Methane to Aromatics

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Methane to Aromatics

Timothy Gunderson, Andrew Mann, Aric Von Buettner, Audra DeStefano

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Executive Summary (Andrew)

The United States currently consumes more benzene than it produces as of the year 2015 [1]. Approximately 25% of the benzene consumed in North America is imported from other countries. Figure 1 shows the amount of benzene produced verses consumed for North America. The process in which BTX type products are produced in the United States is through catalytic reforming of naphtha. This takes higher order hydrocarbons, typically six to twelve carbon hydrocarbons and reforms them from linear type hydrocarbons into ring type hydrocarbons using a catalytic reformer [2]. Naphtha prices are currently around $500 per ton which is slightly lower than the BTX product that it is used to produce [3]. Currently this process yields 50-55% toluene, 30-35% xylenes and only about 10-15% benzene [4]. The process proposed in this paper takes advantage of the current low price of natural gas and uses methane found in natural gas as the feedstock to make BTX. Methane from natural gas about $350 less per metric ton than naphtha ($156/mt). The process also yields about 93% benzene and 4% toluene and negligible amount of xylenes which is about 4.5 times the amount of benzene yielded from the current process. This is a crucial piece to this process due to the shortage of Benzene in the United States and the fact that the US must import almost 25% of the benzene consumed. The plant and process proposed alone can make up for about 15% of the total benzene that must be imported to the United States reducing the extra cost via tariffs that must be paid to import the extra benzene needed for the consumption of the United States. Toluene although a valuable product the United States is able to meet its own demand of Toluene through domestic production. Toluene produced from the current process is often put through a separate process in order to make more benzene due to toluene being three times as abundant as benzene from the reforming of naphtha.
There have been several catalysts researched in the conversion of methane to BTX type products. The Mo/ZSM-5 catalyst was chosen for this process due to the largest combined selectivity to BTX type products and the lack of methane converted to Coke. Two very valuable side products are also created during this process, these are diatomic hydrogen and naphthalene. Using the information provided in the research paper, Aspen Plus, and a full economic evaluation it was determined that the process would have an IRR of 28%, an NPV10 of 680 MM$, and a payback period of about 2.5 years from start up.

The biggest obstacle in this process is the large recycle stream due to the low conversion of methane by the catalyst (7.2%), the recycle stream accounts for about 90% of the methane being fed into the reactor. Despite this large recycle the process proposed seems to be a viable option to create benzene and toluene for profit. It is recommended that the process goes to bench scale for further research on whether this process can perform as well as predicted by the research papers and aspen plus. This future work should include an analysis of the catalyst lifespan and degrading over time due to impurities within the system. Different reactor
conditions should be tested to check the effects of temperature and pressure on the yields. The use of an alternative catalyst should also be tested to determine the most effective one for the job. Due to the promising IRR and Payback period of this project estimated thus far it is recommended that further efforts be put into the development of this process. These efforts should be put into the research of the longevity and performance of the catalyst over time, the use of hydrogen as a fuel source instead of the purged hydrocarbons, and the types of separation used to reduce utility costs.

**Scope of Work (Aric)**

**Design Problem Statement:**

To design a system that converts methane to benzene and toluene such that it will obtain 720 million pounds per year of mixed benzene and toluene, while also maintaining the process such that it will be both safe and economically sound.

**Constraints:**

**Scientific/technical Constraints**

1. *Supercooled Refrigerant* - The flash drum needs to operate at a low temperature in order for the separation to occur. For now, using propane as our flash drum refrigerant fluid works well for reaching the low design temperature.

2. *Reactor Volume Modification* - Involves multiplying the initial calculated volume of the reactor by 2 or 3 times in order to account for guard/inert solid, which prevents the catalyst from being removed from the reactor. Using a minimum factor of 2 to 3 ensures the reactor will be large enough to operate effectively and safely.
3. **Heat Integration** - This constraint ensures that heat input and output is balanced. We need to check our approach temperatures for feasibility. Using heat integration will increase our capital costs, but reduce our variable costs, so we need to determine a reasonable solution for our system. Our current heat integration requires very large heat exchangers, so we may need to consider the feasibility of smaller exchangers.

**Environmental Constraints**

1. **Pollution** - Many of the unit operations of our process are heated by a furnace that is run on natural gas. We will need to apply for an appropriate pollution permit that economically covers the environmental effects associated with dumping our furnace’s effluent gas to the atmosphere.

2. **Energy Consumption** - The feedstock for our process is solely natural gas. We will be consuming natural gas which is a finite resource, this will further accelerate the depletion of this natural resource. While there is currently a glut in natural gas, which makes it unlikely that it will run out / run low anytime soon, it would best to perform a brief analysis of the marketplace in order to put any concerns to rest.

**Economic Constraints**

1. **Cost of natural gas** - The cost of natural gas has a great effect on the profitability of the process. We have addressed this by running preliminary economic sensitivities that demonstrate what effect changing the price of natural gas by 25% from our base case will have on our IRR.

2. **Cost of BTX** - The cost of our BTX product has a significant effect on the profitability of the process. We have addressed this by running preliminary economic sensitivities that
demonstrate what effect changing the price of BTX by 25% from our base case will have on our IRR.

3. *Cost of Byproducts (Hydrogen, Naphthalene)* - This also has a significant effect on the profitability of the process. We have addressed this by running preliminary economic sensitivities that demonstrate what effect changing the price of both of our byproducts by 25% from our base case will have on our IRR.

**Production Constraints**

1. *Product Rate* - This is limited by the need for our process to be economically feasible without overrunning the market. The 2010 global production of benzene alone was about 80 billion pounds. We currently produce about 720 million pounds or BTX product per year. Our product mainly consists of benzene, so our production would account for less than 0.6% of the global benzene market. This means that we will not be flooding the market, so we have some flexibility with adjusting production rate to make our process profitable. While we are currently a profitable venture, there is always room for improvement in this regard, so we could look to manipulate the production rate such that our process becomes even more profitable in the future.

2. *Catalyst Deactivation* - Our catalyst can become deactivated due to coking. We address this by keeping a small percentage (1-1.5 weight percent) of hydrogen in the feed to the reactor which is required in order to prevent/lessen the amount of coking. Our process has been designed so that the hydrogen produced by the reaction is recycled back to the feed stream at the desired rate.

3. *Hydrogen Membrane Temperature and Pressure* - The temperature of the stream entering the hydrogen membrane needs to be between 25 and 400 degrees Celsius and the pressure
of the stream must be between 300 and 600 psig in order for the hydrogen membrane to operate properly. Currently, our recycle stream enters the hydrogen membrane at 30 degrees Celsius and 470 psig which meets this constraint.

**Product/Feedstock Constraints**

1. *Feedstock Rate* - The state of Texas produces an average of 19.7 billion cubic feet of natural gas per day, which far exceeds our current usage of 108,500 cubic feet per day. This means that we have some flexibility in the amount of natural gas our facility will require and can adjust it to meet our production needs.

2. *Reactor Temperature* – Judging from the fact that all of the literature we looked at indicated that they only ran the reactions involving the Mo/H-MFI catalyst at one temperature, our reactor will need to be run at 973 K for optimum catalytic conversion. While we could attempt to perform studies in the future in order to certify this, our process is currently designed so that the reactor currently operates at 973 K.

**Safety Constraints**

1. *Material Compatibility* - The unit operations of our process have to be designed so that the corrosion/fouling does not jeopardize the health of plant personnel and the public at-large, as well as preventing the need to replace unit operations much more often, which will reduce the cost of our process. We have met these constraints by using stainless steel in the majority of the unit operation design.

2. *Flammability* - Many of the chemicals used in our process are extremely flammable. To address the potential hazards associated with leaks, we plan to enforce strict no smoking
rules on the plant site, install detectors for those flammables, and maintain the practices of safe flammable storage and handling.

3. **Unit Op and Pipe Pressures** - This constraint limits the type of material and thickness that will allow any particular unit op or pipe to be handle the operating pressures of the system.

**Practical Constraints**

1. **Reactor Volume** - Due to the low catalytic conversion in our process, a large space time will be required for our desired production rate. This can be an issue if our reactor is designed to be impractically large (i.e. larger than the biggest building in the world.) Our reactor has been designed such that it is very large but not too large.

2. **Tower Height** - There is a 200 foot height limit for our distillation tower due to weather conditions (potential hurricane storms) in the gulf coast. Our tower is designed to be well below 200 ft.

**Introduction (Andrew)**

The recent downturn in natural gas prices has opened up alternative chemistry methods to create higher order hydrocarbon products, including ring structure hydrocarbons and in this process aromatics. Our team is using natural gas as the feedstock to produce about 720 million pounds per year of mixed Benzene and Toluene. These products are very important to the petrochemical industry, with global consumption of benzene being 40,000,000 tons in 2010 which was an 8% growth from 2009 [5]. These products can be used as additives to fuel as well as precursors for several other chemicals as shown in figure 2.
The proposed plant will be located on the Texas Gulf Coast because of existing refinery infrastructure and the positive tax climate of the state. Current production of BTX products in industry is done in a variety of ways however the most common in the US involves using a catalytic reforming of Naphtha. This process provides about 40% of the benzene in the United States, the other 40% is produced by extracting benzene from pyrolysis gas, and the last 20% is provided by the catalytic hydrodealkylation of toluene [6]. In this process most common practice Naphtha is mixed with hydrogen and fed into a reactor containing a catalyst at 425-530 degrees C and 7-35 Bar. The aromatic rich fraction is then separated from the reformate. This process is similar to the one proposed however the feedstock will use a single carbon feedstock (methane) instead of using 6-12 carbon hydrocarbons. This process consumes about 1,025 btu/lb of product produced. This process also emits, benzene, toluene, xylenes and solvents. The largest source of effluents for this process is process water, while the waste and byproducts are raffinate, coke, and spent catalyst. This process often takes the toluene from this and runs it into a catalytic hydrodealkylation of toluene to produce more benzene [7]. This process is shown in figure 4.
Figure 3. Current method for BTX production

The cost of the methane feedstock is less than half of that of naphtha on a per ton basis and the yield of benzene is about 4.5% with this proposed process. A flow chart of the process for refining naphtha into BTX products is shown in figure 3. Several catalysts have been researched in the making of BTX products from methane. These catalysts tend to be Molybdenum zeolite catalysts with very low conversions of 4-12% however, the selectivity from methane to BTX type products is very high. In order to overcome this low conversion our process requires a recycle stream in which unconverted methane is fed back into the front of the process.
The second most common practice involves extracting benzene from pyrolysis gas. This process is shown in figure 8. Pyrolysis gas, also known as Pygas, is a naphtha type product that is high in aromatic content. It is a byproduct of high temperature naphtha cracking during ethylene and propylene production [8].
The main reason this catalyst and process was chosen is due to the high selectivity to benzene as well as the lack of coking when converting methane to other compounds in this reaction. This process also creates valuable side products, diatomic hydrogen and naphthalene. These side products provide an additional $78,000,000 in revenue per year in addition to the $231,000,000 provided by the benzene and toluene mixture. The utilities for this process is also kept to a minimum by using the purge stream as fuel for a furnace to provide heat where needed throughout the process. This purge stream is also used in a generator to provide electricity for the plant and compressors in the process. This helps tremendously on our utility cost due to the massive temperature swings throughout the process.

**Description of Base Case (Audra)**

**Overall Design Description:**

The base case simulation covers the conversion of methane to aromatic products and the purification of the resulting products as shown in Figure 2. First, the natural gas feed (NGFEED), which is almost entirely made up of methane, is mixed with the RECYCLE stream and enters a heater (H101-H), which heats the mixed stream to 973 K. After heating is complete, the stream is ready to enter the reactor R101, where the partial conversion of methane to benzene, toluene, and various byproducts takes place with a Mo/H-MFI-B catalyst. The resulting stream that exits R101 (R101O) enters a condenser (H101-C, H102-C, and H103) which cools the stream down to the required temperature for it to enter the flash drum (D101). D101 separates the cooled-down reactor effluent (H102O) into two streams (D101VO and D101LO). D101VO consists of the unreacted feed and hydrogen, which is recycled back to the front of the process after it is compressed (C101), heated (H102-H), and passes through a hydrogen membrane (S101) which removes most of the hydrogen from the resulting RECYCLE stream. D101LO contains the
aromatic products, which are separated using a distillation column (T101) into a vent stream (TVENT) of light aromatics, a stream primarily consisting our naphthalene byproduct (NAPHPROD), and a stream that contains our desired benzene and toluene products (DISTIL). From there, a benzene recovery system consisting of a cooler and a flash drum will separate out much of the benzene and toluene in the TVENT stream. The recovered chemicals will be combined with the DISTIL product stream to form BTXPROD. The remaining materials of TVENT will be used to power a furnace and electric generator.

