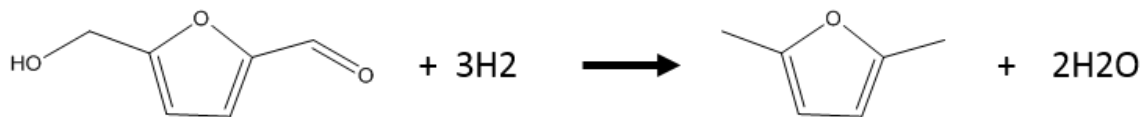


Figure 7. Shows the reaction mechanism of HMF to DMF reaction scheme.

To accomplish reactions with high selectivity, a common approach is synthesizing bimetallic catalysts. Some bimetallic catalysts developed for this reaction include: Pt/Co, CuCrO₄, and Cu/Ru. Pt is often used as an oxygen reduction catalyst due to its high reactivity, however Pt is a precious earth metal and costs are growing daily. To lower the amount of Pt required in the reaction the fundamentals of catalysis are used. Most catalysts only have reactions at the surface, thus to maximize the surface area while still minimizing the amount of Pt needed for the reaction bimetallic catalysts are usually used. Bimetallic catalysts solve this problem, they also allow for optimization as the alloying process shifts the binding energy of the catalyst itself in turn causing different reaction rates than either one of the metals. In this reaction, PtCo bimetallic catalyst was used. PtCo hollow nano-structure catalysts have shown the highest selectivity towards carbon and oxygen bonds while in the presence of C=C bonds [17]. Co/Pt have shown up to 99.1% selectivity of C=O over C=C [16]. This is further represented in Figure 9.







Entry	Catalyst	Temp/time (°C h ⁻¹)	Conversion (%)	Yield (%)					
									
1	PtCo@HCS	120/2	100	5	-	-	70	18	-
2		160/2	100	96	Trace	-	-	3	-
3		180/2	100	98	Trace	Trace	-	-	-
4		220/2	100	95	Trace	Trace	-	-	-
5		220/6	100	91	7	Trace	-	-	-
6		220/10	100	83	8	Trace	-	-	7
7 [†]		180/2	100	98	Trace	Trace	-	-	-
8 [‡]		180/2	100	72	Trace	Trace	13	9	-
9	Pt@HCS	180/2	24	1	-	-	15	1	-
10	Co ₃ O ₄ /HCS	180/2	82	-	-	-	77	-	-
11 [§]	Co ₃ O ₄ /HCS& Pt@HCS	180/2	68	2	-	-	54	4	-
12	Pt/AC	180/2	70	9	1	1	30	6	-
13	Pt/GC	180/2	100	56	-	2	-	-	-
14	PtCo/AC	180/2	100	98	Trace	Trace	-	-	-
15	PtCo/GC	180/2	100	98	Trace	Trace	-	-	-
16	Blank	220/2	0	-	-	-	-	-	-

Figure 8. Shows the reported selectivity and conversion of the planned Pt/Co catalyst. Reactions were done with 2 mmol of HMF, 4.78g of 1-butanol and 50 mg of catalyst. [16]

To further reduce the amount of Pt needed in a bimetallic catalyst nanoparticles are usually used. When bimetallic catalysts are used, in which one is a precious earth metal, nanoparticles are

usually involved to increase the catalytic surface area of the catalysts. This is not conducive to durability due to the low surface adhesion properties of nanoparticles [18]. Thus the durability of the Pt/Co hollow carbon sphere catalyst may be a larger concern when compared to other catalysts. The catalyst may cause a large capital cost, however it has shown the best yield out of all catalysts [16]. To reduce costs the platinum could be regenerated and reactivated, and a much more durable catalyst could be synthesized with a larger amount of Pt, this may alleviate the concern of aggregation and ergo deactivation of the catalyst. While no other studies on just alloyed Pt/Co (without a carbon support) catalysts for HMF to DMF reaction have been conducted, it has been shown that Pt/Co has the highest conversion and selectivity for this reaction and could be synthesized into simpler catalysts. Figure 10 shows the Pt and Co nanoparticles in the hollow carbon sphere (synthesis described later).

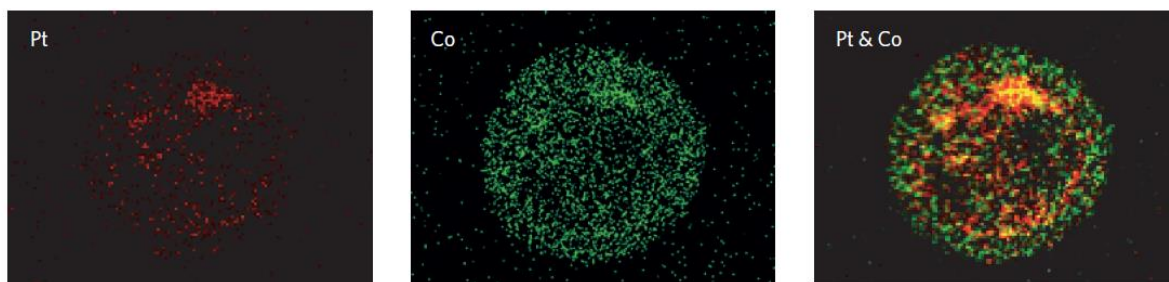


Figure 9. Shows the concentration and roughly the size of cobalt and platinum nanoparticles held in the carbon nano-sphere. [19]

To add to the deactivation via aggregation, Cl^- ions are also a major concern when using precious earth metals. For example, liquid-phase hydrogenolysis experiments using a 3:1 atomic ratio of Cu:Ru/C catalyst produce yields of 71% DMF, 4% 6, and 12% intermediates. Notably, the same catalyst used with a purified 1-butanol solution containing 1.6 mmol of NaCl generates yields of 61% DMF, 4% 6, and 20% intermediates [14]. To alleviate this problem a reaction in the vapor phases due to NaCl staying in the liquid phase may be considered for the future.

Catalyst

A high selectivity for this reaction means lower costs in separation, and a lower number of distillation columns. It should be noted that this reaction was done with low amounts of reactants and was diluted by butanol. The solvent in this reaction is often used to reduce the amount of salts in the reactions, Cl^- are known to deactivate the catalyst and reduce the overall conversion of reactant to product. Since water is usually a byproduct in this reaction it is the hope that any remaining salt that was used for dehydration of fructose in the first section has left in the ion exchanger or is soluble in the water formed by the byproducts. This should further increase the longevity of the reaction by protecting the catalyst from deactivation through poisoning. To alleviate possible Cl^- poisoning, catalysts such as CuRu/C have been developed. These show lower yield but may be used if the future project has a major problem with catalyst deactivation, such a process will be further described in the alternatives section. Pt and chloride are known to be extremely reactive to one another. PtCl_2 is an extremely unreactive compound.

Catalyst Synthesis:

The synthesis for hollow polymer spheres (HPS), Pt nanoparticles with HPS, and PtCo nanoparticle with HPS follow. The process can be broken down into three processes: the first is to produce HPS, this is followed by introducing Pt nanoparticles of roughly 1.2 nm in diameter, and finally Co is introduced into the HPS through ion exchange with carboxylate groups. The HPS can then be further broken down into hollow carbon spheres (HCS) through further heat treatment. The processes are described, starting on the next page.

1. Synthesis of HPS:

The process is started by mixing different amounts of 2,4-dihydroxybenzoic acid (DA) and hexamethylenetetramine(HMT) to 60 ml of deionized water. 20 ml of aqueous Pluronic EO20_PO70_EO20 (P123) and SO are added to are added under slow stirring, after 10 minutes the solutions is put into a autoclave of 120ml capacity that is Teflon-lined and is heated to 600° C at a rate of 1° C/min and maintained at this temperature for roughly two hours. The autoclave is allowed to reach equilibrium with the room and the products are then centrifuged at roughly 16,500 rpm for 10 min. Once centrifuged the solution is washed three times with deionized water and dried at 50° C for 8 hours. [19]

2. Synthesis of Pt nanoparticles with HPS (Pt@HPS)

The process is started by mixing 1.2 mmol DA and 0.5 mmol HMT to 60 ml of deionized water. 20 ml of aqueous solution containing 0.24 mmol SO, 0.0075 mmol Pluronic P123 and 0.06 mmol K₂PtCl₄ are added under slow stirring, after 10 minutes the solutions is put into a autoclave of 120ml capacity that is Teflon-lined and is heated to 600° C at a rate of 1° C/min and maintained at this temperature for roughly two hours. The autoclave is allowed to reach equilibrium with the room and the products are then centrifuged at roughly 16,500 rpm for 10 min. Once centrifuged the solution is washed three times with deionized water and dried at 50° C for 8 hours. [19]

The Pt@HPS is converted to Pt@HCS by carbonization. This is done by heating Pt@HPS to 600° C with a heating rate of 2° C/min and held at this temperature for 3 hours in an argon atmosphere.

3. Synthesis of Platinum and Cobalt nanoparticles with HPS (PtCo@HPS)

The process is start by mixing 1.2 mmol DA and 0.5 mmol HMT to 60 ml of deionized water. 20 ml of aqueous solution containing 0.24 mmol SO, 0.0075 mmol Pluronic P123 and 0.06 mmol K₂PtCl₄ are added to are added under slow stirring, after 10 minutes the solutions is put into a autoclave of 120ml capacity that is Teflon-lined and is heated to 600° C at a rate of 1° C/min and maintained at this temperature for roughly two hours. The autoclave is allowed to reach equilibrium with the room and the products are then centrifuged at roughly 16,500 rpm for 10 min. Once centrifuged the solution is washed three times with deionized water and dried at 50° C for 8 hours. This was done to create Pt@HPS, the Pt@HPS was then suspended in 8 ml of water containing 0.18 mmol Co(NO₃/₂_6H₂O) and 2 ml of ammonium hydroxide solution (28.0_30.0%) and was stirred for 4 hours at 50° C. The solution was then centrifuged at roughly 16,500 rpm for 10 min and dried for 8 hours again.

