Green Production of Terephthalic Acid for the Synthesis of PETE

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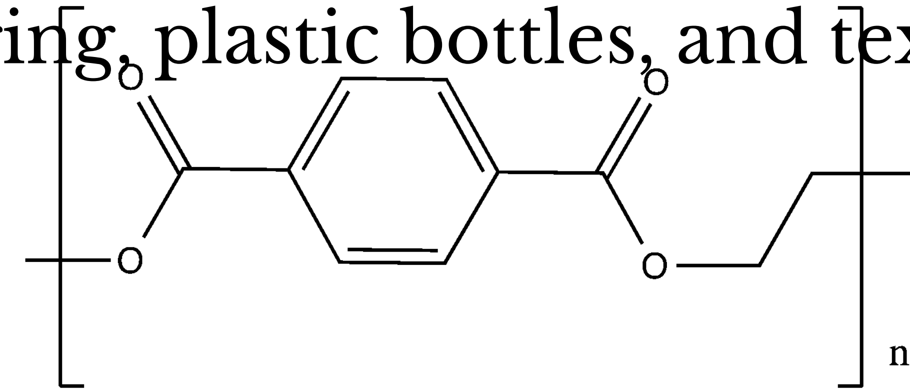
Outline

- PETE Production
- Green Routes
- Isobutanol to P-xylene Process
- CHEMCAD Simulation
- Economic Analysis
- Environmental, Health, and Safety Concerns
- Sustainability and Concluding Remarks

Polyethylene Terephthalate (PETE)

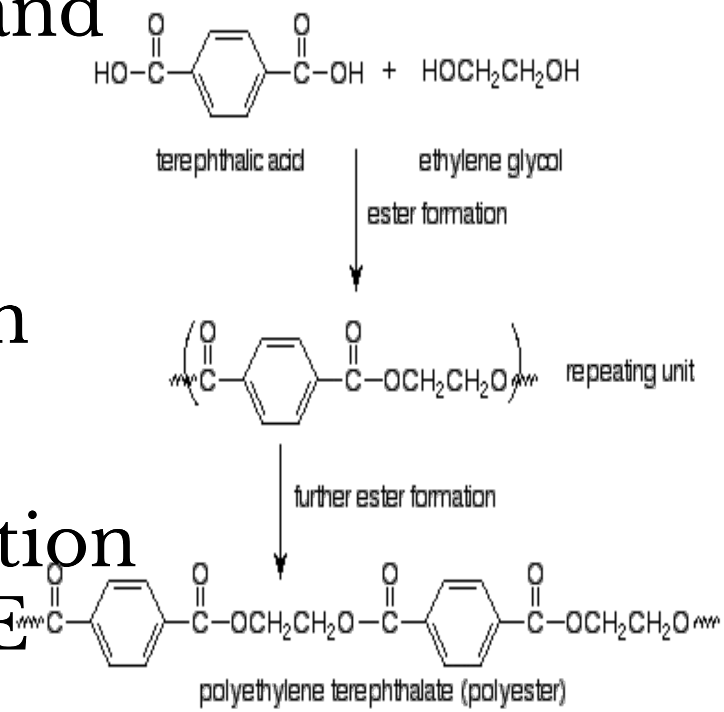
- One of the most common types of polymers
- Global PETE production in 2015 was estimated to reach 24.39 million tons†
- Lightweight, impact resistance, and chemical resistance make it ideal for food packaging, plastic bottles, and textiles



† Merchant Research & Consulting, Ltd. http://mcgroup.co.uk/news/20140117/global-pet-supply-exceed-2439-mln-tonnes-2015.html