**Basic Chemistry and Separations:**

**Reaction Chemistry**

Aromatic products are produced from methane as part of a five reaction system using Mo/H-MFI-B as a catalyst. Along with the desired toluene and benzene, naphthalene, hydrogen, ethylene, and ethane are also produced as shown in Table 1. The MFI zeolite has a 3-dimensional pore structure, with openings of 6 angstroms. It also possesses a SiO$_2$/Al$_2$O$_3$ ratio between 20 and 1000, and a surface area to weight ratio of over 300 m$^2$/g. The molecular structure of the zeolite is shown in Figure 6 with defined pores and channels. The yellow balls represent silicon and red balls represent oxygen atoms in Figure 6 [9, 10].
Mo/H-MFI catalysts can be prepared by impregnating H-MFI support with ammonium heptamolybdate solution, which would then be followed by drying it overnight and performing calcination at 773K for 3 hours. The mixture would then be stirred for 3 hours at ambient temperature to form a gel, after which it would be treated hydrothermally at 443K for 1 week in a stainless autoclave. The resulting product (Na-MFI) would then be dried overnight and Na+ removed using NH4Cl solution. Finally, the product should be dried and calcined at 873K for 3 hours. Once exposed to methane gas, the molybdenum catalyst initiates conversion of methane to benzene and other products. The proposed mechanism for the production of benzene and hydrogen, shown in Figure 7, begins by polarizing one of methane’s C-H bonds. After that, the polarized methane reacts with a Bronsted acid site, forming carbene-like intermediates which are dimerized to produce ethylene, which in turn is aromatized to produce benzene and hydrogen [11].
Five reactions occur when methane is exposed to Mo/H-MFI-B to produce benzene, toluene, naphthalene, ethylene, ethane, and hydrogen, with the highest selectivity shown for the benzene product. These reactions along with their methane conversions are listed in Table 1. All five reactions have low conversion rates, with a total methane conversion rate of 6.18%. This conversion can drop even lower due to the coking of the catalyst’s active sites, which deactivates it. Coking can be mediated through adding a hydrogen co-feed to the reaction [11,13].

Table 1. The five reactions occur when methane is exposed to the Mo/H-MFI-B catalyst used in the reactor along with their proposed conversions [13].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$</td>
<td>4.78 %</td>
</tr>
<tr>
<td>$10\text{CH}<em>4 \rightarrow \text{C}</em>{10}\text{H}_8 + 16\text{H}_2$</td>
<td>0.80 %</td>
</tr>
<tr>
<td>$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$</td>
<td>0.20 %</td>
</tr>
<tr>
<td>$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2$</td>
<td>0.20 %</td>
</tr>
<tr>
<td>$7\text{CH}_4 \rightarrow \text{C}_7\text{H}_8 + 10\text{H}_2$</td>
<td>0.20 %</td>
</tr>
</tbody>
</table>

Separations

Four major separations occur throughout the process: 2 flash drums, a hydrogen membrane, and a distillation tower. The first is the separation of produced aromatics from the hydrogen and unreacted feed accomplished through use of a flash drum. As a result of the very
low conversion rate in the reactor, less than 5% of the material leaves the flash drum as liquid in stream D101LO. Of that liquid stream, about 80% is benzene, 13% is naphthalene, and 3% is toluene, with the remainder consisting of small amounts of hydrogen, ethylene, ethane, methane, propane, and butane. The significantly larger vapor stream (D101VO) contains large amounts of methane and hydrogen, and is recycled. Due to large amounts of light compounds, the drum operates at 430 psi and -30°F.

A second separation system is the hydrogen membrane used to separate hydrogen from the recycle stream. This ceramic membrane splits the stream and produces a very high purity stream of greater than 99.5% hydrogen, while leaving enough hydrogen in the recycle stream to maintain a 1% mass concentration in the feed to the reactor in order to reduce catalyst deactivation via coking.

Another separation takes place with a distillation tower, T101. This tower is designed to separate the process’s naphthalene byproduct from the benzene and toluene mixture (BTX mix) product. Stream D101LO, which consists of approximately 80% benzene, 3% toluene, and 13% naphthalene by mass fraction, with the remainder consisting of small amounts of hydrogen, ethylene, ethane, methane, propane, and butane enters the distillation column for separation. Three streams, DISTIL, NAPHPROD, and TVENT leave the column. The naphthalene byproduct stream, NAPHPROD, is 99% pure naphthalene by mass has a mass flowrate of about 13,400 pounds per hour. The BTX mix stream, DISTIL, is 93% benzene and 4% toluene and flows at a rate of about 90,000 pounds per hour. A vent stream, TVENT, of mostly (89%) benzene, ethane, ethylene, and methane vapors leaves the top of the column at a rate of 4,700 pounds per hour. Including a vent stream increases the purity of the benzene and
toluene in the BTXPROD stream by purging a majority of the methane, ethane, and ethylene from the D101LO stream.

The TVENT stream is used as a fuel source for the electric generator used to power the process's compressors and reboiler after removing most of the benzene with another flash drum, D102. Feeding the vent stream to the generator as a fuel source makes use of a stream that would otherwise be wasted. The BTXREC stream leaves the bottom of D102 and is added to the T101 distillate stream for a final production rate of about 91,000 pounds per hour. Adding D102 to recover benzene and toluene reduces the burned vent by about 1,200 pounds per hour.

**Assumptions and Approximations:**

We made several assumptions in the use of our catalyst due to a lack of literature meeting our needs. The research paper we based our conversions on studied the catalyst at atmospheric pressure [13]. Conducting the vapor phase reaction at atmospheric pressure resulted in very large volumetric flow rates through the reactor, so we increased the pressure to 450 psi and assumed that the conversion would only decrease by 5%. We also assumed that 1% hydrogen present in the reactor feed would be sufficient to reduce coking enough to prevent catalyst replacement and that catalyst regeneration would be inexpensive. Realizing the potential difference this assumption could make, we ran economic sensitivities for catalyst replacement every 5 and 10 years.

Most of the process utilizes stainless steel unit operations due to corrosive effects of methane on stainless steel [14]. One of the exceptions to this is the distillation tower because the feed to the tower is only 2% methane by mass, which we assumed to be low enough to negate the negative effects of methane on carbon steel. This assumption would need to be confirmed before installing a real distillation tower.
Our economic analysis also required making an assumption. The cash flow diagram we developed assumes nameplate production will be reached during the first year of operation. An economic sensitivity was conducted with a more gradual startup to account for this assumption. We also assumed that equipment prices were scalable from 2002 using cost indices.

**Solution Procedure:**

Aspen Plus was used to model the methane to aromatics plant. The Soave-Redlich-Kwong (SRK) property method was used for the simulation. This method uses a cubic equation of state for all thermodynamic properties and is recommended for hydrocarbon and light gas mixtures. Our reaction occurs at high pressure and contains components with a variety of boiling points which the SRK method is capable of handling. The steam property method used with SRK is STEAMNBS and requires that temperatures be below 2000 K and pressure under 10,000 bar. Both of these requirements are met by our system.

An Aspen simulation for the process was developed in a piecewise fashion. First, the main reactor loop was made using an estimated recycle stream rate. For this preliminary design, we used three heaters to control the temperature and pressure of the streams going into the reactor, exiting the reactor, and exiting the flash drum. After convergence of the recycle stream, we added the distillation tower used to further separate the aromatics. This tower was originally simulated using a large enough number of trays to easily separate our products. When this tower converged successfully, we optimized its size by specifying the reflux ratio to 1.2 and minimizing the reboiler duty.

Next, changes in temperature and pressure throughout the system were further specified. A pressure drop of 5 psi per unit operation was instituted and a compressor (C101) was added to the recycle loop to compress the vapor leaving D101. Heaters were further broken down using a
heat integration. The high reaction temperature and low flash drum separation temperature require significant temperature changes throughout the process. Before the feed stream enters the reactor, it is heated from 60°F to 1292°F, which is the temperature required by the MO/H-MFI-B catalyst used in the reactor. After the reaction, the stream leaving the reactor is cooled to -30°F. This low temperature is required to flash separate the benzene, toluene, and naphthalene products from the lighter recycle stream, primarily composed of methane and hydrogen. The recycle stream is then heated before being mixed with the feed stream. A heat integration analysis determined that the hot reactor effluent could be used to partially heat the reactor feed and completely heat the recycle stream. Final cooling of the reactor effluent was accomplished using a propane refrigeration cycle. The final heating configuration consisted of one furnace, three heat exchangers, and propane recycle system. These components were added to the simulation and used to replace the original heat exchangers.

Final fine tuning of the simulation was made by reducing the purge stream and adding a benzene recovery system following the distillation tower. Reduction of the purge increased flow through the rest of the system and required resizing the distillation column and changing the amount of hydrogen removed by the membrane apparatus. Adequate cooling of the increased reactor effluent required increasing the quantity of propane used by the propane refrigeration system. Effects of flowrate changes on unit operation sizes were made automatically by Aspen.

**Process Flowsheets and Descriptions:**

An overall process flow diagram for the main process is shown in Figure 8. This flowsheet includes the main reactor and separation systems. Heat exchangers used in sizing the heaters and the propane refrigeration system were modeled outside of the main flowsheet. All unit operations in the main reactor and recycle loop, except the ceramic membrane, were
constructed from stainless steel due to the corrosive effects of methane on carbon steel [14].

Figure 8. Process flow diagram for the main reaction and separation steps.

Reactor:

The reactor itself is a fixed bed, plug flow reactor made of stainless steel which has an approximate volume of 2,500 m³. This volume is large due to the volume of high temperature gas being flowed through the reactor. Stream M101O enters and leaves the isothermal reactor at 1291.7°F while the pressure drops from 460 psi to 450 psi. Several reactions are catalyzed by MO/H-MFI-B within the reaction vessel. The main reactions are shown in Table 1, with our main products benzene and toluene having conversions of 4.78% and 0.20% respectively. Naphthalene, ethane, and ethylene are also produced with conversions of 0.80%, 0.20%, and 0.20% respectively, resulting in an overall per pass methane conversion of 6.18%. Hydrogen is produced in each of these reactions in anywhere from 0.5 methane to hydrogen mole ratio all the way up to 1.6 methane to hydrogen mole ratio.

Recycle:

A recycle stream is essential to the operation of the process due to the very low conversion of methane feed in the reaction. The recycle stream accounts for about 94% of the mass flow into the reactor. The recycle stream starts when the light components are flashed off.
the top of our D101 Flash tank. Stream D101VO consists of mostly unreacted methane and leaves D101 at -30°F and 430 psi. D101VO then enters a compressor which increases the pressure to 480 psi in order to maintain a pressure gradient throughout the whole system. A heat exchanger then warms the stream. The recycle stream contains hydrogen which is a valuable byproduct, which is partially removed from the stream using a ceramic hydrogen membrane. The membrane splits the stream and produces a very high purity stream of greater than 99.5% hydrogen, while also leaving enough hydrogen in the recycle stream to maintain a 1% mass concentration in the feed to the reactor in order to reduce catalyst deactivation via coking. After the hydrogen membrane the stream comes to a tee where about 1% of the stream is split off to a purge to prevent impurities from building up in our system. The purge stream is not wasted, as it is sent to a furnace and combusted in order to heat the reactor feed. Finally, the recycle stream is sent to another tee in order to mix it with the incoming fresh feed.

**Heat Integration:**

The high reaction temperature and low flash drum separation temperature require significant temperature changes throughout the process. Before the feed stream enters the reactor, it is heated from 60°F to 1292°F, which is the temperature required by the MO/H-MFI-B catalyst used in the reactor. After the reaction, the stream leaving the reactor is cooled to -30°F. This low temperature is required to flash separate the benzene, toluene, and naphthalene products from the lighter recycle stream, primarily composed of methane and hydrogen. The recycle stream is then heated before being mixed with the feed stream. A heat integration analysis determined that the hot reactor effluent could be used to partially heat the reactor feed and completely heat the recycle stream. The final heating configuration consisted of one furnace and three heat exchangers.
In the Aspen Plus simulation, the first two heat exchangers were represented by two heaters in the process flow diagram, but were modeled separately using HeatX heat exchangers to calculate the heat transfer coefficients and log mean temperature difference used in sizing and pricing the exchangers. The third heat exchanger was only modeled as one heat exchanger because only one side of the heat exchanger utilized process fluid, although this heat exchanger was also modeled outside of the main loop using a HeatX heat exchanger.

The first heat exchanger (H101-HX) uses the hot reactor effluent (R101O) to partially heat the mixed feed to the reactor (M101O). This heat exchanger is represented in the process flow diagram by H101-H and H101-C. H101-H is the side of the heat exchanger that is heated while the stream going through H101-C is cooled. The desired temperature for the reactor feed is equal to the reactor effluent temperature, so the heat exchanger is unable to completely heat the reactor feed without a temperature crossover. This results in the necessity of a furnace to complete the heating of the reactor feed. Stream H101H-O leaves H101-HX and is immediately heated to the reaction temperature of 1291.7°F using a furnace (F101). This furnace has a process duty of 87 MMBTU/hr. An area of about 500,000 ft² was calculated for the heat exchanger. On the hot side of the heat exchanger, a portion of the cooling required for the reactor effluent is completed.