To develop PtCo@HCS the pyrolysis of PtCo@HPS is done under hydrogen and argon atmosphere (5%/95%). To accomplish this the sample was first heated to 400° C with a heat increase rate of 2° C/min and kept at this for 2 hours; this was followed by an increase of temperature to 500° C that was done at a rate of 1° C/min and left for another 2 hours. The sample was then allowed to cool with an atmosphere of 1% oxygen in argon for 2 h. The sample was finally crushed in liquid nitrogen. [19]

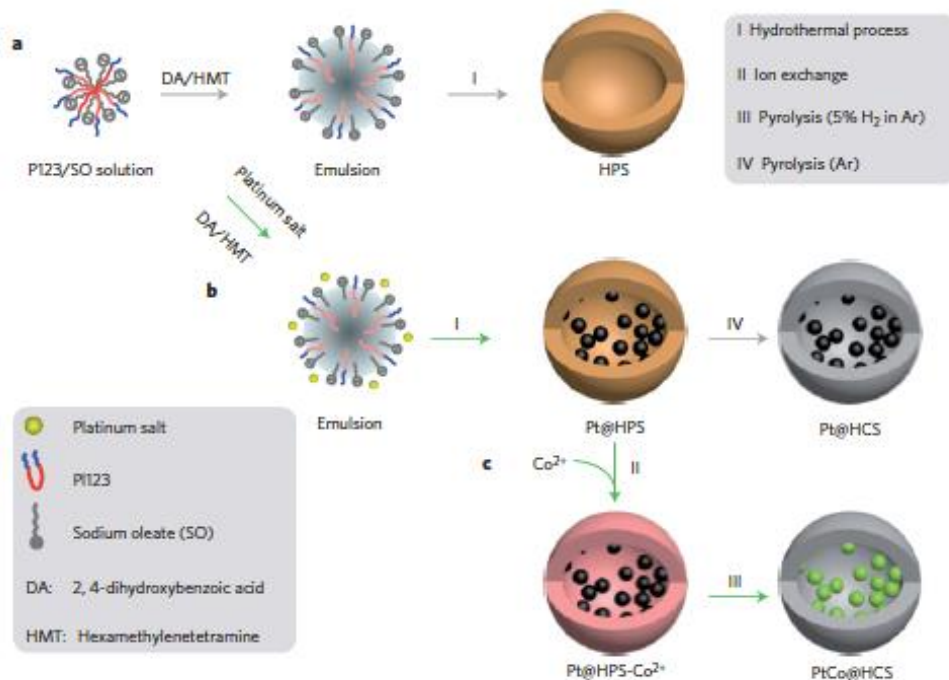


Figure 10. Shows the different methods of synthesis of HPS, Pt@HPS, Pt@HCS, PtCo@HPS, and PtCo@HCS. [19]

Catalyst Durability

To further increase the longevity of the catalyst it has been absorbed onto a carbon sphere. Both Pt and Co have been absorbed to allow the selectivity benefits due to the electronic properties of the two metals together. Durability tests were conducted on the catalyst to get an idea about its decrease in yield over time. Results have shown that PtCo@HCS is effective at obtaining high yields of DMF (98%) after only two hours. The most ideal conditions for these tests were done in a hydrogen atmosphere of 10 bar and a temperature of 180° C. After obtaining data from the first reaction the PtCo@HSC was recycled back into the reactor. Due to poor durability, pellet size catalyst will be considered in the future, however in this analysis it is assumed that the nanoparticle catalyst will be sufficient. Recycling was done by centrifuging the catalyst out of solution and washing a number of times. The second reaction parameters are shown in Figure 6. The catalyst shows a large decrease in yields, a reduction from 98% to only 72%. The surface area decreased from 542 m²/g (fresh, entry 2 in Figure 6) to 413 m²/g (entry 8 in figure 6), indicating some pore blockage of the catalyst. To alleviate this

problem it may be worth considering greatly increasing the amount of Pt in the catalyst to increase durability. The problem may be due to the aggregation of nanoparticles in the catalyst as well.

Reaction Byproducts

The reaction from fructose to HMF involves one major byproduct other than water. A byproduct known as IMF is produced. However as previously mentioned the PtCo@HCS is known to be extremely selective to C-O and C=O bonds. This reaction has been modeled to happen as a 100% conversion, same as HMF to DMF, with propane and water being the only byproducts. No other byproducts are predicated, however the reaction scheme will need to be done in lab to confirm this. This will further increase the yield of DMF and decrease the overall wasted products of the system. We hypothesize that this byproduct will react during the reaction of HMF to DMF. The hypothesized reaction scheme is shown in Figure 12. This reaction will need to be further tested in the lab to confirm products.

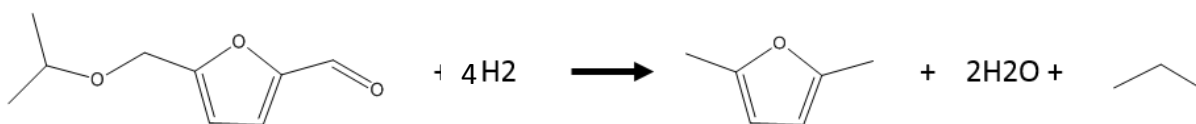
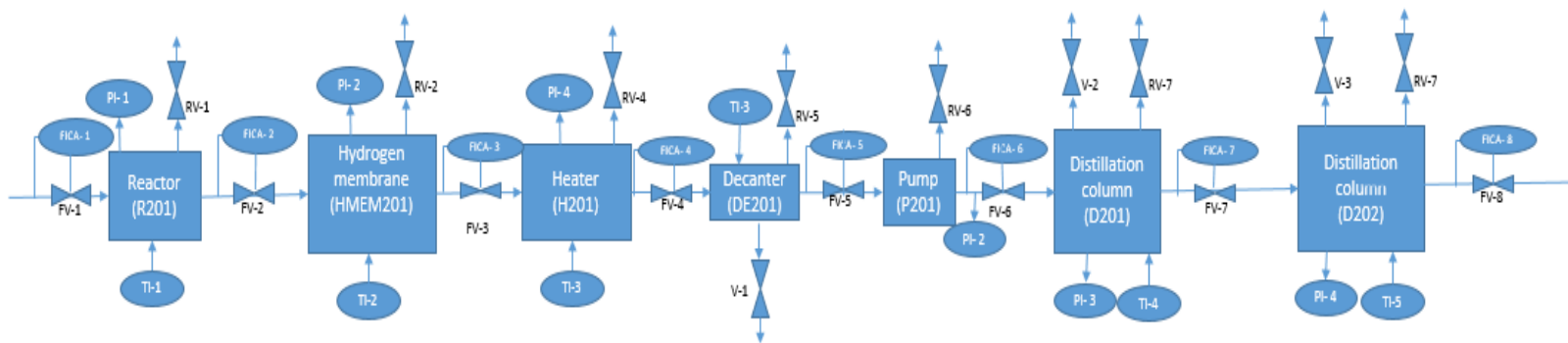


Figure 11. Shows the reaction scheme of IMF to DMF, water, and propane. This is predicted to happen in a 100% conversion.

Control Schemes

The control schemes are shown in Figure 13 on the next page.

Please see Appendix #1 for the HAZOP on this section.



Stream Tables and Duty Tables

Table 6. Overall Stream tables for Section 2.

	D103HMF	HYDROGEN	H2OPURG2	D201T	D202T	D202B
Temperature F	519.5	356	100	58.2	156.7	220.8
Pressure psia	55.9	145.04	135.04	235	15	19.9
Vapor Fraction	0	1	0	0	0	0
Mass VFraction	0	1	0	0	0	0
Mole Flow lbmol/hr	350	1074.08	692.47	17.751	18.248	338.891
Mass Flow lb/hr	4.47E+04	2165.216	12475.03	677.961	1153.273	32587.23
Mass Flow kg/sec	5.64E+00	0.273	1.572	0.085	0.145	4.106
Mass Flow kg/sec		0.273				
Mass Flow kg/sec	5.636		1.57E+00	8.50E-02	1.45E-01	4.11E+00
Volume Flow cuft/hr	448.851	65105.71	2.01E+02	23.321	21.861	717.118
Enthalpy MMBtu/hr	-58.646	2.089	-84.803	-0.903	-1.565	-21.172
Density lb/cuft	99.651	0.033	6.13E+01	29.07	52.756	45.442
Mass Flow lb/hr						
ISOPROP	9.00E-03			< 0.001	0.009	trace
NH4CL						
HMF	42373.58					
IMF	2354.695					
DMF				0.108	659.982	32339.04
DMTF				< 0.001	8.84E+01	2.48E+02
2MF				0.032	2.76E+02	9.00E-03
CH4				53.904		
H2O	trace		12475.03	7.331	128.331	trace
H2		2165.216				
PROPANE				616.586	0.766	trace
Mass Fraction						

ISOPROP	202 PPB			15 PPB	8 PPM	
NH4CL						
HMF	0.947					
IMF	0.053					trace
1-BUT						
DMF				159 PPM	0.572	
DMTF					205 PPB	0.077
2MF				47 PPM	0.239	
CH4					0.08	0.992
H2O	trace		1	0.011	0.111	0.008
H2			1			264 PPB
PROPANE			0.909	664 PPM	trace	

Table 7 Duties of process equipment in Section 2.

Duties of Equipment	Design	BTU/hr
H201	Condenses DE201 Feed	-2.2E+07
H202	D201 Reboiler	5829834
H203	D201 Condenser	-357030
H204	D202 Reboiler	14249170
H205	D202 Condenser	-1.8E+07
DE201	Water decanter	-1370694
R210	Reactor	-3.1E+07
P102	D103 Feed Pump	386.254

Section 3 is described below, beginning on the next page.

Section 3 –Wyatt Keller

The third section of the design is where the 2,5-dimethylfuran (DMF) produced in Section 2 is reacted in a packed bed reactor with ethylene to produce para-xylene, and subsequently purifies this product to 99.8 mass percent. This section consists of a packed bed reactor, a decanter to separate water and organic phases, and a series of several distillation columns. The distillation columns are used to separate and recycle large amounts of solvent and to purify product streams, including the target product (para-xylene) and various byproduct streams. The overall scheme of the third section of this process will be discussed in this section, along with descriptions of each piece of equipment on an individual basis. The flowsheet for Section 3 is shown in Figure 14.

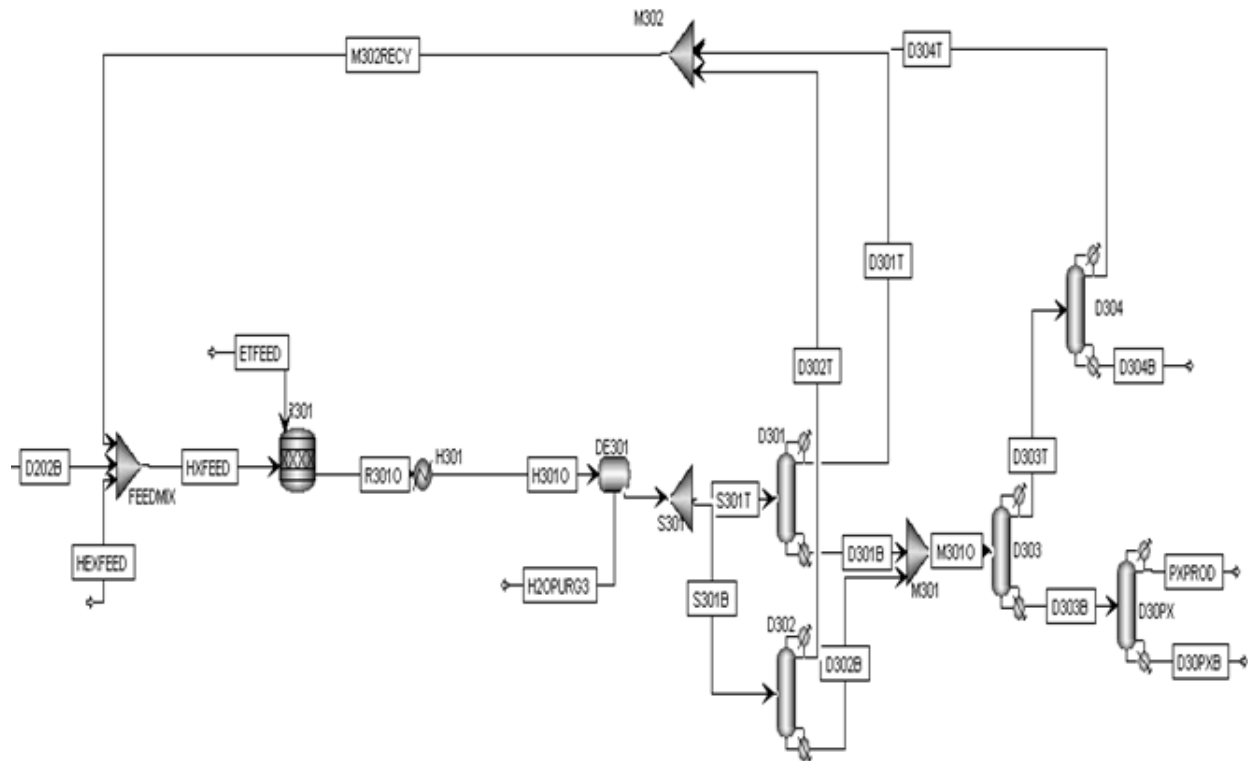


Figure 13. Process Flow diagram for section 3.

