CHE 4080

William Duncan, Wyatt Keller, Rachael Weber, Zach Witters
Project Definition

- Produce 261 MMlb/year of 99.8% mass purity para-xylene from biological feedstock with an overall conversion of 75%
- The bio-feedstock for this project is fructose.

Need for this Process

- PX demand growth of 6-8% yearly
- Glucose, fructose, and other organic compounds can be used as a feedstock option and considered a renewable resource
  - Can be derived from sugar cane and maize starch
Broader Impact & Contemporary Issues

- Para-xylene is normally distilled from crude oil sources
- The US has consumed about 2.5 times more crude oil than we have produced
- Biological feedstock provides greater market price stability
- High purity of PX is required for making terephthalic acid
- Terephthalic acid is used to make polyethylene terephthalate (PET) for clothing, bottles, and textiles
Plant Location

- Our plant is located in Houston, Texas
- Access to Gulf shipping lanes and existing equipment that could be repurposed
- Sugar cane and High Fructose Corn Syrup (HFCS) can be used as fructose source (which is then used to produce fructose) and is grown in Southern Texas, Louisiana, and Florida
Process Overview

Section 1: D-Fructose to HMF

- Reaction to HMF in Batch Reactor
- Water decant & HMF separation

Fructose

Byproducts & Purge

Water

Section 2: HMF to DMF

- Reaction to DMF in Trickle Bed Reactor

HMF

Section 3: DMF to Para-Xylene

- Water Decant and PX Separation via Distillation

PX

Recycle

Water

DMF

Water decant & DMF separation

Purge
Conversion of Fructose to HMF

- **Reactions (CSTR)**
  - 1 Fructose $\rightarrow$ 1 HMF + 3 $\text{H}_2\text{O}$
  - 1 Fructose + 1 isopropanol $\rightarrow$ 1 isoproxymethylfurfural (IMF) + 4 $\text{H}_2\text{O}$

- **Reaction Conditions**
  - Feed = 10 wt% Fructose in isopropanol
  - 2 L of Isopropanol per mole of fructose (approximately 88.4 wt%)
  - Salt ratio to fructose is 0.5 (approximately 1.6 wt%)
  - Temperature = 248°F
  - Pressure = 14.7 psi

- **Feeds**
  - Fructose, Isopropanol (organic solvent)
  - Catalyst: Amonium Chloride (Salt Catalyst)

- **Products**
  - HMF
Reaction of Fructose to HMF - (2)

- Byproducts
  - Isoproxymethylfurfural (IMF)
  - Water

- Conversions
  - Conversion is modeled at 100% due to batch reactors with 12 hour residence time and literature.

- Approximate Yields for Main Product in Each Reaction
  - Total yield of HMF is 65%
  - Total yield of the byproduct IMF is 6%

- Alternatives: Biphasic system. This was previously analyzed and proven to be infeasible both for economics and practicality.
Design Alternative

Extractive distillation: Uses 2-octanone to increase the relative volatility of isopropanol for easier separation.

- Needs four more distillation columns and make up octanone.
- Obtained 92% isopropanol recovery
  - Not good enough for economic analysis
- Towers are large and will increase capital costs greatly.
Conversion of HMF to DMF - Flowsheet
Conversion of HMF to DMF

- Overall Reaction (based on 100 mol of HMF)
  - (100) HMF + (303) H2 → (98) DMF + (200) H2O + (1) CH4 + (1) 2-methyltetrahydrofuran + (1) 2-methylfuran
  - (1) IMF + (4) H2 -> (1) DMF + (4) H2O + (1) C₃H₈

- Reaction Conditions
  - The reactor is a trickle bed reactor with a hydrogen atmosphere
  - The reaction will run at 356°F and 145 psi.

- Feeds
  - 94.7% mass HMF, 5.3% IMF and 202 PPB of Isopropanol

- Products
  - DMF (2,5-dimethylfuran)
Conversion of HMF to DMF - (2)

- **Byproducts**
  - Water, 2,5-dimethyltetrahydrofuran, 2-methylfuran, Methane and Propane

- **Catalyst**
  - PtCo@HCS Platinum Cobalt Hollow Carbon Spheres
    - Cu/Ru catalysts only have a 71% yield and a 80% conversion
    - Durability results are poor due to nanoparticle aggregation

- **Conversions**
  - 100% conversion of both HMF and IMF
Design Alternatives

- A CSTR reactor can be used for this process with 5 wt% reactant and 95 wt% solvent (Butanol)

- This is not economically feasible as butanol has an azeotrope with water, 2-methyltetrahydrofuran, and DMF

- Pressure shift distillation is required

- Future research could look into liquid-liquid extraction
Conversion of DMF to Para-xylene

Hexane Recycle

Reactor Section

PX Purification
Conversion of DMF to Para-xylene

- **Reaction Conditions**
  - 10 mass % DMF in Hexane. Reaction takes place at 482°F and 899psi

- **Feeds**
  - DMF, Hexane (solvent), Ethylene

- **Products**
  - Para-xylene

- **Byproducts**
  - Water, 1-methyl-4-n-propylbenzene

- **Catalyst**
  - H-BEA (Beta Zeolite)