A second heat exchanger (H102-HX) is used to continue cooling the reactor effluent and to heat the recycle stream. The H101C-O stream moves the reactor effluent from the first heat exchanger to the second. In this heat exchanger, the stream is partially condensed while heating the recycle stream to the temperature of the natural gas feed. The recycle stream enters the heat exchanger after being compressed in C101 and before entering the hydrogen membrane. About 367,000 ft² was the calculated area.
A third heat exchanger is required for the reactor effluent to reach the required flash drum temperature. When stream H102C-O enters the third heat exchanger, its temperature is approximately 17°F and it is cooled to -30°F using propane as the cold side fluid. Propane at -40°F was used to avoid the formation of a vacuum and a compression system was required to recycle vaporized propane in the heat exchanger [15]. The resulting heat exchanger area was about 27,000 ft².

Propane Refrigeration:

Propane is used as the cooling fluid in H103-HX. The process vaporizes propane, making a refrigeration unit necessary to recycle the propane in the heat exchanger. After the propane is vaporized in H103-HX, it is condensed to 200 psi using a 7,200 horsepower compressor and then cooled with an air cooler. The air cooler needs to have about 33,000 ft² of surface area. A valve then releases the pressure on the stream to reduce the temperature before recycling the propane back to the heat exchanger. This process is shown in Figure 9. With the exception of the heat exchanger, all equipment in the propane recycle can be made of carbon steel because there is no corrosive methane present.

Figure 9. Process flow diagram for the propane refrigeration cycle.
Flash Drum, D101:

A flash drum is used to separate the produced aromatics from the hydrogen and unreacted feed. The drum operates at 430 psi and -30°F. As a result of the very low conversion rate in the reactor, less than 5% of the material leaves the flash drum as liquid in stream D101LO. Of that liquid stream, about 80% is benzene, 13% is naphthalene, and 3% is toluene, with the remainder consisting of small amounts of hydrogen, ethylene, ethane, methane, propane, and butane. The significantly larger vapor stream (D101VO) contains large amounts of methane and hydrogen and is recycled.

The sizing of the flash drum is based on the process outlined in *Separation Process Engineering* [16]. Sizing was based on the permissible vapor velocity which was calculated using the densities of the liquid and vapor streams and a constant calculated using empirical constants and liquid and vapor flow rates and densities was also used in the calculation of the permissible vapor velocity. This value was used to calculate the drum volume, cross sectional area, and diameter. From there, a rule of thumb ratio of height to diameter of 3 was used to determine the drum height. A vertical drum was used because the liquid load is small compared to the vapor load. The resulting drum had a diameter of 19 feet, height of 56 feet, and drum volume of about 15,900 ft³.

Distillation Tower:

The final separation takes place with a distillation tower, T101. This tower is designed to separate the process’s naphthalene byproduct from the benzene and toluene mixture (BTX mix) product. Stream D101LO, which consists of approximately 80% benzene, 3% toluene, and 13% naphthalene by mass fraction, with the remainder consisting of small amounts of hydrogen,
ethylene, ethane, methane, propane, and butane goes through a valve before entering the distillation column for separation. This valve reduces the pressure and temperature of the stream to prevent coking of naphthalene inside the tower. Three streams, DISTIL, NAPHPROD, and TVENT leave the column. The naphthalene byproduct stream, NAPHPROD, is 99.8% pure naphthalene by mass has a mass flowrate of about 13,400 pounds per hour. The BTX mix stream, DISTIL, is 93% benzene and 4% toluene and flows at a rate of about 90,000 pounds per hour. A vent stream, TVENT, of mostly (89%) benzene, ethane, ethylene, and methane vapors leaves the top of the column at a rate of 4,700 pounds per hour. Including a vent stream increases the purity of the benzene and toluene in the DISTIL stream by purging a majority of the methane, ethane, and ethylene from the D101LO stream. After separation of benzene from TVENT, the VENT stream is used as a fuel source for the electric generator used to power the process's compressors and reboiler. Feeding the vent stream to the generator as a fuel source makes use of a stream that would otherwise be wasted.

The distillation tower, T101, has 17 stages including a reboiler and a partial-vapor-liquid condenser. D101LO will feed into stage 10 of the distillation tower as a liquid. This design for T101 was created with the intention of minimizing the heat duty of the reboiler and obtaining an R to R minimum ratio of approximately 1.2, where R refers the reflux ratio and R minimum refers to the measured reflux ratio of a tower with infinite stages. An economic analysis of the tower determined that a sieve tray tower would be used instead of a packed tower. Assuming a tray efficiency of 75%, T101 will contain 20 sieve trays that are approximately 11 feet in diameter. Each tray will be four-pass in order to manage a high volume flow rate. With each tray being spaced two feet apart from the other, the tower shell will be 54 feet tall. Although methane has a severe effect on the durability of carbon steel, T101 will still be made with carbon
steel because methane accounts for less than 2% of the stream through the tower [13]. Constructing T101 with carbon steel instead of stainless steel significantly reduces capital costs.

Flash Drum, D102:

A second flash drum is required to recover most of the benzene and toluene from the TVENT stream. A stream named BTXREC leaves the bottom of D102 at a rate of 1,200 pounds per hour and consists mostly of benzene. BTXREC is added to the T101 distillate stream for a final production rate of about 91,000 pounds per hour. Adding D102 to recover benzene and toluene reduces the burned vent by about 1,200 pounds per hour. D102 was sized using the method outlined in Separation Process Engineering [16]. The resulting flash drum had a volume of 13 cubic feet with a length to diameter ratio of 3.

Overall Material Balance:

An overall material balance is shown in Table 2. The natural gas feed to the system is 165,000 pound per hour and from that, about 91,000 pounds per hour of benzene and toluene product is produced. In addition to this, about 25,000 pounds per hour of hydrogen and 13,000 pounds per hour of naphthalene can be sold. The process currently vents and purges almost 37,000 pounds per hour. The feed natural gas stream is mostly composed of methane, but also contains small amounts of nitrogen, ethane, propane, and butane [17]. As shown in Table 2, a slight mass balance discrepancy exists, but the error is less than 0.01%.
Table 2. Overall mass balance

<table>
<thead>
<tr>
<th>IN (lb/hr)</th>
<th>OUT (lb/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>165000</td>
</tr>
<tr>
<td></td>
<td>H2PROD</td>
</tr>
<tr>
<td></td>
<td>24602</td>
</tr>
<tr>
<td></td>
<td>PURGE</td>
</tr>
<tr>
<td></td>
<td>32206</td>
</tr>
<tr>
<td></td>
<td>VENT</td>
</tr>
<tr>
<td></td>
<td>3549</td>
</tr>
<tr>
<td></td>
<td>BTXPROD</td>
</tr>
<tr>
<td></td>
<td>90940</td>
</tr>
<tr>
<td></td>
<td>NAPHPROD</td>
</tr>
<tr>
<td></td>
<td>13686</td>
</tr>
<tr>
<td>Total:</td>
<td>165000</td>
</tr>
<tr>
<td></td>
<td>Total:</td>
</tr>
<tr>
<td></td>
<td>164983</td>
</tr>
</tbody>
</table>

This material balance can be broken down to include several internal streams as shown in Table 3. The key streams included are the reactor feed (M101O), reactor effluent (R101O), flash drum vapor stream (D101VO), flash drum liquid stream (D101LO), and recycle stream, along with all streams leaving and entering the system. These streams are representative of changes in stream composition due to the splitting or recombination of streams along with the reaction within the reactor. Temperature, pressure, phase, component mass fraction, and mass flow rate are included for each stream.

Table 3. Key streams summary with temperature, pressure, phase, composition, and mass flowrate.

<table>
<thead>
<tr>
<th>Key Streams Material Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>NGFEED</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Temperature (F)</td>
</tr>
<tr>
<td>Pressure (psia)</td>
</tr>
<tr>
<td>Phase</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Fraction</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Mass Flow (lb/hr)</td>
</tr>
</tbody>
</table>

30
Utility Requirements:

Utility requirements vary throughout the process. Many of the heating and cooling needs are met using large heat exchangers that use the hot reactor effluent to heat other streams, but some additional heating and cooling is required. Excess heat to the reactor inlet stream is provided using a furnace and the reactor effluent is partially cooled using a propane recycle system that utilizes a large compressor. Additional heating and cooling is required by the distillation tower reboiler and condenser, and H104. This is accomplished using a furnace and cooling water. Another compressor with high energy needs is located in the recycle stream. The largest energy requirement for of the system comes from the reactor which houses an endothermic reaction. A complete breakdown of utility requirements is shown in Table 5 where green entries are accounted for using the heat integration, blue represent cooling water needs, and red entries are show electrical requirements of the system.

Table 4. Utility requirements where green entries are accounted for using the heat integration, blue represent cooling water needs, and red entries show heating requirements.

<table>
<thead>
<tr>
<th>ID</th>
<th>MMBtu/hr</th>
<th>Source</th>
<th>Efficiency</th>
<th>MMBtu/hr Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>C101</td>
<td>20.0</td>
<td>Electric Generator</td>
<td>0.4</td>
<td>50.1</td>
</tr>
<tr>
<td>C102</td>
<td>18.3</td>
<td>Electric Generator</td>
<td>0.4</td>
<td>45.6</td>
</tr>
<tr>
<td>T101 Reboiler</td>
<td>35.1</td>
<td>Electric Generator</td>
<td>0.9</td>
<td>39.0</td>
</tr>
<tr>
<td>R101</td>
<td>356.1</td>
<td>Natural Gas Furnace</td>
<td>0.9</td>
<td>395.7</td>
</tr>
<tr>
<td>F101</td>
<td>87.1</td>
<td>Natural Gas Furnace</td>
<td>0.9</td>
<td>96.8</td>
</tr>
<tr>
<td>H104</td>
<td>0.4</td>
<td>Cold Water</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>T101 Condenser</td>
<td>20.8</td>
<td>Cold Water</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H101X</td>
<td>2495.7</td>
<td>Heat Integration</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H102X</td>
<td>154.1</td>
<td>Heat Integration</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H103X</td>
<td>48.0</td>
<td>Heat Integration</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
The energy required to fuel the reboiler, reactor, furnace, and both condensers is supplied by burning the purge and vent streams. A total energy requirement of 627 MMBtu per hour is required to power these unit operations and together the two streams can supply 841 MMBtu per hour. This exceeds our energy requirements, leaving excess energy for fluctuations in utility use and supplementing general electrical needs of the plant. A summary of the energy availability in the purge and vent streams is shown in Table 5.

Table 5. Energy availability of the purge and vent streams.

<table>
<thead>
<tr>
<th>Component</th>
<th>Btu/lb</th>
<th>Purge lb/hr</th>
<th>Total Energy (btu/hr)</th>
<th>Vent lb/hr</th>
<th>Total Energy (MMBtu/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>17270.01</td>
<td>45</td>
<td>778100</td>
<td>208</td>
<td>3583924</td>
</tr>
<tr>
<td>Toluene</td>
<td>17450.14</td>
<td>1</td>
<td>10557</td>
<td>2</td>
<td>42700</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>61000</td>
<td>329</td>
<td>20062900</td>
<td>3</td>
<td>192028</td>
</tr>
<tr>
<td>Ethylene</td>
<td>20290.22</td>
<td>2459</td>
<td>49902842</td>
<td>759</td>
<td>15396665</td>
</tr>
<tr>
<td>Ethane</td>
<td>22400</td>
<td>2270</td>
<td>50846611</td>
<td>956</td>
<td>21420650</td>
</tr>
<tr>
<td>Methane</td>
<td>23900</td>
<td>26779</td>
<td>640021733</td>
<td>1615</td>
<td>38607725</td>
</tr>
<tr>
<td>Naph</td>
<td>17262.35</td>
<td>0</td>
<td>86</td>
<td>5</td>
<td>88677</td>
</tr>
<tr>
<td>Propane</td>
<td>21000</td>
<td>0</td>
<td>3003</td>
<td>0</td>
<td>3654</td>
</tr>
<tr>
<td>Butane</td>
<td>21200</td>
<td>0</td>
<td>657</td>
<td>0</td>
<td>2226</td>
</tr>
<tr>
<td>Total (MMBtu/hr)</td>
<td>761.6</td>
<td>Total (MMBtu/hr)</td>
<td>79.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Process Control:**

Like any process, this process requires many control measures. One of the key control issues is maintaining a mass fraction of 1% hydrogen in the reactor feed, regardless of other fluctuations in the system. For this to occur an on-line gas chromatographs would need to be installed on the M101O stream to measure the composition of the stream. This instrument would determine the hydrogen concentration of the stream relay a signal to control the amount of hydrogen leaving the system through the membrane. Figure 10 illustrates this arrangement where the blue box samples stream composition and the orange box adjusts hydrogen removal.
Figure 10. Purge control scheme where the blue box represents an on-line gas chromatograph and the orange box adjusts the fraction of hydrogen being separated from the recycle stream.