The reaction to produce para-xylene proceeds via a cycloaddition reaction between ethylene and DMF to an intermediate, which is subsequently dehydrated to yield the final para-xylene product. This reaction takes place at 482°F and 899 psia. This high pressure has two benefits: the reaction produces a fewer number of vaporized molecules, so high pressure will favor the products; and high pressure will increase the concentration and solubility of ethylene dissolved in the liquid phase, where the reaction occurs, which increases the reaction rate.

Aside from water, this reaction scheme has two main byproducts that can be produced. These byproducts are 2,5-hexanedione and 1-methyl-4-n-propylbenzene (MPB), as shown in Figure 15 on the next page [20]. 1-methyl-4-n-propylbenzene is produced from the reaction of para-xylene with an additional ethylene molecule, and after it is produced, it is carried through the rest of the process and separated as a byproduct stream. 2,5-hexanedione is the product of an equilibrium reaction between DMF and water. However, this reaction is reversible, so this byproduct can be recycled back through the reactor and dehydrated, allowing us to convert essentially all of this byproduct into the desirable para-xylene. It is important, however, to separate the water out of the system to prevent its buildup, and minimize the side reaction producing 2,5-hexanedione.

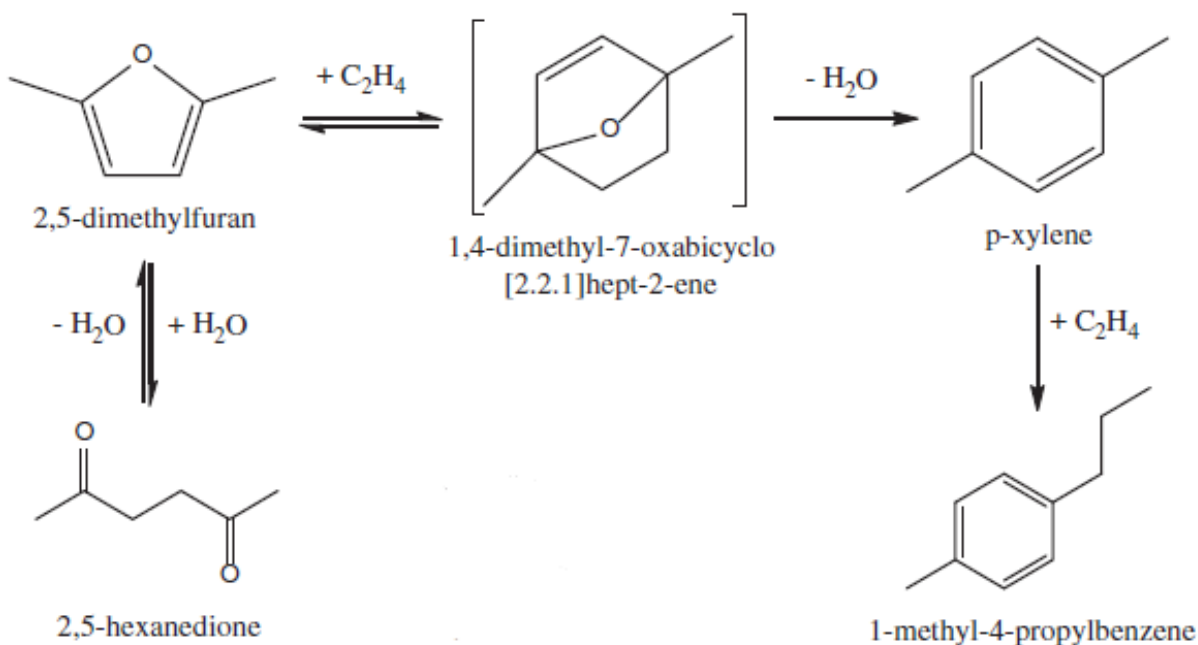


Figure 14. Reaction of DMF and ethylene to para-xylene.

This reaction is carried out in the liquid phase, which utilizes a large volume of hexane solvent. Hexane is used in 90% weight and DMF makes up 10% weight of the solution. By using a nonpolar organic solvent, we can separate DMF out of the aqueous phase into the organic phase during the reaction, and minimize the amount of 2,5-hexanedione that may be produced [21]. H-BEA zeolite is used to catalyze both the cycloaddition and subsequent dehydration reaction of the intermediate to produce para-xylene. H-BEA is a solid-phase zeolite with Bronstead acid sites. This catalyst is composed of a silica-alumina mixture of 25:1 ratio of silica to alumina on a molar basis, and is used in a packed bed reactor design. Chang et al. report that by using this catalyst, in addition to an organic solvent such as hexane, a selectivity and yield of greater than 90% for para-xylene may be achieved, with the principal byproduct being an over-alkylated compound produced by the reaction of para-xylene with an additional ethylene molecule, which we treat solely as 1-methyl-4-propylbenzene for the scope of this project.

Although this catalyst/solvent system achieves complete conversion of DMF with a high selectivity towards para-xylene, the lifetime of the catalyst is short. Literature suggests that in this system H-BEA deactivates in as little as 24 hours [20]. However, research presented by Guisnet and Magnoux suggests that the deactivation of H-BEA is due to significant coking, and therefore the catalyst may be regenerated by the removal of this coke [22]. This catalyst regeneration can be accomplished by passing high temperature steam through the packed bed to remove coke deposits from the surface of the catalyst. Regenerating the catalyst allows us to decrease our operating costs on a yearly basis, since there will be no need to purchase large quantities of catalyst on a regular basis. However, it should be noted that we are assuming that the coking can be totally removed from the catalyst, so no coke is irreversibly deposited on the surface. This assumption is consistent with the information presented by Freese et al. but it would need to be experimentally verified [23].

Therefore, in reality, the reactor for this section (R301) will be two packed bed reactors. One reactor will be used for 24 hours, while the catalyst is regenerated in the other, and then the reactors will be switched so that the catalyst can be regenerated in the first while the process continues to operate through the second reactor. Because the reaction takes place at 482°F and 899 psia, but no unusually corrosive materials are present, the reactor will be treated as a thick-walled carbon-steel vessel capable of withstanding pressures up to 1450 psia.

The DMF feed to the reactor comes from section 2 in the D202B stream, and contains DMF, DMTF, and 2MF at 221°F and 20 psia. This stream is mixed with a recycle stream (M302RECY) containing hexane (solvent), DMTF, 2MF, water, and ethylene at 156°F and 15 psia. Then, this stream (HXFEED) is finally fed to the reactor, in addition to the ethylene feed to the reactor, which we are treating as already compressed and heated to 899 psia and 482°F. Because the liquid stream (HXFEED) is only at

159°F and 15psia, a large heat duty is required by the reactor in order to raise the temperature and pressure necessary for the reaction to proceed. This value is shown in Table 8 below.

Each reactor has a volume of 17,600 cubic feet, and will contain approximately 6400 pounds of H-BEA catalyst. This reactor volume and amount of catalyst should allow for 100% conversion of DMF, with 90% selectivity and yield with respect to para-xylene, with a residence time for the reactants of 20 minutes. One key assumption made here is that DMTF and 2MF do not react in this system, so no additional byproducts are produced. This assumption also simplifies the separation process later in the design since there will be no additional byproducts that need to be separated later. The results of the simulation are consistent with this assumption and expected conversion to para-xylene. They are shown in Table 8 below.

Table 8. Feed flowrate, effluent flow, and conversion of R301.

Feed to R301 (HXFEED and ETFEED)	R301O (R301 effluent)		
	Component	Mole Flow lbmol/hr	Component
DMF	336.413	DMF	0
DMTF	9.431	DMTF	9.431
2MF	1.333	2MF	1.333
H2O	16.576	H2O	352.989
HEXANE	3522.701	HEXANE	3522.701
ETHYLENE	10486.841	ETHYLENE	0.178
PX	trace	PX	299.014
MPB	trace	MPB	37.399
Conversion of DMF		100%	
Selectivity to PX		0.889	
Heat Duty (Btu/hr)		5.01E+07	

It is important to note that because the reactor is operating at high temperature and pressures, temperature and pressure should be monitored to ensure that there are no runaway reactions occurring, or pressure buildup that could lead to a possible explosion. Pressure relief valves and a

cooling jacket should be installed on the reactor as well, in order to reduce pressure and temperature in the event that they reach dangerous levels. However, in addition to the danger of thermal burns from coming into contact with this high temperature liquid, the contents of the reactor should be isolated in the event of a discharge since para-xylene is flammable, an irritant, and carcinogenic.

After the reactor, the effluent enters a water-cooled heat exchanger, modeled as a heater block in Aspen. Because no unusually corrosive materials are present, a carbon steel shell-and-tube heat exchanger may be used. This heat exchanger decreases the temperature and pressure to 250°F and 244 psia, respectively, by utilizing 80°F cooling water and an area of 1530 square feet to remove 6.99E+07 Btu/hour from the system.

Because the pressures around the exchanger are still well above atmospheric pressure, a thick-walled vessel will be used to ensure that it can operate safely. This exchanger is also used to condense the vapor in the effluent stream (R3010), which allows a decanter to be used to separate liquid water from the system after the heat exchanger. Additionally, cooling the effluent stream allows the use of lower pressure vessels later in the process, increases the ease of separation via distillation, and helps suppress further side reactions.

After the reactor effluent is cooled, it is sent into a decanter, which separates the liquid water from the DMTF, 2MF, PX, MPB, and hexane (all organics). By decanting this stream we are able to get a good separation of water (6060 pounds out of 6360) from the stream, so we are able to have fewer distillation towers later in the process, and the towers will be smaller since they will be dealing with a smaller flow rate. DE301 operates at 65 psia, so it will be constructed of thick carbon-steel to compensate for the high pressure present in the system.

Once the water has been removed, the organics stream (DE301O) is split into two by S301 and fed to two identical distillation columns in parallel. D301 and D302 both have the same feeds, number of trays, and distillate and bottoms discharge. Both of the towers have 35 stages, diameters of 10.6 feet, heights of 90 feet, and are specified to recover 90 mass percent of the hexane in their feeds in their distillate streams, so that it may be recycled.