- **Conversions**
  - 100% conversion of DMF
  - 90% selectivity and yield PX
## Equipment Costs

<table>
<thead>
<tr>
<th>ScaledInstalled Costs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pumps</strong></td>
<td>$ 700,000</td>
</tr>
<tr>
<td><strong>Furnace</strong></td>
<td>$ 2,000,000</td>
</tr>
<tr>
<td><strong>Heat Exchangers</strong></td>
<td>$ 5,000,000</td>
</tr>
<tr>
<td><strong>Reactor</strong></td>
<td>$ 14,700,000</td>
</tr>
<tr>
<td><strong>Vessels</strong></td>
<td>$ 2,500,000</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>$ 140,000</td>
</tr>
<tr>
<td><strong>Towers &amp; Trays</strong></td>
<td>$ 21,800,000</td>
</tr>
<tr>
<td><strong>Total Installed ISBL</strong></td>
<td>$ 52,000,000</td>
</tr>
<tr>
<td><strong>Total Installed OSBL</strong></td>
<td>$ 10,500,000</td>
</tr>
<tr>
<td><strong>Total Installed FCI</strong></td>
<td>$ 62,500,000</td>
</tr>
</tbody>
</table>
Economics

- Feed Prices

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Quantity (MMlb/year)</th>
<th>$MM/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>520</td>
<td>198</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>7</td>
<td>6.5</td>
</tr>
<tr>
<td>H2</td>
<td>18</td>
<td>9.80</td>
</tr>
<tr>
<td>Hexane</td>
<td>0</td>
<td>0.012</td>
</tr>
<tr>
<td>Ethylene</td>
<td>87</td>
<td>32.4</td>
</tr>
<tr>
<td>Total</td>
<td>632</td>
<td>246.33</td>
</tr>
</tbody>
</table>

- Product Price

- PX costs $0.70/lb.
- At 8250 operating hours per year, this plant makes ~261 MMlb/year PX which generates ~$180 million dollars in revenue.
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Economics - Production Costs</strong> ($MM/Year)</td>
<td></td>
</tr>
<tr>
<td>Product Revenue</td>
<td>183</td>
</tr>
<tr>
<td>Gross Cost of Raw Materials</td>
<td>246</td>
</tr>
<tr>
<td>Byproduct Credit</td>
<td>29</td>
</tr>
<tr>
<td>Net Cost of Raw Materials</td>
<td>217</td>
</tr>
<tr>
<td>Utilities</td>
<td>12</td>
</tr>
<tr>
<td>Total Variable Costs</td>
<td>229</td>
</tr>
<tr>
<td>Total Fixed Costs</td>
<td>10</td>
</tr>
<tr>
<td>Total Manufacturing Costs</td>
<td>239</td>
</tr>
<tr>
<td>Margin (Sales Price - Variable Costs)</td>
<td>-46</td>
</tr>
</tbody>
</table>
### Economics - Cash Flow

<table>
<thead>
<tr>
<th>NPV Summary ($MM/year)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NPV0</td>
<td>-656.27</td>
</tr>
<tr>
<td>NPV10</td>
<td>-341.47</td>
</tr>
<tr>
<td>IRR</td>
<td>N/A</td>
</tr>
<tr>
<td>PBP (approx) (yrs)</td>
<td>N/A</td>
</tr>
</tbody>
</table>
### Para-Xylene Sensitivities

<table>
<thead>
<tr>
<th>Parameter</th>
<th>High IRR (%)</th>
<th>Low IRR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>-8%</td>
<td>24%</td>
</tr>
<tr>
<td>Para-Xylene</td>
<td>-6%</td>
<td>23%</td>
</tr>
<tr>
<td>MPB</td>
<td>4%</td>
<td>18%</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>9%</td>
<td>14%</td>
</tr>
<tr>
<td>Hexane</td>
<td>12%</td>
<td>11%</td>
</tr>
</tbody>
</table>

The following Tornado Plot Table is for the MPB price of $2.25/lb, which would make this project reasonably, economically feasible.
Safety

- SDS were examined for each chemical present in the system
- Hazards revealed by this include several irritants, carcinogens, toxins, and flammable species
- Process temperatures up to 505°F and pressures up to 899 psia
- Full HAZOP conducted to minimize the risks to operators and equipment
Environmental Concerns

- Large amount of heat needed for the process
- Modeled as combustion of natural gas
- Produce 13 MMlb CO\textsubscript{2} per year
- Utilize low NO\textsubscript{x} burners and Selective Non-Catalytic Reduction technology to minimize NO\textsubscript{x} release
  - Up to 75% reduction compared to no controls
Process Issues and Future Goals

- **Issues**
  - High capital costs due to multiple separation processes
    - High purity means that all byproducts must be separated
    - Contributes to large towers and difficult separations
  - Small margin for profit (fructose is 51% of PX price)

- **Future Research**
  - Trickle bed reactor must be tested
  - Salt recovery for recycling
  - Reduction in conversions and yields due to scale up.
  - Higher reactant concentration in feed streams for section 3
Questions?