Maintaining proper temperatures and pressures is essential to the success and safety of our operation. For this reason, temperature and pressures of all streams should be monitored using thermocouples and pressure gauges. The reactor, flash drums, and distillation tower column, reboiler, and condenser should also be monitored. Thermocouple and pressure gauge locations are represented by blue squares in Figure 11.
Figure 11. Pressure gauges and thermocouples will be located on all streams and certain unit operations as represented by blue squares.

The methane to aromatics set of reactions is endothermic, as confirmed by the positive enthalpy change of our reaction. This means that a runaway reaction will not result in an explosion, so extensive cooling measures are not necessary. With that said, the possibility of the reactor heating system getting out of control would lead to increased temperatures and pressures within the vessel and could lead to problems. For this reason, the temperature of the reactor should control the heating applied to the reactor as shown in Figure 12 where the orange box represents the heat source for the reactor.

Figure 12. Reactor temperature control where the temperature of the reactor (blue) controls the output of the heater (orange).

The distillation tower requires controls to regulate the temperature throughout the tower. Heat enters the tower through the reboiler and the distillate is cooled using cooling water in the condenser, so the heat source and the cooling water source need to be controlled based on deviations in temperature in other areas of the tower. For example, if the temperature in the tower is too low, more energy should be supplied to the reboiler to raise the temperature in the
rest of the tower. Figure 13 shows how temperatures in and around the tower need to influence the heat source (orange box) and cooling water source (green box).

![Figure 13. Temperature scheme for T101 where the orange box represents the reboiler heat source and the green box represents the condenser cooling water source.](image)

Variations in flowrate impact heating and separations, so they need to be monitored and controlled. Flowrate monitors should be installed on every stream in the process to allow for the identification of any abnormalities. One flowrate control scheme is shown in Figure 14. This scheme requires measuring the flowrate of the recycle stream to ensure that the flowrate of fresh feed into the system is adjusted to keep the flowrate into the reactor constant.
Figure 14. Flowrate scheme where the flow into the system is influenced by the recycle stream flowrate. Flowrate monitors are shown as green boxes.

Discussion:

The simulation developed by our group yielded a reasonable view of the methane to aromatics process. A potential problem with our simulation involves the catalyst conversion. Assumptions were necessary regarding catalyst conversion with increased pressure and would need to be validated to confirm our solution. If the 5% decrease that we assumed proved to be significantly inaccurate, our simulation would no longer be representative of the problem. Another problem is the slight discrepancy in mass balance. Resolving this issue would make the simulation more dependable. Physical properties can cause issues in simulation, but the components used in our system fit the property method well, so we were not required to estimate any physical properties, adding to the dependability of our simulation. Overall, if our assumption involving catalyst conversion is accurate, the simulation is a reasonable representation of a methane to aromatics process.
Design Alternatives (Aric)

Size of Purge Stream:

When we first managed to obtain an Aspen model for our process, we originally designed it such that the purge stream was 5% of the stream coming out of the hydrogen membrane (S101). This was for the purpose of preventing impurities from building up within the system, and we intended to use it in order to provide energy to our generator after it was combusted, thus saving on energy costs.

However, when we got feedback for our report from the fall, which was based on this design, we found out that the purge stream was so large that most of it wouldn’t end up going towards energy purposes, and would thus be mostly wasted. Thus, we reduced the purge stream to about 1% of the stream coming out of the hydrogen membrane, such that all of it is combusted and used to heat the reactor feed.

Mo/ZSM-5 Catalyst:

Due to the low yield facilitated by the Mo/H-MFI catalyst, we considered using another Molybdenum catalyst in order to obtain the same amount of product at a lower feed rate to the reactor (R101). For a time, we settled on the Mo/ZSM-5 catalyst, as we had heard from someone who knew another person that used the catalyst, that it did not possess the same problem with coking as the H-MFI catalyst, while still facilitating the conversion of methane to benzene and toluene (along with the byproducts of naphthalene, hydrogen, ethane, and ethylene).

Like the MFI zeolite, this catalyst has a three-dimensional pore structure, with openings of roughly six Angstroms. Mo/ZSM-5 catalysts can be prepared through the procedure outlined by Dingjun Wang. The first step of this process is to prepare a slurry of H-ZSM-5 in an aqueous
solution of ammonium heptamolybdate \([(\text{NH}_2)_6\text{Mo}_7\text{O}_{24}]\) at 85 degrees Celsius for 16 hours. This is followed by drying the solution for four hours at 120 degrees Celsius and then calcining it for another four hours at 500 degrees Celsius in air. The calcined catalyst will then be crushed and sieved through 20/45 mesh granules in order to obtain a purer catalyst. Once it is exposed to methane gas within the reactor, the molybdenum catalyst initiates the conversion of methane to benzene and other products through the same mechanism as the Mo/H-MFI catalyst. In addition to the main reaction from methane to benzene and hydrogen, there are four other side reactions. The yields for these corresponding reactions, obtained from three different sources, are listed in the table below (Table 6).

Table 6. Occurring reactions along with conversions from several sources [18, 19, 20].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2)</td>
<td>5.60%</td>
<td>6.79%</td>
<td>3.85%</td>
</tr>
<tr>
<td>(10\text{CH}<em>4 \rightarrow \text{C}</em>{10}\text{H}_8+16\text{H}_2)</td>
<td>1.04%</td>
<td>0.79%</td>
<td>1.59%</td>
</tr>
<tr>
<td>(7\text{CH}_4 \rightarrow \text{C}_7\text{H}_8+10\text{H}_2)</td>
<td>0.88%</td>
<td>0.32%</td>
<td>0.20%</td>
</tr>
<tr>
<td>(2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2)</td>
<td>0.16%</td>
<td></td>
<td>0.13%</td>
</tr>
<tr>
<td>(2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2)</td>
<td>0.16%</td>
<td></td>
<td>0.13%</td>
</tr>
<tr>
<td><strong>Total CH(_4) Conversion:</strong></td>
<td>7.84%</td>
<td>7.90%</td>
<td>5.90%</td>
</tr>
</tbody>
</table>

When we performed more in-depth research into this catalyst, however, we found out that not only is the Mo/ZSM-5 catalyst prone to coking, but it cokes even more than the Mo/H-MFI. As a result, using this this catalyst would result in less product for the same amount of methane, so we decided to reject this catalyst and stick with the H-MFI catalyst.
Other Catalysts:

In addition to the Mo/ZSM-5 catalyst, we also briefly considered another catalyst in the form of Mo/MCM-22. While this catalyst also helped facilitate the conversion of methane to various aromatic products, it didn’t show as much of a capacity for methane dehydroaromatization as the Mo/H-MFI catalyst, so we settled on the latter instead.

Permitting and Environmental Concerns

Environmental Issues Associated with Design (Audra):

The primary environmental concern for this process under normal operating conditions comes from air pollution due to combustion of the purge stream. A purge stream is removed from the recycle stream to prevent the accumulation of nitrogen in the system and to provide a fuel source for the reaction inlet furnace and a generator used to power other unit operations. While this stream is primarily composed of methane, small amounts of ethylene, ethane, and hydrogen are also present. A vent stream produced in the purification of the BTX product will also be used as fuel for the furnace and generator. Combustion of these streams will result in air pollution, negatively affecting the surrounding environment.

Accidental release of benzene, toluene, and naphthalene throughout the process give cause for concern. During the methane to aromatics process, these compounds can be found in both vapor and liquid form, so contamination of air or groundwater may occur. Benzene is highly flammable and has associated health effects [21]. Toluene is also very flammable, dangerous if ingested, and is toxic to aquatic life [22]. Naphthalene is a dangerous chemical due to its flammable nature and possible complications is ingested or inhaled [23]. All three of these
compounds are considered hazardous air pollutants and their release into the environment requires regulation [24].

**Necessary Permits (Audra):**

The methane to aromatics process requires water use for cooling purposes. While most of this water will be recycled, a purge stream will be necessary to keep mineral concentrations in the water from compiling. Removing water from the system will require a Texas Pollutant Discharge Elimination System (Texas’s NPDES) permit. Another permit will be required for storm water. Facilities of our type fall under standard industrial classification codes, so a Multi-Sector General Permit (TXR050000) can be obtained to allow storm water to be released to municipal drains and Texas surface waters [25].

Currently, no greenhouse gas regulations are in place, but under 40 CFR Part 98, our facility is required to report greenhouse gas emissions [26]. The Clean Air Act defines major sources as sources that have the potential to emit at least 10 tons per year of a hazardous air pollutant or 25 tons per year or a combinations of hazardous air pollutants [27]. Combustion of our purge and vent streams will release NOx and VOCs to the atmosphere, qualifying the plant as a major source of these pollutants. We will need to apply for standard air permits through the Texas Commission on Environmental Quality because of our combustion of natural gas [28]. An Air Quality Standard Permit for Boilers will be needed for our furnace that combusts natural gas to head the reactor feed and an Air Quality Standard Permit for Electric Generating Units will be required for our electric generator [29].

**BACT Analysis for Air Emissions (Andrew):**

The process proposed will have carbon emissions associated due to the burning of hydrocarbon fuels both in the generator and furnace. Using the energy required for these two unit
ops, the EPA’s carbon emission calculator [33] estimated that our furnace will produce about 23,300 metric tons of CO2 per year while the generator will emit about 93,800 metric tons of CO2 per year, with a total of 117,000 metric tons of CO2 per year. This value is similar to that found in other petro-chemical production plants in the Houston, Texas area. Burning of these hydrocarbons can result in other greenhouse gas emissions and other hazards air pollutants including NOx, CO, Volatile organic compounds and Sulfur Oxides. One way to mediate these air pollutants specifically the NOx gases is to add a selective catalytic reduction catalyst to reduce the NOx emitted from the furnace and generator into water and diatomic nitrogen (N₂).

These catalysts are typically made of a ceramic material with the active components being oxides or base metals. Due to the high temperature of our furnace and generator a zeolite catalyst would best fit the process proposed due to the zeolites potential to operate at higher temperatures [34]. The zeolite can withstand prolonged exposure to conditions of 900 K. There are a few limitations when it comes to using these catalysts to reduce the NOx gases which include the clogging of pores and deactivation of the catalyst due to poisons. The reduction of NOx gases by these catalysts are typically between 20%-50% of the total NOx emitted [35]. By reducing the amount of NOx emitted by this process, the amount of acid rain produced by this process will also be reduced saving the environment from this harmful effect. Carbon monoxide can be emitted through the burning of our natural gas in the furnace, the amount of CO released is dependent on the efficiency of the natural gas combustion within the furnace [52]. The furnace chosen for this process has an efficiency rating of 90% which will help mediate the amount of CO being released as most of our fuel will be combusted in this unit. VOC emissions are also dependent on the efficiency of the furnace being used, our furnace is being fed partly by these VOC's and will result in a higher concentration of these leaving our system versus using strictly a natural gas fuel source [52]. To mediate these compounds from being released, high combustion temperatures
will be used to promote the breaking down of these VOC as well as longer exposure or residence
time at these temperatures to once again promote these compounds to break down [52]. SOx
compounds are not of high importance when it comes to emissions from burning natural gas, this
is due to natural gas from pipelines typically containing sulfur concentrations of less than 130
grams per million cubic feet of natural gas [52].

**Safety and Risk Management (Aric)**

For our unit hazard ops analysis we had several unit ops to consider. The most hazardous
unit ops would be our heat exchangers and reactor, as both have the potential to reach high
temperatures several different ways. Our heat exchangers have the potential to have flow rates
change on both the hot and cold side of these exchangers. If this ratio is not in proper balance
there is the potential that it will significantly increase or decrease the difference from the desired
temperature leaving the heat exchangers. The reactor has a similar issue with temperature and
pressure being properties that could deviate from the norm. If the stream entering the reactor has
too high of a flow or temperature the reaction vessel could go beyond the pressure specifications
that the vessel was rated for causing an explosion. Also, due to the high temperature of the
reactor, there is a potential issue for HTHA (high temperature hydrogen attack) in which
hydrogen can permeate into the stainless steel and react with the carbon and create methane,
which can cause stress within the material and cause internal cracks. The issues with the heat
exchangers can be mitigated by adjusting either the hot or cold stream flows, as well as by
installing a flow alarm governing the streams into and out of the exchangers, and also by
performing routine inspections. These risk management strategies can also be applied to the
reactor if it experiences deviations in temperature and pressure from the norm, as well as
stabilizing the feed rate into the reactor. With regards to the risk of HTHA in the reactor, this can
be managed by using stainless steel as material for the reactor, as opposed to the more corrosive carbon steel.