The inlet pressure and temperature for the two towers are 65 psia and 246°F, respectively. The pressure drop per tray is 0.1 psia, and the distillate outlet pressure is 60 psia. The bottoms pressure is 63 psia. Because the distillate and bottoms pressures are still well above atmospheric pressure, the towers will be constructed of thick carbon-steel, which will be accounted for in their costing in the economics section.

The reason two towers in parallel are needed is because of the large distillate flow that must be managed. Before D301O is split and fed to the reactors, there is a flow rate of approximately 304000 pounds per hour of hexane, 90% of which we want to recover in these towers. Because there is such a high flow rate, one tower to handle this is unreasonable, since the diameter of the tower would need to be very large to deal with this issue. So, the flow is split and two smaller towers are used. The flows before and after splitting are shown in Table 9 on the next page, and the distillate, bottoms rates, and heat duty for D301 and D302 are shown in Table 14.

Table 9. Flow rate before and after splitting in S301.

Flow before splitting (DE301O)		Feed to each D301&D302 (S301T & S301B)	
Component	Mass Flow lb/hr	Component	Mass Flow lb/hr
DMTF	944.652	DMTF	472.326
2MF	109.466	2MF	54.733
H2O	298.614	H2O	149.307
HEXANE	303576.383	HEXANE	151788.192
ETHYLENE	5	ETHYLENE	2.5
PX	31745.562	PX	15872.781
MPB	5019.745	MPB	2509.872
TOTAL	341699.421	TOTAL	170849.711

Table 10. Distillate and bottoms flowrates for D301 and D302.

Distillate for each D301 & D302 (D301T & D302T)		Bottoms for each D301 & D302 (D301B & D302B)	
Component	Mass Flow lb/hr	Component	Mass Flow lb/hr
DMTF	132.185	DMTF	340.141
2MF	54.075	2MF	0.658
H2O	149.307	H2O	trace
HEXANE	136609.372	HEXANE	15178.819
ETHYLENE	2.5	ETHYLENE	trace
PX	trace	PX	15872.781
MPB	trace	MPB	2509.872
TOTAL	136947.44	TOTAL	33902.271
Heat Duty (Btu/hr)		-4.05E+07	

The hexane-rich distillate streams from these towers are mixed and recycled back to the reactor, along with the distillate from D304 (this will be examined later). This recycle allows our process to minimize waste of our hexane solvent, which reduces operating costs since this chemical is not being continually depleted and repurchased. The para-xylene rich bottoms from D301 and D302 are mixed and fed to D303.

D303 is a distillation column that has 23 stages, a diameter of 10.8 feet, a height of 66 feet, and is designed to separate the remaining hexane and DMTF into the distillate from the para-xylene in the bottoms. D303 is specified to remove 99.99 % mass of the hexane feed into the distillate stream, and recover 99.8% mole of the para-xylene into the bottoms. The inlet pressure and temperature are 63 psia and 340°F, respectively. The pressure drop per stage is set to 0.1 psi, and the distillate outlet pressure is 20 psia. From Aspen, the bottoms pressure was calculated to be 22 psia. The feed flowrate, distillate rate, bottoms rate, and heat duty for D303 are shown in Table 11 below.

Table 11. Feed rate, distillate rate, and bottoms rate for D303.

Feed to D303 (M301O)		Distillate Rate (D303T)		Bottoms Rate (D303B)	
Component	Mass Flow lb/hr	Component	Mass Flow lb/hr	Component	Mass Flow lb/hr
DMTF	613.714	DMTF	613.665	DMTF	0.048
2MF	1.683	2MF	1.683	2MF	trace
H2O	trace	H2O	trace	H2O	trace
HEXANE	30357.638	HEXANE	30357.335	HEXANE	0.304
ETHYLENE	trace	ETHYLENE	trace	ETHYLENE	trace
PX	31745.562	PX	1.587	PX	31743.974
MPB	5019.745	MPB	trace	MPB	5019.745
TOTAL	67738.342	TOTAL	30974.271	TOTAL	36764.071
Heat Duty (Btu/hr)			-3.49E+07		

The distillate from D303 will be fed to D304, which separates DMTF at 98% mole purity in the bottoms from hexane in the distillate. D304 has 23 stages, a diameter of 5.3 feet, and a height of 66 feet. The pressure drop per stage is 0.1 psia, and the distillate outlet pressure is set to 15 psia. The bottoms stream pressure was calculated by Aspen to be 17 psia. The bottoms stream from this tower is rich in DMTF (an organic byproduct) and is burned to provide heating for the process. The distillate from D304 is rich in hexane, and will be mixed with D301T and D302T. This mixed stream (M302RECY) is then recycled back to the reactor. The results for M302RECY will be presented after all distillation

columns have been presented. The feed flowrate, distillate rate, bottoms rate, and heat duty for D304 are shown in Table 12 below.

Table 12. Feed rate, distillate rate, and bottoms rate for D304.

Feed to D304 (D303T)		Distillate Rate (D304T)		Bottoms Rate (D304B)	
Component	Mass Flow lb/hr	Component	Mass Flow lb/hr	Component	Mass Flow lb/hr
DMTF	613.665	DMTF	365.483	DMTF	248.182
2MF	1.683	2MF	1.683	2MF	< 0.001
H2O	trace	H2O	trace	H2O	trace
HEXANE	30357.335	HEXANE	30354.265	HEXANE	3.069
ETHYLENE	trace	ETHYLENE	trace	ETHYLENE	trace
PX	1.587	PX	< 0.001	PX	1.587
MPB	trace	MPB	trace	MPB	trace
TOTAL	30974.271	TOTAL	30721.432	TOTAL	252.839
Heat Duty (Btu/hr)			-8.84E+06		

The para-xylene-rich bottoms from D303 are fed at 315°F and 22 psia to D30PX. D30PX is the final tower used for the purification of para-xylene. D30PX purifies the distillate stream to 99.8% weight para-xylene and consists of 23 stages, has a diameter of 4.6 feet, and a height of 66 feet. This column is also specified to recover 99.9% mass of the para-xylene present in the feed. The pressure drop per stage is set at 0.1 psi, and the distillate and bottoms pressures are 17 psi and 19 psi, respectively. Because para-xylene has a lower boiling point than 1-methyl-4-propylbenzene, it will be collected in the distillate stream (PXPROD). The MPB-rich bottoms stream (D30PXB) is 99.4% weight pure MPB, and will be sold for byproducts credit. The feed rate, distillate, bottoms rate, and heat duty for D30PX are given in Table 13.

Table 13. Feed rate, distillate rate, and bottoms rate for D30PX.

Feed Rate (D303B)		Distillate Rate (PXPROD)		Bottoms Rate (D30PXB)	
Component	Mass Flow lb/hr	Component	Mass Flow lb/hr	Component	Mass Flow lb/hr
DMTF	0.048	DMTF	0.048	DMTF	trace
2MF	trace	2MF	trace	2MF	trace
H2O	trace	H2O		H2O	
HEXANE	0.304	HEXANE	0.304	HEXANE	trace
ETHYLENE	trace	ETHYLENE		ETHYLENE	
PX	31743.974	PX	31712.243	PX	31.731
MPB	5019.745	MPB	63.184	MPB	4956.561
TOTAL	36764.071	TOTAL	31775.779	TOTAL	4988.292
Heat Duty (Btu/hr)			-7.95E+06		

The total flow rate of PXPROD is approximately 32,000 pounds per hour. When we consider the plant operating 8250 hours in a year, this gives us a total production of 262.15 million pounds per year of para-xylene product.

The hexane solvent recycle stream (M302RECY) is a mixture of D301T, D302T, and D304T, and recycles 99.6% weight hexane from the end of the process back to the reactor, along with some DMTF, 2MF, water, and ethylene. Because we separate out the hexane for recycle, a very small amount is needed for make-up every hour. A mass balance on hexane over section 3 shows that the amount of hexane leaving the system (which must be replaced) is just over three pounds per hour, compared to over 300,000 pounds per hour that flows through the entire process. This shows that approximately 99.99% of the hexane solvent is recycled in the system. This efficiency allows us to drastically reduce our operating costs, since we are not forced to buy large quantities of fresh hexane to replenish the losses every hour. This mass balance is shown in Table 14 on the next page.

Table 14 shows the mass balance on hexane around section 3.

Hexane Feed to Reactor (HXFEED) lb/hr
303576.383
Hexane Out (PXPROD) lb/hr
0.304
Hexane OUT (D30PXB) lb/hr
trace
Hexane OUT (D304B) lb/hr
3.069
Make-up Feed (lb/hr):
3.373

Design Alternatives – William Duncan

One alternative design that was analyzed was using extractive distillation to remove isopropanol from water. Extractive distillation works by adding another component that increases the relative volatility for one of the components with azeotropic behavior [10]. This makes distillation more successful because higher purities and recovery of the solvent isopropanol can be reached. The design that was tested used 2-octanone as the extractive solvent [10]. The addition of this solvent changes the relative volatility to 1.22 [10]. The figure for the design can be seen below in Figures 14 and 15.

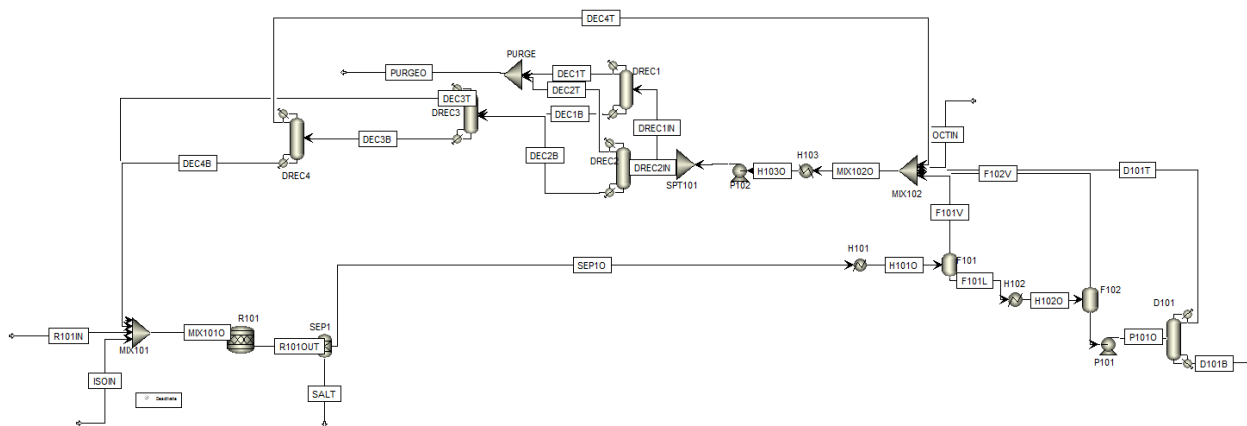


Figure 15. The flow sheet for section one using extractive distillation.

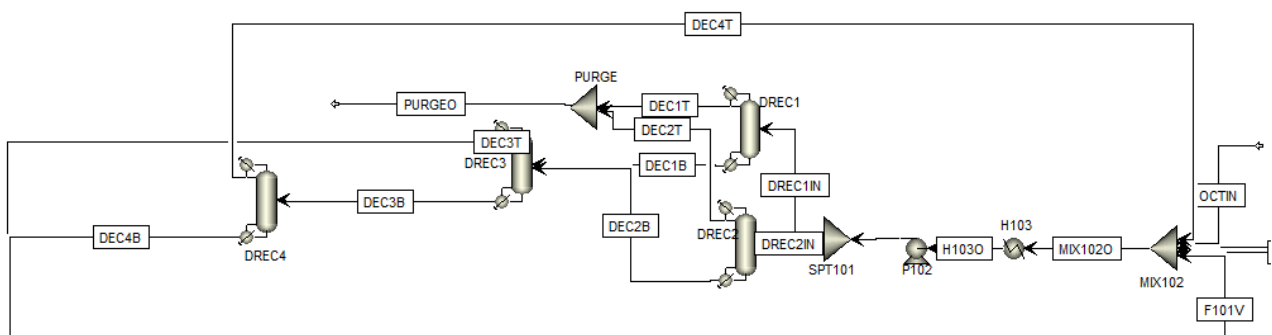


Figure 16. A more detailed flow sheet of the extractive distillation section.

To model the system, a series of 4 distillation columns were used. The first two columns are run in parallel to lower tower sizes. The towers DREC1 and DREC2 have 28 theoretical sieve trays with total condensers and reboilers. The feed enters on stage 15 and diameter of the tower is 16 feet. The pressure in the condenser is 145 psia with a 0.1 psia pressure drop per stage. A design specification of 95% mole recovery of water was selected to separate as much isopropanol as possible in the first stage of distillation. The first two towers were able to extract 87.7% of the isopropanol while keeping recycled water to a minimum in the bottoms of the towers. The reflux ratio of the tower is 0.005 and the distillate rate is 1038 lbmol/hr. Afterwards, the tops is purged because of the water and isopropanol that cannot be recovered even with increased recovery using the extracting solvent.

The bottoms are sent to another tower DREC3 that has 18 ideal sieve trays with the feed entering on stage 10 with a tower diameter of 25 feet. The tower has a reboiler and a total condenser that operates at 20 psia with a pressure drop of 0.1 psia per stage. The change in pressure allows for easier separations and higher recoveries of isopropanol. The reflux ratio is 0.5 and the distillate rate was found using a design specification of 99.9% mole recovery of isopropanol in the tops. The tops from DREC3 recycle isopropanol back to the reactor and the bottom go to another tower DREC4 for extractive solvent recycling.

The last tower DREC4 has 8 ideal sieve trays with a 25-foot diameter. The feed enters on tray on 3. The tower has a distillate rate of 8270 lbmol/hr and a reflux ratio at 0.11. The condenser operates at 16 psia and the tower has a pressure drop of 0.1 psia per stage. The tops from the DREC4 has a high octane purity and is recycled back to the first tower to help separation of isopropanol. The bottom stream is isopropanol, which is fed to the reactor.

This alternative process was analyzed but not used in the design for multiple reasons. Firstly, the process still required that almost 62,000 lb/hr of isopropanol was added as make up to the lost solvent

in extraction. This makes the process very uneconomical even though 92% of the solvent was recovered. Also, this method involves towers that are very large in diameter, which would add lots of capital costs to the overall process. Accordingly, it was decided that the process would use salt separation instead of extractive distillation.

Another design alternative is to use the same process from CHE 4070 and use a biphasic reactor set up with higher concentrations of feed reactants. The biphasic reactor consists of an aqueous phase and an organic phase that extracts the HMF from the aqueous phase. In the aqueous phase, a Lewis Acid catalyst and HCl catalyzes the dehydration reaction of fructose to HMF. The acidity of the reaction condition results in a low pH. The feed conditions of the reactor are 5% weight glucose or fructose in water that has been saturated with salt (NaCl).

The organic counterpart phase consists of 1-butanol and is used as the extracting phase. Once HMF is formed in the aqueous phase, it is extracted into the organic phase to separate it from the aqueous layer. One major byproduct in the reaction is levulinic acid (LA), which is produced from the reaction of HMF with water. We selected to change the solvent to 1-butanol because it has similar azeotropic properties with water which reduces the ability for complete purification of HMF before the next section and adds multiple unit costs. This organic phase is fed at a mass ratio of 2 to 1 with the aqueous phase. A picture of the two-phase system (Figure 18) can be seen on the next page.

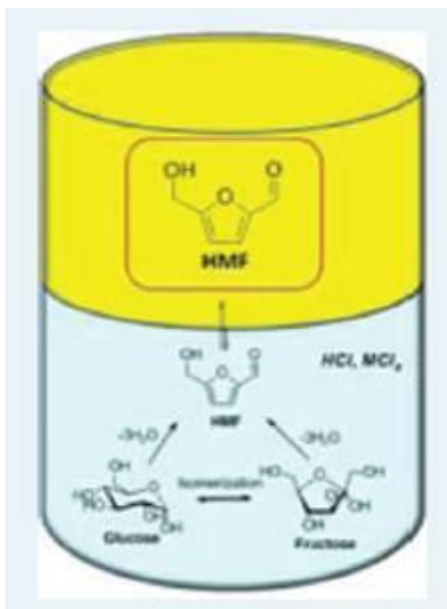


Figure 17. A schematic of the biphasic reactor

The new design would need a much less dilute concentration of feed reactant. Last semester, 5 wt% was used and results in unreasonably large reactors and units. For a biphasic reactor to work the concentration would need to be much higher to reduce capital costs. Also, research would need to be done to ensure that similar conversions and selectivity's are obtained using higher concentrations of feed materials.

Permitting and Environmental Concerns – Wyatt Keller

To determine the amount of CO₂ that is produced for this process, we took the amount hydrocarbons in our purge streams that we plan to combust for heating purposes and then converted that to CO₂ and H₂O. Using the EPA greenhouse gas equivalencies calculator [24], we can estimate that we produce approximately 13 million pounds of CO₂ per year. This is a large environmental concern due to the effect of CO₂ as a greenhouse gas. However, at this time, there are no EPA endorsed technologies for controlling the production of CO₂ [25]. This means that anticipating the requirements for permitting is quite difficult, if they can be anticipated at all. For this reason, more information would be required to evaluate the criteria for permitting in the Houston area. More work would need to be done for this, at a date closer to construction.

In addition to CO₂, this plant will also produce NO_x products due to the combustion of natural gas in air, which contains high levels of nitrogen. All NO_x produced will be the result of thermal NO_x formation and its emissions should be controlled. In order to control the amount of NO_x released, we will utilize low NO_x burners in conjunction with Selective Non-Catalytic Reduction technologies (SNCR). SNCR uses a reducing agent in the flue gas stream to reduce any thermal NO_x back to N₂ and O₂. When SNCR is used in addition to low NO_x burners, the amount of NO_x released can be reduced by as much as 75% compared to no controls, which is the reason this type of control technology was selected for our application [26].

Safety and Risk Management – Wyatt Keller

All chemicals in an industrial process should be considered hazardous. This is especially true for our process, where numerous chemicals are classified as flammable, irritants, carcinogens, or toxins. Due to the wide variety of chemicals used in this system, their individual risks should be examined in Appendix 1, where the SDS for each chemical can be found. Additional hazards are present due to high temperatures and pressures in the system. These risks are accounted for in the design and costing of each piece of equipment, where a pressure multiplier has been used to account for the thickness of vessel walls needed based on pressure.

During the design of this process, a Hazard and Operability study (HAZOP) was conducted, which examines deviations from the normal operating conditions and evaluates potential consequences on the piece of equipment being examined. In addition to the information presented regarding safety associated with the chemical species present in the system, the HAZOP examines safety concerns that result from deviations from designed operating parameters, focusing on a single piece of equipment at a time and presenting the findings in tabular form. These results are presented in Appendix 1, since the tables are quite large.

Some of the most serious safety concerns in this process result from the high temperatures and pressures being used, which can be as high as 519°F and 899 psia, respectively. These temperatures and pressures will put a significant amount of strain on the equipment and, if not controlled, can easily lead to an explosion. In addition to the physical damage inflicted by an explosion (regarding both pieces of equipment and personnel), the chemicals will be released at high temperature, which poses the risk of thermal burns for anyone coming into contact with them, as well as possible chemical burns. Close

monitoring of this reactor and every other process will be done to prevent explosions, fires, and other hazardous outcomes.

HAZOP: See Appendix 1 for HAZOPS for each section.

Project Economics – Rachael Weber

General Information

The calculations for this process have shown that this project is economically infeasible. The unit operations for this project have all been sized according to the appropriate equations as well as utilizing information given in Aspen. The prices were estimated using the appropriate figures in Peters, Timmerhaus and West [27] or, if prices were given, they were used and modified to fit the year 2016 using an inflation calculator [28] or the Chemical Engineering Plant Cost Index [29]. The Fixed Capital Investment (FCI) of this project was approximately \$63 Million and there was a yearly \$183 Million revenue, with about \$250 million in yearly costs. There is no payback period because this plant never generates enough in revenue to exceed its costs. Since the plant never breaks even, there is no IRR.

Major Equipment Cost

Major Equipment

The major equipment required for this project is listed and the purpose of each unit is described in Table 15 on the next page. In all, there were 52 total units sized for this project. This amount includes the reboilers, condensers, and reflux drums in the distillation columns. In each section, there was one reactor. Beyond the reactors, in Section 1, there were two pumps, one furnace, five heaters, five vessels, and three distillation columns. In section two, there was one pump, five heat exchangers, three vessels, and two distillation columns. In section three, there were 11 heaters, six vessels, and five distillation columns. In total, there were three pumps, one furnace, 21 heaters, three reactors, 14 vessels, four catalysts, and ten distillation columns.

It should be noted that although there are eight mixers and splitters through this process, they were not sized or priced because the sizes would theoretically be large enough to hold the correct capacity of fluids flowing through them (plus a little extra volume in case of problems with the plant) and prices were assumed to be negligible compared to the costs of the other units. Also, there were no

compressors simulated throughout this process. This simulated plant deals mostly with the liquid phase, and if needed at any time, pressure was increased using pumps.

Table 15. The list of major equipment sized for this project along with a description of the unit.

Reactors:	Description
R101	Batch reactor which converts fructose to HMF
R201	Trickle bed reactor which converts HMF to DMF
R301	Packed bed reactor which converts DMF to PX
Distillation towers:	Description
D101	Separate HMF and IMF from Isopropanol and Water
D102	Separate HMF and IMF from Isopropanol and Water
D103	Further purifies HMF to be sent to the second section
D201	Separates DMF from propane and other reagents/solvents
D202	Further purifies DMF to be sent to the third section
D301	First round of PX purification
D302	First round of PX purification
D303	Second round of PX purification
D304	Stream to burn DMTF for burning
D30PX	Final purification of product and profitable byproduct
Heaters/Heat Exchangers:	Description
H101	Condenses Separator Outlet
H201	Condenses DE201 Feed
H301	Condenses DE301 FEED
Vessels:	Description
SALTOUT	Water and salt decanter
SEPOR1	Cat. and Water Decanter
DE201	Water decanter
DE301	Water Decanter

Equipment Features

Almost every unit for this process has a sub-unit that needed to be sized and priced. Table 16 on page 71 shows the list of the secondary components needed for each of the major units in this process as well as a description of each component.