The distillation tower used in our process is also vulnerable to safety hazards, with the most significant of these being a low liquid level. This can be the result of a leakage or the obstruction of the feed stream, and is potentially hazardous because, in the latter case, it could result in a back flow of the material in the feed stream if it is blocked, which would prevent the products from getting separated from any impurities. More significantly, as applied to the former case, a leak can result in the release of dangerous chemicals into the environment. These risks can be mitigated by installing a level alarm and incoming flow-rate meter to monitor the level and feed-rate into the reactor, respectively.

Another primary safety hazard is the potential for our process's Hydrogen Membrane to become completely blocked. With larger molecules than hydrogen present in the inlet stream to the membrane, there is a potential that fouling could occur on or around the membrane which over time would continue to block the passage of hydrogen through the membrane. This could have undesired consequences such as a larger hydrogen content in the recycle stream entering the reactor, thus contributing to HTHA. Another undesired consequence would be that without an operating hydrogen membrane, no other unit operations are present in the process that collect the hydrogen, so there would be no chance to sell the excess hydrogen as a credit to our process. To mitigate the effects of a potentially blocked hydrogen membrane we have considered installing a hydrogen membrane that can easily been removed and replaced by a new membrane apparatus upon plant shutdown.

Potential for dangerous leaks are present throughout our system. One such chemical is natural gas. As a primary component throughout most of our system, leaks in many locations
could lead to release of large amounts of flammable natural gas. Another flammable gas present in large amounts is the propane required by our reactor effluent refrigeration system. Our process also produces large amounts of benzene. Benzene is a carcinogen, aspiration hazard, and mutagen, so its release would be dangerous to plant personnel. As a gas more dense than air, any leaked benzene will be dangerous and require adequate alarm and ventilation systems. In order to help mitigate the likelihood of a leak, we have implemented the use of stainless steel equipment to reduce structural damage due to corrosion, but routine equipment inspections should be performed to monitor mechanical integrity of all unit operations.

**Project Economics (Tim)**

**General Information and Approaches:**

All economic analysis done on this project was completed using estimations of process parameters using a simulation in the computer program Aspen Plus. This program was used to create a working model to get an estimation of variables of economic interest. The Aspen Plus model was used to determine the flow rates of the feed, purge and product streams. The feed flow rate was determined initially to be 165,000 pounds per hour of natural gas so that the amount of aromatic product produced per year would be near 500,000,000 pounds. This feed flow rate is very high because the catalyst in the process model was set to a conversion rate of reactants to products of approximately six percent. Low conversion rates led to designing abnormally large reactors, and other unit ops in the Aspen Plus model. Large reactor and unit operation vessels in the design led to large capital investments in the economic analysis. Using large unit operations also posed many questions about the feasibility of the design. One problem that the design group faced was that the reactor would be larger by volume than the largest building in the world. To lower the amount of volume needed for the initial reactor design the
group decided to use a plug flow reactor model instead. By making this change the size and price of the reactor vessel was lowered significantly, thereby improving the economics of the project. Another issue the group faced in designing the reactor was that all the research articles that were referenced in this paper ran their catalyst testing at atmospheric air pressure. However, this is infeasible in a large process because the flow of the gases through the reactor could be slowed significantly. To troubleshoot this issue, the reactor pressure was increased to 450 pounds per square inch. It was assumed that by raising the pressure the expected conversion rates should be lowered by five to ten percent. After making the correction to the conversion rate, given the same natural gas feed rate of 165000 pounds per hour, the nameplate production per year was lowered temporarily to 480,000,000 pounds of aromatic product. This sacrifice of the nameplate production value turned out to have only a slight effect on the profitability of the project.

One of the largest parts of the process simulation is the recycle loop. The majority of the gases that flow out of the reactor effluent are unreacted species and must be recycled if the project is expected to make a profit. However, recycling the unreacted materials can be very costly because of all of the added unit operations required for preparing the recycle stream to mix with the feed stream, especially if the stream is very large. In the design of the simulation it was decided that a purge stream would be necessary to remove some of the inert byproducts of the side reactions in the reactor section. This turned out to be very fortunate for the profitability of the project because the purge line consisted of enough natural gas fuel that the heating and power requirements for the process could be met with the use of generators and furnaces. The addition of a generator and furnace increases the initial capital investment but decreases the utilities cost. The group also used heat integration in the design of the process to increase capital investment costs but decrease utilities cost. With heat integration and by using natural gas as a heat and
power source the utilities cost was close to zero. Initially the purge was set to remove five percent of the recycle stream. This was a problem though, because five percent of the recycle stream amounted to a purge stream of 76,000 pounds per hour. This would mean that approximately half of the feed gas was leaving in a purge stream, not to be converted to product. The purge stream flow rate was so great that the power and heating needs were met by tenfold and was not economical to have so much of the feed gas go to waste. So the purge stream was reduced to be only 1.3% of the recycle stream. This significantly cut down on waste and improved the economic feasibility of the project. With the adjusted purge stream, the process then yielded approximately 728,000,000 pounds of aromatic product per year.

After the basic process design was finished, and most of the major noticeable flaws in the economic feasibility were addressed, the group worked on the sizing estimations of the unit operations of the process. The majority of the sizing information was collected using charts from Peters and Timmerhaus’s book. In Microsoft Excel sizing calculations were completed using values from the Aspen Plus model. Flow rate, surface area, number of trays, pressure, and vessel type are some examples of the kinds of information taken from Aspen Plus to determine the proper sizing values. The reactor sizing was determined using the Aspen Plus model, the weight hourly space velocity from literature, and a few other key assumptions. The mass of catalyst needed was used to determine the volume of catalyst which was then used to produce an estimate of reactor volume required. To size the hydrogen membrane, information from an online source was retrieved in order to get an estimate [42]. The distillation tower had to be optimized before it could be sized. The distillation tower was determined to be seventeen trays in total, with a feed tray at seventh level, because it yielded the lowest reboiler duty and had a reflux to reflux minimum ratio of 1.2. The reflux minimum ratio refers to the reflux ratio when the number of tower trays is extremely large. The ratio of 1.2 was chosen in order to follow the typical
distillation tower sizing conventions. Many of the heat exchangers that were designed as a part of the heat integration required very large surface areas for heat transfer. All of the sizing values determined for the unit operations were rough estimates.

After sizing was completed, the group used online sources and Peters and Timmerhaus to develop pricing estimates. Logarithmic charts in Peters and Timmerhaus were used to estimate the prices for the compressors, heat exchangers, furnace, reactor, flash drum, and distillation column from the year 2002 [36]. To adjust the value for 2015 the prices of the 2002 unit operations were multiplied by a ratio of the chemical engineering plant index (CEPCI) of 2015 over that of 2002 [37]. Many of the pricing charts accounted for the operating pressure, and the type of the material used to determine price. Every unit operation in the project uses stainless steel 316 for safety reasons having to do with poor material compatibility between methane and cheaper materials such as carbon steel. The only unit operation that uses carbon steel is the distillation column because the flow in to the column is very low in methane content. Another reason for using the carbon steel for the distillation tower is that it is cheaper especially for a unit operation that contains many trays and valves. The price of catalyst was calculated based on prices from the website “infomine” for molybdenum oxide catalysts [38]. The catalyst was included in the price of the reactor. Based on the suggested operating conditions from literature (having a feed composition of 1-1.5% hydrogen by weight) it is assumed that replacement of catalyst due to deactivation would not be an issue [11]. However, various economic sensitivities were examined in which the catalyst would have to be replaced every five or ten years. The price of the hydrogen membrane was calculated using cost estimates from an online article about palladium membranes [42]. Once price estimates were calculated, the values were compiled to create values for the fixed capital investment, working capital, and startup.
The streams were the next major component to work on in order to complete the economic analysis of the project. The natural gas feed flow rate was set already. Prices for natural gas were easy to find from government websites for the gulf coast area of Texas [39]. In the past few years the price of natural gas has been consistently decreasing. Using a few calculations and conversions the approximate cost of natural gas on a per pound basis was determined to be seven cents. This assumption for the price of natural gas in the gulf coast area makes this project design profitable. Using price listings from the organization ICIS, the price of the aromatic product stream was estimated to be 32 cents per pound of product [40,41]. The product stream price is over four times greater than the feed stream’s price which is a good indicator that this project can be profitable. The byproduct streams of this process also add to the profitability. From the recycle stream, hydrogen is exclusively separated by membrane separation and can be sold at a price of fifteen cents per pound [42]. One of the side products that comes from the bottom of the distillation column is naphthalene. The naphthalene side product can be sold for 45 cents a pound [43]. The hydrogen and naphthalene byproducts were added to the total variable costs as credit, effectively lowering the costs. All of these factors, including the extremely low utility costs, suggest that the process is very profitable.

The costs and revenues were used then to create a cash flow table for a twenty-year period. The net present value (NPV0) of the project was determined to be 2194 million dollars. The net present value discounted at a rate of ten percent (NPV10) was determined to be 689 million dollars. The internal rate of return (IRR) was determined to be 29%. A 29% internal rate of return is an indicator value that suggests that the project is very profitable based on the current analysis.
Major Equipment Costs:

The following table, table 7, contains a list of all of the major equipment parts for the process described in the previous sections with all of the associated costs.

Table 7. Major unit operations pricing list with flow sheet names, descriptions and price in dollars.

<table>
<thead>
<tr>
<th>ID</th>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>T101</td>
<td>Distillation Tower</td>
<td>217000</td>
</tr>
<tr>
<td>H101</td>
<td>Heat ex 1</td>
<td>9202085</td>
</tr>
<tr>
<td>H102</td>
<td>Heat ex 2</td>
<td>6748716</td>
</tr>
<tr>
<td>H103</td>
<td>Heat ex 3</td>
<td>490589</td>
</tr>
<tr>
<td>H104</td>
<td>Heat ex 4</td>
<td>15500</td>
</tr>
<tr>
<td>AC101</td>
<td>Air Cooler</td>
<td>85000</td>
</tr>
<tr>
<td>F101</td>
<td>Feed Furnace</td>
<td>1500000</td>
</tr>
<tr>
<td>R101</td>
<td>Reactor, catalyst</td>
<td>6144000</td>
</tr>
<tr>
<td>D101</td>
<td>Flash Drum</td>
<td>376854</td>
</tr>
<tr>
<td>D102</td>
<td>Flash Drum</td>
<td>23553</td>
</tr>
<tr>
<td>C101</td>
<td>Compressor</td>
<td>2125000</td>
</tr>
<tr>
<td>C102</td>
<td>Propane Compressor</td>
<td>1700000</td>
</tr>
<tr>
<td>S101</td>
<td>H2 Membrane</td>
<td>302827</td>
</tr>
<tr>
<td>G101</td>
<td>Generator</td>
<td>67707</td>
</tr>
<tr>
<td>MISC</td>
<td>Pumps</td>
<td>2899883</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>31898716</td>
</tr>
</tbody>
</table>

Each of the values for cost in table 7 are the purchased cost values for 2002. From the table it is apparent that the most expensive pieces of equipment are the reactor, pumps, compressors, and heat exchangers. To find the specific cost of the distillation tower, T101, many parts were needed. The number and type of trays were needed to determine the price. Seventeen sieve, four-pass trays made of carbon steel were decided to be used in the tower. Therefore, the height of the tower was determined to be 54 feet. Using a packed tower instead of trays was determined to be inefficient economically. The tray diameter was collected from the Aspen Plus model. The pressure and volume flow rate were used to determine the price of the reflux drum for the distillation tower. The duty, and temperatures of inlet and outlet streams of the condenser
were used to determine the heat transfer area and eventually determine the price of the condenser portion of the tower. A similar process was used to determine the area of heat transfer and the price of reboiler attached to the distillation tower. Peters and Timmerhaus’s book was used in conjunction with the information collected to determine estimates for the prices [36]. Once the price was determined, the sum of all of the parts made up the cost of the distillation tower.

The duties and inlet and outlet stream temperatures of heat exchangers H101, H102, H103 and H104 and air cooler AC101 were used to determine the areas of heat transfer. Once the areas of the heat transfer were determined the prices of each exchanger could be estimated using charts from Peters and Timmerhaus [36].

The feed furnace, F101, price was determining the required heating value according to the Aspen Plus model. From there, the price was determined using a chart in Peters and Timmerhaus, knowing that the feed furnace is designed to be made of stainless steel [36].

To determine the size of the reactor the weight hourly space velocity (WHSV, mass flow divided by mass of catalyst), feed flow rate, and density of the catalyst were used. The WHSV multiplied by the feed flow rate gave the catalyst weight. Multiplying the catalyst’s weight by its density gave the volume of the catalyst. Multiplying the volume of the catalyst by 2-3 to account for the addition of an inert solid at the front and end of the reactor gave the calculated reactor volume. The volume of the reactor gave the reactor price using Peters and Timmerhaus [36]. The catalyst price was obtained from a source online called “info mine [38].” The reactor and catalyst price together give the value for R101.