The reactors in Sections 1 and 3 were sized and the prices were estimated using Figure 12-54 in Peters & Timmerhaus [27] as a horizontal storage vessel. Since the reactors for this project are vertical

vessels, a vertical multiplier of 1.1 was applied to the FOB cost of each reactor estimated using the figure. The prism membrane in Section 2 was modeled separately as its own membrane and was not modeled as a storage vessel. The catalyst price for Section 1 was estimated by finding a bulk price on Alibaba [30]. The catalyst price for Section 2 was estimated by finding the elemental price of each element in the catalyst, and then multiplying that value by a factor of 1.2 as an assumed buffer. The H-beta zeolite catalyst price for Section 3 was given directly from Professor Lobo from the University of Delaware, who is an engineer who helped develop the process of converting DMF to PX using the catalyst. He is also a co-author of the peer-reviewed research article [31].

The distillation columns were sized using the information calculated by Aspen (including the diameter) and the appropriate equations, assuming a tray efficiency of 80%, as well as the appropriate equations to find the height and number of trays needed for each tower. Then, the columns were priced using Figures 15-11, 15-12, and 15-13 [27] to estimate the FOB prices of the vertical columns (assuming a carbon steel column), manholes (assumed flanged nozzles), and the cost of trays in the tray columns (assuming stainless steel Sieve Trays and applying appropriate quantity factors), respectively.

For each tower, condensers and reboilers were sized and priced as heaters or a furnace, and reflux drums were sized and priced as vessels. The only furnace in this process was the column D103 reboiler, modeled as the furnace. It was modeled this way due to the high temperature needed for the reboiler. If a steam heater had been used as a model, then superheated steam would have to be used at an unrealistic pressure which would also increase utility costs, the number of units, and therefore the capital costs of this project. Thus, the furnace was used to avoid this problem with the steam. Similar to the reactors, the vessels for the columns were priced using Figure 12-54 [27] with the vertical multipliers as needed. The reboilers and condensers were priced using Figure 14-18 [27], assuming the equipment was made from carbon steel and applying the correct pressure adjustment factors where needed.

The decanters for this project were sized according to the reflux and overhead distillate volume flows given by Aspen, and then finding the appropriate length and diameter of the vessels. The pricing of the decanters came from Figure 12-54 [27]. Similar to the reactor pricing, appropriate pressure, vertical, and material factors were applied to the base pricing of the unit. The material for these separators was assumed as carbon steel, as well.

As stated earlier, no compressors were used in this process. The vast majority of this process is in the liquid phase and no compression between phases was needed unless a unit operation (i.e., a distillation tower) could condense its own stream. Also, although there were eight mixers and splitters in this project, the prices of these were deemed negligible compared to the prices of the rest of the units in the process so they were not estimated.

Not very many pumps were used in this project. The pumps used in the project were assumed as centrifugal. In Section 1, pump P101 was modeled as an API-610 Cast steel casing as a horizontal pump and is designed to withstand up to 150 psi. Pump 102 was priced as a centrifugal, cast iron pump with the appropriate pressure adjustment factors. Pump P201 was priced similarly to Pump P101. Pumps P101 and P201 were priced using Figure 12-20 [27] pump P102 was priced using Figure 12-23 [27].

Table 16. Components of the major units in this process.

Pumps	Description
P101	S101 Feed Pump
P102	D103 Feed Pump
P201	D201 Feed Pump
Furnaces	Description
F101	D103 Reboiler
Heat Exchangers	Description
H101	Condenses Separator Outlet
H102	D101 Reboiler
H103	D101 Condenser
H104	D102 Reboiler
H105	D102 Condenser
H107	D103 Condenser
H201	Condenses DE201 Feed
H202	D201 Reboiler
H203	D201 Condenser
H204	D202 Reboiler
H205	D202 Condenser
H301	Condenses DE301 FEED
H302	D301 Reboiler
H303	D301 Condenser
H304	D302 Reboiler
H305	D302 Condenser
H306	D303 Reboiler
H307	D303 Condenser
H308	D304 Reboiler
H309	D304 Condenser
H310	D30PX Reboiler
H311	D30PX Condenser
Vessels	Description
SALTOUT	Water and salt decanter
SEPO1	Cat. and Water Decanter
DR101	D101 Reflux Drum
DR102	D102 Reflux Drum
DR103	D103 Reflux Drum
DE201	Water decanter
DR201	D201 Reflux Drum
DR202	D202 Reflux Drum
DE301	Water Decanter
DR301	D301 Reflux Drum

DR302	D302 Reflux Drum
DR303	D303 Reflux Drum
DR304	D304 Reflux Drum
DR30PX	D30PX Reflux Drum

Equipment Estimated Cost

The estimated Freight on Board (FOB) cost of all of the hardware for this process is listed, according to the appropriate type of equipment, in Table 17 on the next page. The total FOB for this process is approximately \$7.1 Million. The FOB costs for everything but the raw catalysts and the prism membrane (not included in the table because the price found for this was an installed price) were found in Peters & Timmerhaus from the respective figures. The pumps cost includes the spares needed for each pump. The Total ISBL FOB is the amount from 2002, so it was scaled to match appropriate costs for 2016 using the Chemical Engineering Plant Cost Index [[32] [33]]. The raw catalyst prices were current market prices so those processes were not scaled.

By a large margin, the largest FOB cost comes from the catalysts. This section includes the solvents used for the process, which were included as capital costs. Although the majority of the solvents are recovered in the recycle streams, a little bit of the solvents are lost throughout the process, so the first bulk influx cost of the solvents were calculated as capital costs since they will only be a one-time, larger purchase. The replenishing amount is what was included in the Production Cost Statement for each of the solvents, hexane and isopropanol. The most expensive catalyst in this process is for Section 2 and this makes up approximately 78% of the entire FOB cost of just the catalysts, excluding the solvents.

The second-most expensive component of the FOB for this process are the distillation columns and the large FOB for these units comes in part from running some of the columns in parallel to decrease the diameter of the tower which was given by Aspen. The reactors are the third-most

expensive components of the system and this is mainly due to the multiple, large reactors in the batch system in Section 1 with a long residence time. This FOB cost for this plant does not include the prism membrane needed for Section 2 of the process. As explained earlier, the price given for this unit was an installed cost.

Table 17. FOB Prices for all components of this system.

Unit Type	FOB Scaled Cost
Pumps	\$105,000
Furnace	\$300,000
Heat Exchangers	\$750,000
Reactor	\$2,200,000
Vessels	\$370,000
Catalyst	\$100,000
Towers & Trays	\$3,200,000
Total Scaled ISBL FOB	\$7,025,000.00

Fixed Capital Investment

The total Fixed Capital Investment (FCI) of this process is described in Table 18 on the next page but has totaled to approximately \$62.8 Million. The Prism Membrane price was scaled up from the year when it was priced, which was from 2009. As previously stated, the catalyst prices were not scaled to recent years as they were current market prices.

After the FOB costs were estimated for each unit type, they were summed together to get the unit type-specific total Inside Boundary Limit (ISBL) FOB cost. Once these values were calculated, they were added together and scaled appropriately to the current year of 2016 by the Chemical Engineering Plant Cost Index. Then, this “Total ISBL FOB” value was multiplied by the appropriate installation factors (1.1 and 5.04) to get an Installed ISBL cost. To find the total Installed ISBL cost, the Installed ISBL FOB was added to the time-scaled and installed prism membrane cost. The Outside Boundary Limit (OSBL) cost was assumed as 20% of ISBL. Then, the ISBL and OSBL costs were added for each section to get the grand total FCI for the entire process.

Intuitively, a very low FCI would be preferred, but having such a low FCI this semester poses different problems with the profitability of this project. With a low FCI, the product and byproduct (Para-Xylene and 1-methyl-4-propylbenzene, respectively) prices have a large impact on determining the feasibility of this project. Small changes in the unit price of the product and byproduct cause drastic changes in the revenue of this project. This is explained more in depth the sensitivities section. One way to fix this is to assume more durable and expensive hardware for this project. Then, the scrap value could also potentially be higher and the maintenance costs could decrease.

Table 18. Fixed Capital Investment for the Process

Total Installed ISBL	\$52,300,000
Total Installed OSBL	\$10,500,000
Total Installed FCI	\$62,800,000

Operating Costs

The total operating cost estimate is approximately \$245 Million. This encompasses feedstock, utility, manpower, maintenance and miscellaneous fixed costs. These are explained in deeper detail in the following subsections. Table 19 below shows the breakdown of these costs on a million-dollar-per-year basis.

Table 19. Total operating costs for this plant.

Operation Cost Segment	\$MM/Year
Gross Cost of Raw Materials	246
Byproduct Credit	29
Net Cost of Raw Materials	217
Utilities	12
Total Variable Costs	229
Total Fixed Costs	10
Total Manufacturing Costs	239

Feedstock and Utility Costs

The feedstock prices of this process are listed in Table 20 below on a million-dollar-per-year basis. On a unit price basis, isopropanol is the most expensive raw material by a large margin (It costs approximately \$0.93/lb [34] (with appropriate inflation factors [28], and the next most expensive raw material is hydrogen gas at \$0.55/lb [35]). However, based on the production of this process and the consumption of the raw materials, fructose is the most expensive raw material. However, this is based on a food-industry price so it may be beneficial in the future to look at an industrial price and source to decrease the initial feedstock costs. Fructose also has the greatest impact of all of the different parameters on this project. The fructose price for this process per year exceeds the revenue it generates, so finding a lower fructose price will help this project's feasibility immensely. It should be noted here also that we have projected to use the total cost of raw materials per year for this process is approximately \$250 million.

Table 20. Feedstock prices and quantities for this process.

Raw Material	Quantity (lb/year)	\$MM/Year
Fructose	5.20E+08	198
Isopropanol	6.94E+06	6.5
H2	1.79E+07	9.80
Hexane	2.78E+04	0.012
Ethylene	8.65E+07	32.4
Total	6.32E+08	246.33

The utility prices of this process are listed in Table 21 on the next page on a million dollar per year basis. On both a unit cost and consumption basis, steam is the most expensive utility at \$8.00/lb. The next most expensive utility is natural gas which is used to combust unsellable side products to carbon dioxide, which is \$3.00/lb. The total utility cost per year for this process is approximately \$11.6 million.

Table 21. Utility costs for this process.

Utilities	Quantity (per year basis)	Unit	\$MM/year
Electricity	4.75E+05	KW	0.019
Steam	1.49E+12	BTU	9.9
Natural Gas	5.00E+10	BTU	0.17
Cooling Water	-3.72E+12	BTU	1.5
Total Cost			11.6

Manpower Costs

With 10 men working on this plant per shift at \$50/hour, with 8250 working hours on the plant each year, the labor costs will only be \$7 million/year. Only having 10 men per shift working on this larger plant is very low, so increasing this number will help the plant run more smoothly, but it will also drive up the fixed costs which will further hurt the feasibility of this plant.

Maintenance Costs

The maintenance costs for this plant are projected as 4% of the installed ISBL cost plus 2% of the installed OSBL cost. This leads to approximately \$2.3 Million per year based on maintenance alone. Using stronger materials in the unit operations of this process will drive up capital costs, but hopefully the maintenance needed on the machines will be less. Then, this could also decrease the labor costs for employees if they are not going to maintain the units as much. Also, miscellaneous fixed costs are assumed at \$1 Million per year which gives a total of \$3 Million per year of additional operating costs.

End-Of Life Value

Assuming this plant has a profitable lifetime of 20 years, the salvage value will not be very high. The scrap value of this plant is assumed to be 10% of the FOB cost for the plant, which approximately calculates to \$950,000. The decommissioning cost of the plant is assumed at 5% of the FOB which approximately calculates to \$475,000. Adding these two numbers together results in the end-of-life value of this plant as \$1.45 Million.

Year-to-Year Cash Flow Analysis

The year-to-year cash flow analysis for this project with a product price of \$0.70/lb [36] is attached in Appendix 3. The discounted cash flow rate analysis is included. The cash flow without a discount factor is highlighted in green whereas the cash flow with a 10% discount factor is highlighted in orange.

Discounted Cash Flow Analysis

The discounted cash flow analysis including IRR and NPV is shown in Table 22 below. It is also the same worksheet analysis as in the year-to-year cash flow analysis. As it has been stated previously, due to the low FCI cost, changing the selling prices of the product and byproducts are crucial to the success of the project. With a low product and byproduct selling price, this project is infeasible, as it can be seen in the table. Originally, the reasonably high purity of 1-methyl-4-propylbenzene (MPB) price was much higher than is actually used in this project. From TCI Chemical, at 99.0% purity, MPB was sold for \$142.00 in a 5-mL container [37]. Since the purity coming out of the bottoms of column D30PX has 99.4% purity, the product was sold at a higher price. But, this seems unreasonable, so the price of MPB was decreased to \$0.70/lb assuming that it can be used for the same processes as para-xylene [36]. Dropping this price to \$0.70/lb unfortunately took away the feasibility of this project when keeping Para-Xylene price market-competitive. [36]

With all of these costs and profits, in its current design, this plant does not generate an Internal Rate of Return (IRR), and a Net Present Value with a discount factor of 10% (NPV10) at the end of the 20-year lifespan is approximately -\$350 Million.

Table 22. Discounted Cash Flow Analysis Including IRR and NPV.

NPV Summary (\$MM/year)	
NPV0	-\$662
NPV10	-\$349
IRR	N/A
PBP (approx) (yrs)	N/A

Sensitivity Analysis

Profitability of Project

As it was previously stated, the low FCI of this plant causes extreme volatility in the profits of this process. With high para-xylene and MPB selling prices, this plant can make a lot of money in a short amount of time, or with low para-xylene and MPB selling prices, this plant will prove to be infeasible. Table 23 on page 81 shows the IRR fluctuation of this process as the parameters of this process are changed by +/- 10%. As it was stated earlier, this project was feasible if the MPB price was increased to \$2.25/lb. This selling price is what the tornado plot was based on. Using the current MPB selling price of \$0.70/lb, since there is no IRR, there is no tornado plot based on the IRR, so the older tornado plot with the \$2.25/lb MPB price was used for this analysis. As you can see, if the feasibility of this project is completely changed by changing the third-most important constituent of this process, it is imperative to find a stable and lower feedstock price and to keep the para-xylene selling price competitive in the market since they affect the system more than the MPB.

The parameters changed to determine their impact on the feasibility of this plant are fructose, Para-Xylene, MPB, raw material, isopropanol, and hexane prices as well as changing the installed ISBL cost. The fructose, isopropanol, and hexane components also fit in the "Raw Materials" category, but this category also covers hydrogen and ethylene flow into the system. The parameter that has the greatest impact on the feasibility of this project is the price of fructose, and the parameter that has the smallest impact on the project is the price of hexane. Assuming the fructose price and market remains relatively constant, the next two parameters with a great impact on the process are Para-Xylene and MPB prices. As it has been stated throughout this report, these two parameters determine the feasibility of the plant.

Also, the fructose cost was assumed to be \$0.38/lb, but this price is based on only 42% pure High Fructose Corn Syrup (HFCS) and based on Corn Naturally's website, which seems to be a food

industry-based website. So, if another price of fructose is found that is not with the food industry, this could give a feasible project. It has been discussed that an Ion Exchange column will be sized and priced to obtain 99%+ purity HFCS. This will adjust the capital costs, but will also hopefully generate much more money in the long run for the plant so that it is easier to produce more Para-Xylene. This is discussed more in detail in the future work section. Figure 19 below shows the market prices for Beet Sugar, HFCS-42, and HFCS-55 ranging from 2004 to February 2016.

MONTHLY REFINED SUGAR AND HFCS PRICES From January 2004 to Present



Figure 18. HFCS and Sugar Beet market prices from 2004 to February 2016. [37]

The reason hexane does not have a substantial impact on the process is that compared to the amount of Para-Xylene hexane produced is that very little hexane is consumed. Thus, its price per year does not have much of an impact on the plant (besides the capital investment). Similar to hexane, very

little isopropanol is consumed compared to the production of Para-Xylene, despite it being much more expensive than hexane.

Something to confirm with this report is the large impact of MPB price has on the feasibility of this project compared to the other components. Before, this project was feasible when the price of MPB was \$2.25/lb. Assuming that even upgrading to stainless steel appliances will not greatly affect the capital investment of this process, this proves the power of the prices of the main feedstock and sellable product and byproduct. Keeping the MPB selling price at \$2.25/lb constant, changing the Para-Xylene selling price from \$0.70/lb to \$0.65/lb changes the IRR from 11.8% to 0.85%. Also, keeping the Para-Xylene price constant but changing the MPB selling price from \$2.25/lb to \$0.70/lb removes the possibility of an IRR for this process. Although the MPB price does not have as much of an impact on this process as Para-Xylene does from an IRR standpoint, they both still affect the profitability of this process in very large ways.

According to Figure 20 below, it is obvious that fructose has the greatest impact of profitability of this plant over any other fluctuating parameter. However, the price of HFCS has only steadily and predictably increased over the last 12 years with intermittent plateaus [37]. Since 2004, the price of HFCS-42 has gone from approximately \$0.20/lb to \$0.38/lb [37]. Although this price has nearly doubled, compared to Beet Sugar, this trend is substantially much more stable which shows how substances with fundamentally similar backbones can fluctuate in market prices [37]. Also, since it is a lower purity than HFCS-55, the price of HFCS-42 is lower than HFCS-55, but they increase and decrease according to the same trend. Assuming the price of fructose predictably increases, appropriate precautions will take place to account for the increasing change in fructose prices and the focus of the money making for this process will be on the selling prices of Para-Xylene and MPB.

Table 23. Profitability and IRR sensitivity analysis for changing certain parameters by +/- 10%.

Change in (+/- 10%)	Low	Base	High	Swing	Swing^2	Variance
ISBL	12%	12%	12%	24%	0.0572	17%
MPB	4%	12%	18%	22%	0.0505	15%
PX	-6%	12%	23%	17%	0.0287	9%
Fructose	24%	12%	-8%	17%	0.0284	9%
Hexane	12%	12%	12%	24%	0.0557	17%
Isopropanol	12%	12%	11%	24%	0.0557	17%
Raw Materials	14%	12%	9%	23%	0.0551	17%
Sum Swing^2					0.3313	

As stated earlier, there are specific raw materials listed in this sensitivity analysis, but the “Raw Materials” category covers these raw materials listed as well as hydrogen and ethylene feeds.

Tornado Sensitivity Plot

Figure 20 below shows the Tornado Sensitivity Plot run for this process.

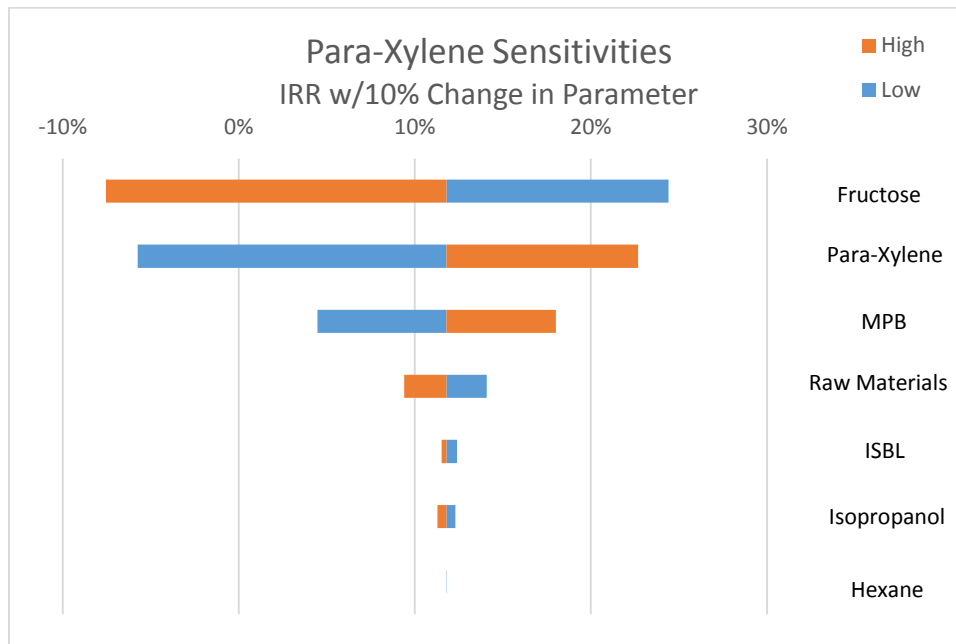


Figure 19. Tornado Profitability and IRR sensitivity plot for changing parameters by +/- 10%.

Global Impacts – Zach Witters

Greenhouse gas emissions are becoming a growing concern due to the climate change over the past few years. CO₂ is a greenhouse gas as it does have an IR spectra and absorbs additional light that is being emitted from the sun. As of 2012 the Department of Energy projected United States' greenhouse gas (GHG) emissions from the US energy industry to drop 28 percent from its 2007 value by 2030. [38] To do this there are many things that must take place. Our energy infrastructure is set up to primarily burn fossil fuels and generate electricity and other forms of energy via combustion. To help prepare for future energy infrastructures, implementing systems that can be changed to develop and use renewable fuels while still allowing for the use of hydrocarbons will be extremely important to the future energy infrastructure. Figure 21 below shows what industry greenhouse gases are emitted from.