To calculate the price of the flash drums, D101 and D102, the group used the flow rate to estimate a volume value. Then this volume was used to make an estimate for the price of the flash drum.
The price of the compressors, C101, and C102, used the Aspen Plus models inlet volume actual flow, braking horsepower, kilowatt used and material type. Once this data was compiled, charts from Peters and Timmerhaus were used to determine estimates for the price [36].

The hydrogen membrane was priced using information from an online source and the volumetric flow rate from the Aspen Plus model [44]. The cost per foot squared of membrane material is 1000 dollars [44]. The flux of the volume of hydrogen allowed to slip through a square foot is 245 standard cubic feet hours per unit area [44]. From this information the cost of the hydrogen membrane was easily calculated.

The generator price was found by contacting Rocky Mountain Power using the amount of electricity needed [45]. To find the approximate costs of all the pumps needed for the process the sum of all the other unit operations was multiplied by ten percent.

**Fixed Capital Investment:**

The fixed capital investment (FCI) for the project was estimated to be 358 million dollars. The 2002 purchased cost values were taken scaled up to their 2015 estimates and multiplied by the installation factor given by Peters and Timmerhaus of 5.04 to get the inside battery limits (ISBL) [36]. The ISBL was then multiplied by ten percent to give the outside battery limits (OSBL). Both the ISBL and OSBL were then summed to form the fixed capital investment. The values for each of the terms described are presented below in table 8.
Table 8. Values of Inside and Outside Battery Limits, Fixed Capital Investment, Working Capital and Start-up for 2015 in dollars.

<table>
<thead>
<tr>
<th></th>
<th>2015 Installed</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISBL $</td>
<td>325148731</td>
</tr>
<tr>
<td>OSBL $</td>
<td>32514873</td>
</tr>
<tr>
<td>FCI $</td>
<td>357663605</td>
</tr>
<tr>
<td>WC $</td>
<td>63117107</td>
</tr>
<tr>
<td>Startup $</td>
<td>35766360</td>
</tr>
</tbody>
</table>

**Operating Costs:**

The feed stock cost was estimated using number of dollars per million British thermal units produced from natural gas in Texas. Next the amount of million British thermal units per pound of natural gas burned was found. With both of these values, the cost of the natural gas feedstock could be calculated in dollars per pound. The table below, table 9, shows the information associated with the calculation of the feedstock price.

Table 9. This table contains all of the values of the intermediate steps that led to the calculations of the price of the natural gas feedstock in dollars per pound.

<table>
<thead>
<tr>
<th>Price of Natural Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTU/lb</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>23900</td>
</tr>
</tbody>
</table>

A large amount of the feedstock is released in the purge stream and this purge stream feeds the generator and the furnace for all of the unit operations. So, the assorted utilities costs normally associated with a project of this magnitude are already covered and aren’t accounted for the economic analysis. The only other utility cost is very small and that is the cost of cooling water. Table 10, contains a detailed breakdown of all the costs associated with the process.
Table 10. This table is the yearly production cost estimate report for the process. All of the values in the two columns to the right are in millions unless otherwise stated.
# Production Cost Estimate Report

<table>
<thead>
<tr>
<th>Product</th>
<th>Name BTX Location Houston, TX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>CH4 to BTX</td>
</tr>
<tr>
<td>Nameplate Production</td>
<td>727.52 m/yr 8000 hr/yr Operating Factor 90940 /hr</td>
</tr>
<tr>
<td>ISBL, m$</td>
<td>325.15</td>
</tr>
<tr>
<td>OSBL, m$</td>
<td>32.51</td>
</tr>
<tr>
<td>Working Capital, m$</td>
<td>63.12</td>
</tr>
<tr>
<td>Start-Up Cost, m$</td>
<td>35.77</td>
</tr>
</tbody>
</table>

## Product and Revenue

<table>
<thead>
<tr>
<th>Product</th>
<th>Unit</th>
<th>Unit Price</th>
<th>Revenue m$/yr of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTX</td>
<td>lb</td>
<td>32 c/lb</td>
<td>233.22 32.06</td>
</tr>
</tbody>
</table>

## Raw Materials

<table>
<thead>
<tr>
<th>Feed</th>
<th>Unit</th>
<th>Unit Price</th>
<th>Consumption per</th>
<th>c/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lb</td>
<td>7 c/lb</td>
<td>2 lb/ product</td>
<td>93.38 12.84</td>
</tr>
</tbody>
</table>

## Gross Cost of Raw Materials

|          | 93.38 12.84 |

## Byproducts

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Hydrogen</th>
<th>Unit</th>
<th>Unit Price</th>
<th>Consumption per</th>
<th>c/</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillate</td>
<td>Naphthalene</td>
<td>lb</td>
<td>0.270524 lb/ product</td>
<td>-30.12 -4.14</td>
<td></td>
</tr>
<tr>
<td>Total Byproduct Credits</td>
<td>-79.00 -10.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Net Cost of Raw Materials (NRM)

|          | 14.38 1.98 |

## Catalysts and Chemicals

<table>
<thead>
<tr>
<th>Regenerating our catalyst so little to no cost in production statement</th>
<th>Unit</th>
<th>0 c/unit</th>
<th>0 unit/ product</th>
<th>0.00 0.00</th>
</tr>
</thead>
</table>

## Utilities

**Note:** *Additional steam will not be needed. NG Purge will heat unit ops.

<table>
<thead>
<tr>
<th>Steam*</th>
<th>mBTU</th>
<th>800 c/mBTU</th>
<th>0 mBTU/ product</th>
<th>0.00 0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling Water</td>
<td>mBTU</td>
<td>40 c/mBTU</td>
<td>0.000229 mBTU/ product</td>
<td>0.067 0.01</td>
</tr>
</tbody>
</table>

## Total Utilities

|          | 0.07 0.01 |

## Miscellaneous Variable Costs

<table>
<thead>
<tr>
<th>Misc name</th>
<th>Unit</th>
<th>0 c/unit</th>
<th>0 unit/ product</th>
<th>0.00 0.00</th>
</tr>
</thead>
</table>

## Total Misc. Variable

|          | 0.00 0.00 |

## Total Variable Costs (VC)

|          | 14.44 1.99 |

## Fixed Costs

<table>
<thead>
<tr>
<th>Labor</th>
<th>Basis</th>
<th>9 men/shift @ 30$/hr <em>1.6</em>8760hr/yr</th>
<th>3.78 0.52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maintenance</td>
<td>4% FCI</td>
<td>14.31 1.97</td>
<td></td>
</tr>
<tr>
<td>Utilities</td>
<td>Ignored</td>
<td>0.00 0.00</td>
<td></td>
</tr>
<tr>
<td>Laboratory</td>
<td>1 man/shift @ 36$/hr <em>1.2</em>8760hr/yr</td>
<td>0.38 0.05</td>
<td></td>
</tr>
<tr>
<td>Plant Overhead</td>
<td>30% of (labor, maintenance, lab)</td>
<td>1.14 0.16</td>
<td></td>
</tr>
<tr>
<td>Taxes and Insurance</td>
<td>3% FCI</td>
<td>10.73 1.47</td>
<td></td>
</tr>
</tbody>
</table>

## Total Fixed Costs (FC)

|          | 30.33 4.17 |

## Total Manufacturing Cost (TMC)

|          | 44.78 6.16 |

## Total Product Cost (TPC)

|          | 44.78 6.16 |

## Margin (sales price - VC)

|          | 218.77922 30.07 |

54
Other fixed or operating costs are the cost of labor, maintenance costs, laboratory costs, plant overhead, and taxes and insurance. The cost of labor is calculated assuming nine men each work a shift. It is assumed that they are paid 30 dollars an hour and that they work for 8760 hours a year. The cost of maintenance is just four percent of the fixed capital investment total. Utilities can be ignored, as discussed earlier. Laboratory fees are calculated assuming one man a shift paid 36 dollars an hour for 8760 hours a year. Overhead fees are 30% of the labor, maintenance and lab fees. Taxes and Insurance cost 3% of the fixed capital investment.

**Project Value:**

It was determined that the end-of-life value for this project would be very small. All values of scrapping each individual component in the project added up would only amount to a small value. If, for some reason the plant would need to shut down, then steep decommissioning fees would need to be paid for the clean-up and the potential environmental impact. It is difficult to predict with any absolute certainty whether shutting down the entire plant would end with a net positive or negative value. However, it is more than likely that the scrapping values minus the decommissioning costs would balance to close to zero.

**Cash Flow Analysis:**

The two-part table below, table 11, contains a year to year cash flow analysis over the economic life of the project.
Table 11. The first section is the cash flow analysis for years -1 to 10 and the second table contains the cash flow analysis for years 11 through 20.

<table>
<thead>
<tr>
<th>NPV</th>
<th>Tax Rate</th>
<th>35.00%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year (for discounting)(year end)</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>FID</td>
<td>-178831802</td>
<td>-178831802</td>
</tr>
<tr>
<td>StartUp</td>
<td>-35766390</td>
<td></td>
</tr>
<tr>
<td>Depr Amount</td>
<td>71553721</td>
<td>114452353</td>
</tr>
<tr>
<td>Depr Tax Credit</td>
<td>25106452</td>
<td>40018324</td>
</tr>
<tr>
<td>Revenue</td>
<td>233224169</td>
<td>233224169</td>
</tr>
<tr>
<td>Variable Costs</td>
<td>-14442593</td>
<td>-14442593</td>
</tr>
<tr>
<td>Fixed Costs</td>
<td>-30334500</td>
<td>-30334500</td>
</tr>
<tr>
<td>Total Expenses (including SU)</td>
<td>-80343503</td>
<td>-44777049</td>
</tr>
<tr>
<td>Tax Credit on Above Expenses</td>
<td>-28190209</td>
<td>-15671983</td>
</tr>
<tr>
<td>Cash Flow</td>
<td>-178831802</td>
<td>-241948809</td>
</tr>
<tr>
<td>CumCF (PV0)</td>
<td>-178831802</td>
<td>-41070711</td>
</tr>
<tr>
<td>DF10</td>
<td>1.10</td>
<td>1.00</td>
</tr>
<tr>
<td>PV10</td>
<td>-15671983</td>
<td>-241948809</td>
</tr>
<tr>
<td>CumPV10</td>
<td>-15671983</td>
<td>-438663891</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NPV</th>
<th>Tax Rate</th>
<th>35.00%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year (for discounting)(year end)</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>FID</td>
<td>-178831802</td>
<td>-178831802</td>
</tr>
<tr>
<td>StartUp</td>
<td>-35766390</td>
<td></td>
</tr>
<tr>
<td>Depr Amount</td>
<td>71553721</td>
<td>114452353</td>
</tr>
<tr>
<td>Depr Tax Credit</td>
<td>25106452</td>
<td>40018324</td>
</tr>
<tr>
<td>Revenue</td>
<td>233224169</td>
<td>233224169</td>
</tr>
<tr>
<td>Variable Costs</td>
<td>-14442593</td>
<td>-14442593</td>
</tr>
<tr>
<td>Fixed Costs</td>
<td>-30334500</td>
<td>-30334500</td>
</tr>
<tr>
<td>Total Expenses (including SU)</td>
<td>-80343503</td>
<td>-44777049</td>
</tr>
<tr>
<td>Tax Credit on Above Expenses</td>
<td>-28190209</td>
<td>-15671983</td>
</tr>
<tr>
<td>Cash Flow</td>
<td>-178831802</td>
<td>-241948809</td>
</tr>
<tr>
<td>CumCF (PV0)</td>
<td>-178831802</td>
<td>-41070711</td>
</tr>
<tr>
<td>DF10</td>
<td>1.10</td>
<td>1.00</td>
</tr>
<tr>
<td>PV10</td>
<td>-15671983</td>
<td>-241948809</td>
</tr>
<tr>
<td>CumPV10</td>
<td>-15671983</td>
<td>-438663891</td>
</tr>
</tbody>
</table>

Discounted Cash Flow Analysis:

The table below, table 12, contains information on the net present value zero (NPV0), the net present value discounted at a rate of ten percent (NPV10), and the internal rate of return (IRR).
Table 12. Values are determined from using the data from table 11. “MM$” means millions of dollars.

<table>
<thead>
<tr>
<th></th>
<th>NPV0</th>
<th>$</th>
<th>NPV10</th>
<th>$</th>
<th>NPV10</th>
<th>MM$</th>
<th>IRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>2194082506</td>
<td></td>
<td>689213406</td>
<td></td>
<td>689</td>
<td>MM$</td>
<td>29%</td>
</tr>
</tbody>
</table>

The table shows that the net present value of investing in this twenty-year project would be valued at 2.19 billion dollars. This does not take into account the time depreciation of money however. A better picture of the profitability of the project is made by the net present value discounted at a certain interest rate. The net present value of this project based on a ten percent discount rate is 689 million dollars. These two pieces of information suggest that the project may be very profitable. Another indicator of profitability is the use of the internal rate of return. The internal rate of return is based off of the cash flow of the project. For a project to be considered by investors, usually the internal rate of return must be greater than zero. In some cases, investors can suggest a minimum acceptable rate of return (MARR), of twenty percent. The projected internal rate of return of this project is 29%. This means that this process is potentially very profitable.

**Sensitivity Analysis:**

It is often important to look at the project and see how sensitive the project’s profitability is to certain market impacts. This is good way to evaluate the robustness of a project. Robust projects are also much more attractive to potential investors because the investor might be less worried that his or her investment could be lost. Some very basic market impacts to look at are how the cost of feedstock or price of product can affect net present values and internal rate of return values.
The table below, table 13, shows the base case’s net present values and internal rates of return as compared to other various conditions. Using the solver function on MS Excel, it was determined that the price of natural gas would have to be $8.28 per million British thermal units before the net present value and internal rate of return become both zero. This is the critical threshold for the project to turn a profit, with all other parameters being the same. On the other hand, the price of natural gas could possibly go down too. If the price of natural gas dropped to two dollars per million British thermal units, then the profitability of the project could rise. The projected net present value discounted at ten percent is 853 million dollars. The internal rate of return would be 33%.

Table 13. Includes base case profitability indicators as compared to the profitability indicators taken from economic analyses of two other prices of natural gas.

<table>
<thead>
<tr>
<th></th>
<th>Base Case NG Price 2.96/MMBTU ($0.07/lb)</th>
<th>NG price where IRR becomes 0: $8.28/MMBTU</th>
<th>NG price $2.00/MMBTU ($0.05/lb)</th>
<th>NG Price where MARR 20% is met: $4.94/MMBTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPV0 (MM$)</td>
<td>2194</td>
<td>3</td>
<td>2580</td>
<td>1374</td>
</tr>
<tr>
<td>NPV10 (MM$)</td>
<td>689</td>
<td>-243</td>
<td>853</td>
<td>340</td>
</tr>
<tr>
<td>IRR</td>
<td>29%</td>
<td>0%</td>
<td>33%</td>
<td>20%</td>
</tr>
</tbody>
</table>

The chart below, figure 15, shows how the IRR is affected by the price of natural gas. With a MARR of 20% the price of natural gas has to reach $4.94 per million British thermal units before the process is found to be unprofitable.
Figure 15. The price of natural gas feedstock compared to the economic profitability of the designed process.

The table below, table 14, shows the base case’s net present value and internal rates of return as compared to slight changes in the product’s sales price. If the sales price of the aromatic product increased by even five cents the internal rate of return increases by four percent. If the sales price of the aromatic product decreases, for whatever reason, the internal rate of return is decreased by five percent. This seems to be a factor that the profitability is particularly sensitive to, because each cent approximately corresponds to losing or gaining a percent of internal rate of return.

Table 14. Includes base case profitability indicators as compared to the profitability indicators taken from economic analyses of two other product sales prices.

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>Product Sales Price +5c</th>
<th>Product Sales Price -5c</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPV0 (MM$)</td>
<td>2194</td>
<td>2659</td>
<td>1713</td>
</tr>
<tr>
<td>NPV10 (MM$)</td>
<td>689</td>
<td>887</td>
<td>485</td>
</tr>
<tr>
<td>IRR</td>
<td>29%</td>
<td>33%</td>
<td>24%</td>
</tr>
</tbody>
</table>
The table below, table 15, shows the base case’s net present value and internal rates of return as compared to cases in which the catalyst may be replaced every five or ten years. This impact seems to have very little impact on the profitability of the project. This could be due to the price of catalyst being dwarfed by the project having a very large fixed capital investment. Table 15. Includes base case profitability indicators as compared to the profitability indicators taken from economic analyses of cases in which the catalyst would be replaced every five or ten years.

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>Catalyst replaced every</th>
<th>Catalyst replaced every</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NPV0 (MM$)</strong></td>
<td>2194</td>
<td>2141</td>
<td>2163</td>
</tr>
<tr>
<td><strong>NPV10 (MM$)</strong></td>
<td>689</td>
<td>670</td>
<td>680</td>
</tr>
<tr>
<td><strong>IRR</strong></td>
<td>29%</td>
<td>28%</td>
<td>29%</td>
</tr>
</tbody>
</table>

The table below, table 16, shows the base case’s net present value and internal rates of return as compared to the case in which the start-up of the plant is more realistic. In this case it is assumed that in the first year only 50% of the expected yearly revenue is generated. In the second year 75% of the expected revenue is generated. In the third year 90% of the expected revenue is generated. In the fourth and following years it is assumed that all of the expected revenue is generated. In this case the profitability is decreased but the process would still be deemed as profitable. Table 16. Includes base case profitability indicators as compared to the profitability indicators taken from economic analysis of the case in which production start-up is more realistic.

<table>
<thead>
<tr>
<th></th>
<th>Base Case</th>
<th>Realistic Production Start up 1(50%), 2(75%), 3(90%), 4+(100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NPV0 (MM$)</strong></td>
<td>2194</td>
<td>2057</td>
</tr>
<tr>
<td><strong>NPV10 (MM$)</strong></td>
<td>689</td>
<td>574</td>
</tr>
<tr>
<td><strong>IRR</strong></td>
<td>29%</td>
<td>24%</td>
</tr>
</tbody>
</table>
To compare all of the major market impacts against each other the formation of a tornado plot was necessary. The figure below, figure 16, shows the ranking of the effect of various market impacts on the profitability of the project. Each of the factors were either increased or decreased by 25% while the other factors remained the same. The effect on internal rate of return was then plotted, and the price of the aromatic product was determined to have the greatest effect on profitability.

![Figure 16. IRR with 25% Change in Parameter](image)

Figure 16. This figure contains the effect of various parameters on the internal rate of return.

The parameters of interest were aromatic product price, hydrogen price, naphthalene price, natural gas cost, and fixed capital investment.

**Global Impacts (Andrew)**

Currently BTX hydrocarbons are typically produced from a feed stream of naphtha to a catalytic reformer which converts the liquid petroleum products into reformates, this allows for straight linear hydrocarbons to be converted into higher octane aromatic compounds [46]. Natural gas is a cleaner burning fuel than all other hydrocarbon compounds. Using natural gas as a feedstock
rather than naphtha will allow for these BTX products to be produced without the side products of the reforming of naphtha. Methane is also a lot cheaper to buy and use as a feedstock than naphtha. Using this feedstock and process can create more competition and possibly lower prices for BTX type products in the United States, forcing other competitors to research other alternatives to create BTX hydrocarbons. This process is also very similar to the current process used, so switching over to this new process wouldn’t be an overbearing task for current producers. Using natural gas as a feedstock is also a lot safer for human exposure, methane doesn’t really have any negative effects on human health until higher concentrations in which the negative impact on health just comes from lack of oxygen [47]. However methane is a fuel and when combined with oxygen has the potential to explode and cause fires. Allowing for this new technology to be used and implemented will bring a lot of jobs into the job market boosting the economy of the United States. The production of benzene in the US is estimated at 101,760 barrels per day with a consumption estimate of 138,760 barrels per day leaving a deficit of 37,660 barrels per day as of June 2014[48]. This leaves the United States in a deficit and requires the country to have to import some of benzene in order to meet production demand. By producing more in the United States there will be less need to import benzene into the US strengthening our economy by relying less on other countries for this product. The process proposed will produce about 5,627 barrels per day of benzene which will make up for about 15% of the benzene that must be imported to the United States. This process yields a much higher percentage of benzene than the traditional current process used to create BTX type products. As stated before since the current process and this proposed process are similar if several competitors switched to this process and were able to have higher yields of benzene the United States could become independent when comes to the production and consumption of benzene and possibly start exporting benzene to other countries instead of importing. This can provide
more tax money for the American people through tariffs and the creation of new jobs. Although methane is the cleanest burning fuel of all the hydrocarbons, the “global warming potential” of methane is 21 times that of carbon dioxide. The United States currently emits about 5.3 million Kilo-Tons of CO2 each year, this project is estimated to emit about 117 kt of CO2 equivalent [49], this is equal to about 0.0022% of the United States total and 0.00033% of the global emission per year [50]. This is just a drop in the bucket compared to the total United States emission and world emission, this value is also similar to petro-chemical plants found in the Houston Texas area. The United States government passed the clean air act was first introduced in 1955 with several changes since then [51]. Figure 17 below shows the EPA’s goal as far as carbon reduction per state. Complying with the EPA’s goal of reduction of 30-36% this process could potentially use the hydrogen by product as a fuel source for a drastic reduction in carbon emissions.
Due to the nitrogen within the system there is also the potential to release NOx type gasses into the atmosphere during the burning process in both the furnace and generators. In order to reduce these types of harmful gases from being released to the atmosphere an SCR type catalyst will be used to reduce these gases into diatomic nitrogen and water. Converting these harmful gases to these inert products will further reduce the negative impact that NOx type gases have on the environment, mostly acid rain. Acid rain can have a negative impact on the local environment by reacting with water and oxygen in the atmosphere to form nitric acid. Nitric acid if inhaled can cause significant damage to the lungs, and can possibly aggravate heart disease. NOx can also react with organic compounds and sunlight in the atmosphere to form ozone. Ozone can do significant to the lungs especially in the elderly and young. As seen in figure 18, The Houston Texas area has rain with a pH lower than most of the country indicating that the formation of
Acid rain is already impacting the environment. Acid rain can also impact local fish life by lowering the pH of the gulf coast and lakes in the Houston, Texas area.

Figure 18. pH of rain throughout the United States

Figure 19. World Consumption of Toluene
Conclusions and Recommendations (Audra)

Due to the promising IRR and market for this process, we recommend further effort be put into developing this process. The process is currently feasible, but future work for this process should include research into exact catalyst performance, especially over time. Better understanding of the catalyst may allow for a smaller reactor which would lower capital expenses and add to the profitability of our process. Detailed energy needs for the plant should also be evaluated to optimize the purge and vent streams to meet this energy demand. With proper consideration and planning this process has the potential to help fill a void in America's aromatic market at a great profit.

Future Work (Andrew)

Several things should be further researched before a pilot plant or full commercial use is considered for this process. The first and most important is the deactivation and lifespan of the catalyst under conditions proposed. There was very limited information in the papers found indicating the lifespan of these catalysts for this process. The research papers used for this process used atmospheric pressure as the operating condition, while this is how most research is done this is not the most effective way for mass production of a gas phase reaction. Increasing the pressure within our reactor could dramatically decrease the capital cost of the process by decreasing the size of the reactor required. Looking into how the temperature of the reactor changes the kinetics of the process is another thing that should be researched since the research papers only provided one temperature condition. If the temperature of the reactor is able to be reduced not as much fuel will need to be combusted to raise the temperature of the reactor and maintain it thus saving utility cost as well as lowering the environmental impact. Another design alternative that could be looked into would be using the hydrogen as a fuel source to provide
electricity and heating for our process instead of using the purge stream hydrocarbons. Hydrogen is a much cleaner burning fuel than any hydrocarbon as the byproduct is water and would therefore leave a much smaller carbon footprint than the current proposed method. Alternative methods of separation might be looked into to improve the separation of desired compounds, possibly yielding a higher purity product and possibly not having to cool the stream coming out of the reactor for separation thus reducing utility cost and carbon footprint. Currently a distillation tower and flash drum are being used for separation, however molecular sieves might be used to separate the smaller hydrocarbon compounds from the higher order hydrocarbons. Molecular sieves would be advantages to a tower or flash drum because the stream entering does not need to be cooled before entering thus possibly reducing utility cost. An adsorption tower might also be considered for the separation of compounds, this might be able to provide a higher selectivity and thus again providing a higher quality product.

Acknowledgements

We would like to thank Dr. Holles and Professor Myers for their guidance in developing our process and for sharing their industrial experience.

References

3. Platts, Naphtha prices a double-edge sword for European industry
4. Eere, The BTX chain: Benzene, Toluene, Xylene
5. Platts, The changing dynamics of global benzene supply
   http://blogs.platts.com/2015/07/14/changing-dynamics-global-benzene-supply/
6. Eere, The BTX chain: Benzene, Toluene, Xylene
7. Eere, The BTX chain: Benzene, Toluene, Xylene
8. Eere, The BTX chain: Benzene, Toluene, Xylene
17. Center for Energy Economics. Composition of natural gas and LNG.