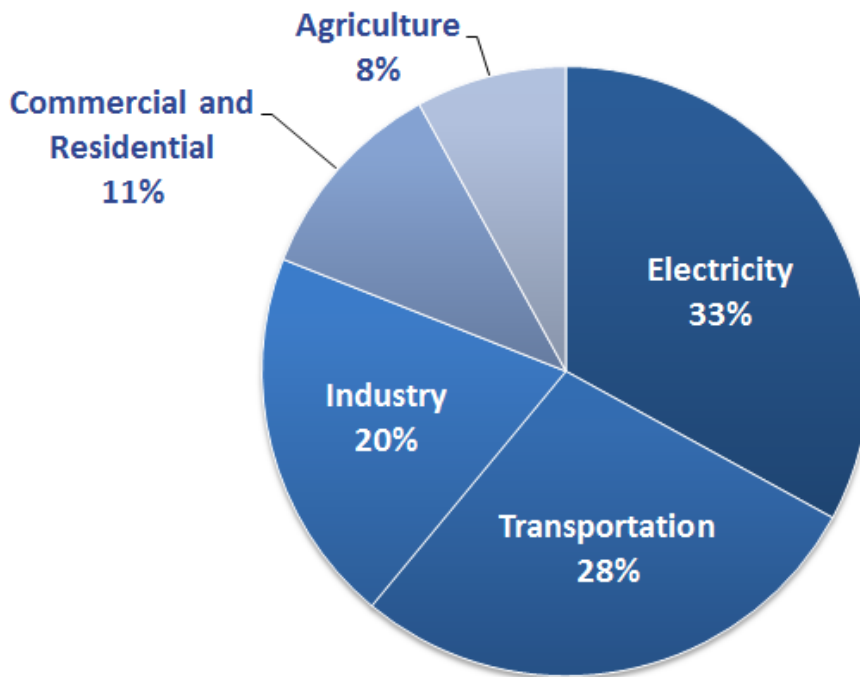


Figure 20. Percentage of U.S.'s global greenhouse gas emissions by industry. [39]

The production of PX from renewable sources allows for the development of this energy infrastructure. As more expensive sources of oil are mined and the price of gas rises, renewable biofuels will be more and more economical. Continuing to develop this process's efficiency will allow for more competitive markets to open. With rising oil prices and lower synthesis costs' PX from fructose can allow for a biofuel that can be integrated into combustion engines for electricity generation or be used in the transportation industry. However, currently PX is too expensive to be used in the biofuel market and this is a long ways out. Selling high purity PX to be used for DMT, PTA, and for other industrial chemicals will allow for research in the catalysis and separation processes involved in the production of PX. This will further lower its costs making it a promising source of biofuel in the future.

Accomplishing the U.S's goal to reduce carbon emissions by 28% in 2030 will be important not only to lower our emissions but to promote lowering greenhouse gas emissions of other countries. This can be done through the development of renewable sources of pure hydrocarbons that can be developed and optimized for industrial use and later integrated into the transportation and energy infrastructure. This allows for the use of carbon neutral sources of energy to decrease global greenhouse gases and ultimately providing infrastructure for the U.S. to meet its goals.

Conclusions and Recommendations – Rachael Weber

The production of PX from fructose and glucose have been considered in past projects, but have not yet been created on the industrial scale. In the research of this semester, the only company that is somewhat close to making this project real is Virent, and they are on the pilot-plant scale. With the current petroleum bust, biorenewable production of para-xylene is a very attractive industry to enter. This way, para-xylene production will be more independent so more products can be made from it without depending on the fluctuating petroleum industry.

The FCI of a plant that produces 262 MMlb/yr of 99.8% pure PX is estimated to be approximately \$62.5 million. There are no payback period or internal rates of return because the yearly costs for this project exceed the revenue generated by the plant. The net present value with a discount factor of 10% after twenty years gives a \$350 million deficit. The project is estimated to make \$183 million/year when at full production rate. The importance of the price of PX to the economics of the plant can be described by the changing the price of the PX by \$0.05/lb, this produces a change in the IRR of 11% (IRR ranges from 0.8 to 11.8%). Thus, with lower feedstock fructose prices and future price increases of PX, this plant may be feasible.

These results are not very promising for a research project that has as little published data on the reactions and separation processes as this process has. While the process of producing PX from fructose is relatively new, little research has been done, and the pilot plants that do run this process are trying to develop experimental breakthroughs that will make their process even more economically friendly. Based on the little amount of research published on the process, it is recommended to look further into catalysts and more economically friendly ways of reaction procedures and separation processes. With the development of lower-cost catalysts that are longer lasting, better and more

efficient separation processes, and lower solvent concentrations, the FCI will decrease and profit margins will increase. This process will become only more promising as further research is being done and as biofuels become a larger part of the energy industry.

Future Work – William Duncan

Work that still needs to be completed for this design includes sizing and pricing an ion exchange column for section one to purify HFCS 42 to greater than 99% fructose. This will add additional costs to the economics and will be further researched. Also, evaporation systems or ion exchange columns for catalyst regeneration and salt recovery for the first section also needs to be sized and included in economics. A simulation may be conducted on the side to determine the size of the vessels due to flow rates to help assist in more accurate economic analyses, but more information on the ion exchange resin needs to be researched and determined.

There needs to be additional research conducted as well to verify that assumptions that were made for the simulation. For section one, the scalability of the reaction needs to be tested at higher levels rather than just 10 grams of fructose. This will ensure the ability to scale up to industrial size. Scalability should be analyzed for each reaction. Also, more research needs to be done to ensure that the catalyst is not being coked by humin formation. It is important that we acknowledge there may be poisoning of the catalyst that occurs because we will need to burn it off to regenerate the catalyst. Another area that could be researched is running the reaction with less solvent. If it does not affect the reaction yields, this would greatly reduce the costs and size of equipment as well as raw materials.

For section two, the most important assumption that needs to be verified is that the reaction will still occur at the same selectivity and conversion using a trickle bed reactor with no solvent compared to a CSTR with solvents that cause difficult separation. This is important because it simplifies the process and reduces capital cost and utilities. If a solvent is used, the separation of solvent and products is incredibly difficult due to the possibility of multiple azeotropic interactions. Accordingly, the verification of a trickle bed reactor is crucial to the feasibility of the design. Further research and economic analysis needs to be done to determine the type of catalyst used (nanoparticle or pellet size),

and then recycling or reactivating this catalyst will also have to be understood. Finally, experimental results on the prism membrane may be important to reaction conditions and recycle compositions. Solving all of these unknowns will be important to finalize results on section 2.

For section three, research needs to be done that verifies that no side reactions occur from byproducts sent from section 2. More byproducts could affect the purity production of para-xylene for the overall process. Also, more research needs to be done to test that the coking can be removed from the zeolite bed reactor without degrading the catalyst. These factors all affect the overall recovery of para-xylene and yield of the design.

For the economics of this project, a big assumption that we are making is that the fructose market will stay predictably stable. As it was stated in the sensitivity analysis, the market price of fructose is steadily and predictably increasing if obtained from high fructose corn syrup, but it also has the largest impact on the IRR of this project. Accordingly, the prices of fructose will be monitored to ensure appropriate action can be taken to combat any sudden changes.

Obtaining research on the 3 sections involved with this process will allow for better estimations of economic variables and in turn the overall availability of developing an industrial sized plant. Overall, research needs to be conducted in hopes of lowering our costs and reducing uncertainties before this process should be considered. Due to a low margin of revenue and many unknown conditions for reactions, this process is not plausible for possible construction. However, this paper presents the future research areas that require development for the future industrial feasibility of this project to be seen.

Additionally, a different price of HFCS should be gathered from a bulk supplier. It seems that the HFCS price from Corn Naturally is geared more toward the food industry, so the price is assumed to be higher than an industrial price of the syrup. Since our HFCS is used to produce PX, a better bulk price

from another supplier should be found. With a lower price point of the feedstock, this could decrease the feed prices and therefore make the process more feasible.

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Appendices

Appendix 1 - Safety

The following items can be found attached:

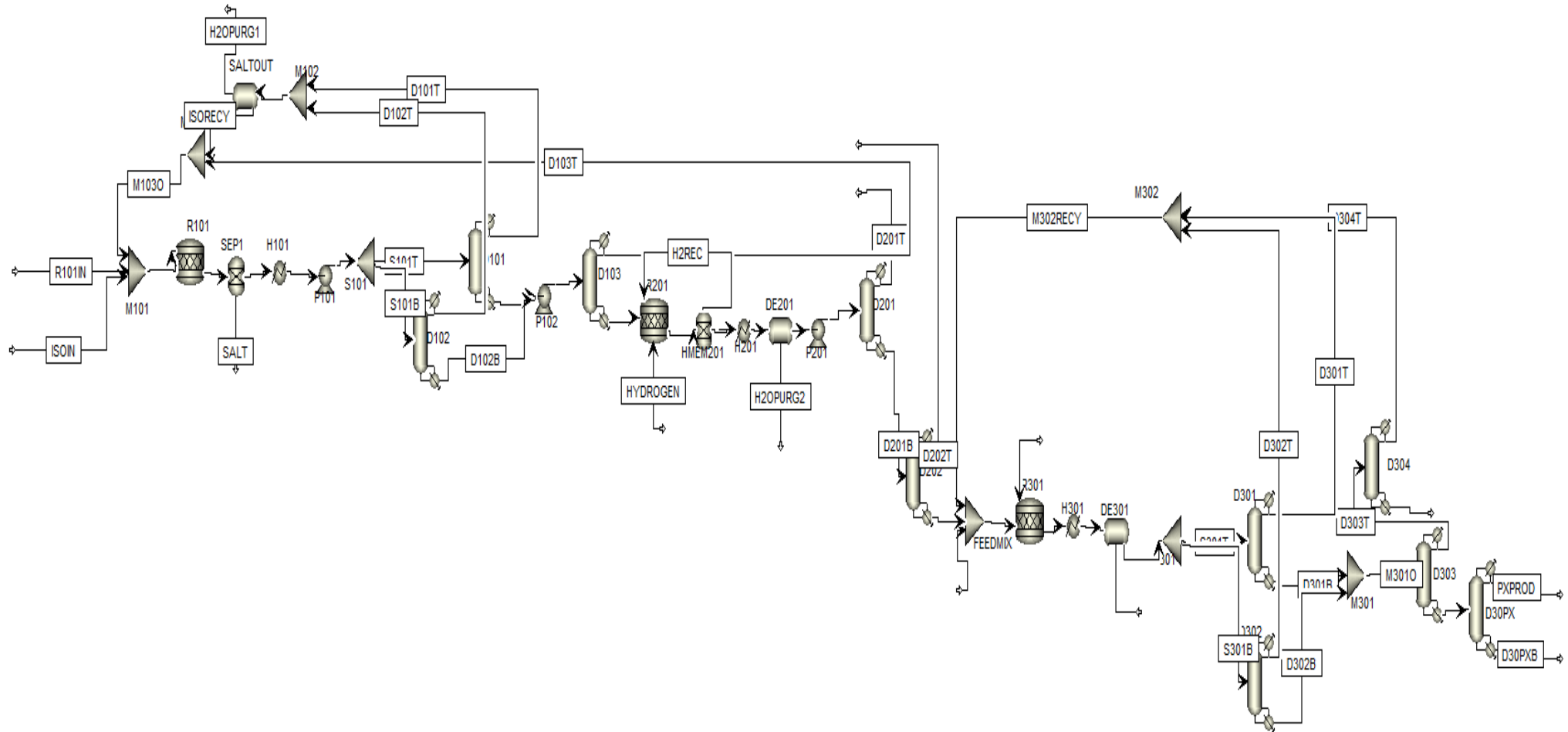


SafetyDataSheets.zip



HAZOPResults.zip

Appendix 2 – Overall Process Diagram



Appendix 3 – Material Balance and Economics

Please see the following for material and energy balance, economics, and pollution calculations.



Final LCGPM Econ.zip