24. 42 U.S.C. § 7412


27. Clean Air Act of 1990


34. www1.eere.energy.gov
49. EPA, Overview of Greenhouse gases https://www3.epa.gov/climatechange/ghgemissions/gases/co2.html
51. EPA, Summary of the Clean Air Act https://www.epa.gov/laws-regulations/summary-clean-air-act
Appendices

A. HAZOP Analysis Table (Aric):

<p>| Unit Op     | Guideword | Deviation | Causes                                   | Consequences                                                   | Action Required                                  |
|-------------|-----------|-----------|------------------------------------------|                                                               |                                               |
| M101 - Mixer| Agitation | Fast mixing| Too much power to mixer                  | Going out of range of designer spec                           | Fix power supply                                 |
|             | Agitation | Slow mixing| Too little power to mixer                | Lack of proper mixing of components                           | Fix power supply                                 |
|             | Agitation | No Mixing | No power to mixer                        | No mixing of components                                        | Fix power supply                                 |
| H101 - Heat Exchanger | Temperature | High | Wrong ratios of CW and hot stream | Less energy efficient and potential explosion or weakening of equipment | Adjust either CW or hot stream flow |
|             | Temperature | Low | Wrong ratios of CW and hot stream | Not enough heating for required chemistry or process to occur normally | Adjust either CW or hot stream flow |
|             | Flow | Low | Tube leak or blockage | Release to atmosphere and decreased performance | Install flow alarm and routine inspections |
| F101 - Furnace | Temperature | High | Too much fuel being fed | Over heat the reaction, create unwanted products and waste energy | Valve to control the fuel flow to furnace |
|             | Temperature | Low | Too little fuel being fed | Under heat the reaction and not get the reaction rate or conversion desired | Valve to control the fuel flow to furnace |
| R101 – Reactor | Flow | Low flow | Blockage from earlier unit op, low feed rate, etc. | Less product formed, potential hazard to following unit ops and recycle stream | Increase flow rate to reactor to within the acceptable range |</p>
<table>
<thead>
<tr>
<th>Flow</th>
<th>High flow</th>
<th>High feed rate, excess recycle</th>
<th>Less product formed, potential hazard to following unit ops and recycle stream</th>
<th>Decrease the flow rate to reactor to within the acceptable range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>No flow</td>
<td>Complete blockage of earlier unit op, no feed rate</td>
<td>No product formed, potential over heating of reactor resulting in degradation of catalyst and/or reactor shell integrity</td>
<td>Turn off heating of reactor and introduce feed flow to reactor gradually raising the heat</td>
</tr>
<tr>
<td>Temperature</td>
<td>High</td>
<td>High heating flow rate, low feed flow rate</td>
<td>Less product formed, potential hazard to following unit ops and recycle stream, possible explosion due to HTHA, and possibility of methane corroding stainless steel</td>
<td>Increase cooling flow, decrease heating flow, stabilize feed rate</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low</td>
<td>Low heating flow rate, high feed flow rate</td>
<td>Less product formed, potential hazard to following unit ops and recycle stream</td>
<td>Increase heating flow, decrease cooling flow, stabilize feed rate</td>
</tr>
<tr>
<td>Pressure</td>
<td>High</td>
<td>Blockage of outlet from reactor, increased feed flow rate</td>
<td>Less product formed, could stress structural integrity of reactor shells</td>
<td>Lower flow rate, check for blockage on shutdown</td>
</tr>
<tr>
<td>Pressure</td>
<td>Low</td>
<td>High flow from outlet (inability to hold pressure), low feed flow</td>
<td>Less product formed, potential hazard to following unit ops and recycle stream</td>
<td>Increase flow rate to reactor, check pressure building mechanism on shutdown</td>
</tr>
<tr>
<td>Reaction</td>
<td>Slow</td>
<td>Catalyst deactivation</td>
<td>Less product formed, potential hazard to following unit ops and recycle stream</td>
<td>Reactivate catalyst or replace on shutdown</td>
</tr>
<tr>
<td>Reaction</td>
<td>No reaction</td>
<td>Complete catalyst deactivation</td>
<td>No product formed, Potential hazard to following unit ops and recycle stream</td>
<td>Reactivate catalyst or replace on shutdown</td>
</tr>
<tr>
<td>Component</td>
<td>Condition</td>
<td>Issue Description</td>
<td>Solution</td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Start-up</td>
<td>Too fast</td>
<td>Heating too quickly, introducing feed rate too quickly</td>
<td>Slow down the time taken to stabilize the reactor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Too slow</td>
<td>Heating too slowly, introducing feed rate too slowly</td>
<td>Speed up the time taken to stabilize the reactor</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Unwanted reaction</td>
<td>Temperature of reactor too high</td>
<td>Increase cooling flow, decrease heating flow, stabilize feed rate</td>
<td></td>
</tr>
<tr>
<td>H102 - Heat Exchanger</td>
<td>Temperature</td>
<td>High</td>
<td>Adjust either CW or hot stream flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Wrong ratios of CW and hot streams</td>
<td>Adjust either CW or hot stream flow</td>
<td></td>
</tr>
<tr>
<td>H103 - Heat Exchanger</td>
<td>Temperature</td>
<td>High</td>
<td>Adjust either CW or hot stream flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Wrong ratios of CW and hot streams</td>
<td>Adjust either CW or hot stream flow</td>
<td></td>
</tr>
<tr>
<td>Flow</td>
<td>Low</td>
<td>Tube leak or blockage</td>
<td>Install flow alarm and routine inspections</td>
<td></td>
</tr>
<tr>
<td>D101 - Flash Drum</td>
<td>Pressure</td>
<td>High</td>
<td>Adjust flow of stream going into drum or fix patches</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>Too little flow into the drum</td>
<td>Adjust flow of stream</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------</td>
<td>------------------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>High Pre-cooling propane might not be functionally properly</td>
<td>Low Pre-cooling propane might not be functionally properly</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>High temperature could allow for lower MW molecules to go up the tower rather than below</td>
<td>Low temperature could allow for higher MW molecules to go down the tower rather than below</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C101 - Compressor</strong></td>
<td>Utility failure Failure Too little power supplied</td>
<td>Loss of pressure gradient uniformity throughout the system, more impurities in feed stream</td>
<td>Install pressure gauge</td>
<td></td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>High Too much power being fed to the compressor</td>
<td>Could go beyond manufacture recommended settings, possibly damaging the equipment</td>
<td>Have a cap on power allowed to flow to compressor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Too little power being fed to the compressor</td>
<td>Does not allow for all the gas to be compressed back to liquid</td>
<td>Add another power source for the compressor</td>
<td></td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>High Inlet flow temperature too high</td>
<td>Won’t allow for full condensation of gases being flowed through</td>
<td>Ensure gas is cooled sufficiently before entering the compressor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Inlet flow temperature too low</td>
<td>Not energy efficient since the stream does not need to be that cool</td>
<td>Ease up on cooling process before entering the compressor</td>
<td></td>
</tr>
<tr>
<td><strong>Flow</strong></td>
<td>High Compressor not able to condense all the gas</td>
<td>Having gas flow through pipes that should be all liquid</td>
<td>Put valve on to regulate stream flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Compressor not being used at optimum efficiency</td>
<td>Energy would be wasted</td>
<td>Put valve on to regulate stream flow</td>
<td></td>
</tr>
<tr>
<td><strong>S101 - Hydrogen Membrane</strong></td>
<td>Flow</td>
<td>No flow</td>
<td>Fouling of larger molecules</td>
<td>Blockage of flow</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------</td>
<td>---------</td>
<td>-----------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Flow</td>
<td>Low</td>
<td>Fouling of larger molecules</td>
<td>Blockage of flow</td>
<td>Clean frequently</td>
</tr>
<tr>
<td>Flow</td>
<td>High</td>
<td>Flow controller fault</td>
<td>Loss of efficiency, membrane may get damaged</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td>Pressure</td>
<td>Low</td>
<td>Decreased flow to membrane or damage allowing undesired reactants through membrane</td>
<td>Impure Hydrogen product stream</td>
<td>Monitor pressure and product quality</td>
</tr>
<tr>
<td>Pressure</td>
<td>High</td>
<td>Excess pressure from compressor or pore fouling</td>
<td>Damage to membrane and possible reduction in product stream</td>
<td>Clean frequently and monitor pressure</td>
</tr>
<tr>
<td>Temperature</td>
<td>High</td>
<td>Excess heating in H102</td>
<td>Reduced membrane performance if outside temperature range</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low</td>
<td>Insufficient heating in H102</td>
<td>Reduced membrane performance if outside temperature range</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td><strong>T101 - Distillation Tower</strong></td>
<td>Level</td>
<td>High</td>
<td>Outlet pipe blockage</td>
<td>Over pressure of reflux drum, condensate flow back to distillation</td>
</tr>
<tr>
<td>Level</td>
<td>Low</td>
<td>Leakage or inlet flow blocked</td>
<td>Back flow of material if blocked, and chemical release if a leak exists</td>
<td>Install level alarm and incoming flow-rate meter</td>
</tr>
<tr>
<td>Temperature</td>
<td>High</td>
<td>Low flow to tower</td>
<td>Impure product</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low</td>
<td>High flow to tower</td>
<td>Low reboiler level, impure product</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Flow</td>
<td>High</td>
<td>Flow controller fault</td>
<td>Increased level and reduced temperature, reboiler may reach capacity and liquid</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td>Component</td>
<td>Condition</td>
<td>Cause</td>
<td>Impact</td>
<td>Corrective Action</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------</td>
<td>-----------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Flow</td>
<td>Low</td>
<td>Flow controller fault or inlet flow blockage</td>
<td>Reduced flow could cause increased tower temperature and result in off-spec product, any flow blockage could increase pressure in the inlet pipe and lead to structural damage</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td></td>
<td>No flow</td>
<td>Leakage or inlet flow blocked</td>
<td>Increased temperature and reduced liquid levels</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td>Utility failure</td>
<td>Failure</td>
<td>Cold water to condenser reduced or stopped</td>
<td>Insufficient condensation resulting in vapor product</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Utility failure</td>
<td>Failure</td>
<td>Power to reboiler stopped</td>
<td>Insufficient reheating resulting in impure bottoms product</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>AC101 - Propane Air Cooler</td>
<td>Low</td>
<td>Air cooler leak or inlet pipe blockage</td>
<td>Propane release to atmosphere if leak, reduced propane recycle flow limits cooling in H103</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td>Flow</td>
<td>High</td>
<td>Flow controller fault</td>
<td>Increased mass flow through the air cooler could result in a higher outlet temperature insufficient for the cooling required by H103</td>
<td>Install temperature sensor and flow alarm</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low</td>
<td>Long residence time</td>
<td>Over cooling of H103 impacting the operation of D101</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Temperature</td>
<td>High</td>
<td>Short residence time</td>
<td>Insufficient cooling in H103 impacting separation in D101</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Utility failure</td>
<td>Failure</td>
<td>Too little power supplied</td>
<td>Insufficient cooling of propane, which in turn limits cooling in H103</td>
<td>Install pressure gauge</td>
</tr>
<tr>
<td>C102 - Propane Compressor</td>
<td>Failure</td>
<td>Too little power supplied</td>
<td>Insufficient propane compression leading to reduced cooling in H103</td>
<td>Install pressure gauge</td>
</tr>
<tr>
<td>Pressure</td>
<td>High</td>
<td>Outlet blockage or increased power supply</td>
<td>Increased pressure leads to increased cooling in H103 and potential structural damage</td>
<td>Install pressure gauge</td>
</tr>
<tr>
<td>------------</td>
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<td>-------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Pressure</td>
<td>Low</td>
<td>Low inlet feed or reduced power supply</td>
<td>Higher volume of gas being fed to air cooler resulting in reduced propane cooling and therefore reduced cooling in H103</td>
<td>Install pressure gauge</td>
</tr>
<tr>
<td>Temperature</td>
<td>High</td>
<td>Warmer hot or cold side or reduced cold-side flow-rate in H103</td>
<td>Insufficient propane cooling leading to decreased cooling in H103</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low</td>
<td>Cooler hot or cold side or increased cold-side flow-rate in H103</td>
<td>Insufficient propane cooling leading to decreased cooling in H103</td>
<td>Install temperature sensor</td>
</tr>
<tr>
<td>Flow</td>
<td>Low</td>
<td>Inlet flow controller error, pipe blockage, or reduced propane in system</td>
<td>Insufficient propane to H103, pipe blockage could damage equipment</td>
<td>Install flow alarm</td>
</tr>
<tr>
<td>Flow</td>
<td>High</td>
<td>Inlet flow controller error or increased propane in system</td>
<td>Increased power required to reach same pressure or desired pressure will not be reached</td>
<td>Install flow alarm</td>
</tr>
</tbody>
</table>

**B. Supporting Documents**

1. Spring 2016 Final.bkp
2. Process Considerations – Spring Updates.xlsx
3. Sizing and Economics Final.xlsx