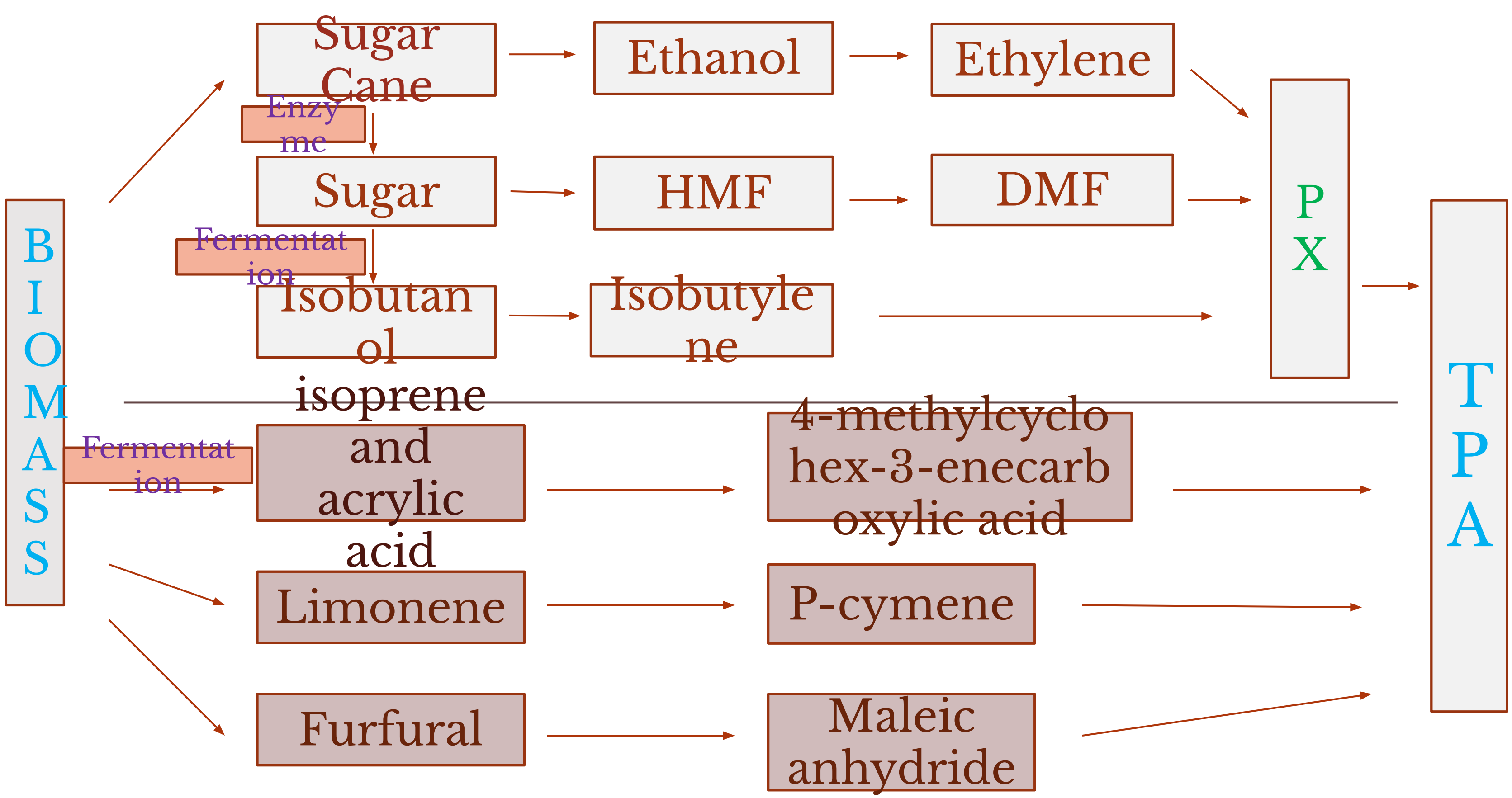
PETE Production

- Typically produced with terephthalic acid (TPA) and ethylene glycol (EG)
- Undergo condensation reactions in esterification vessels forming BHET
- Followed by polymerization in reactors to form PETE



†U.S. Environmental Protection Agency, "Compilation of Air Pollutant Emission Factors," Publication AP-42, https://www3.epa.gov/ttnchie1/ap42/ch06/final/c06s06-2.pdf, EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC (Jan. 1995).

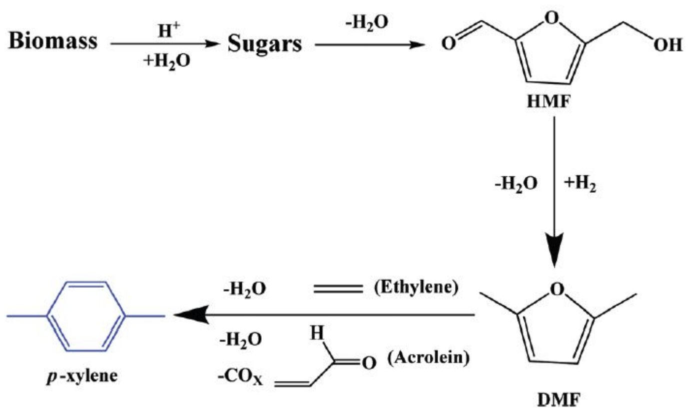
Green Routes Overview



†Based on figure from Pang et.al. Synthesis of ethylene glycol and terephthalic from biomass for producing PET. *Green Chem.* ***2016***,*18*, 342.

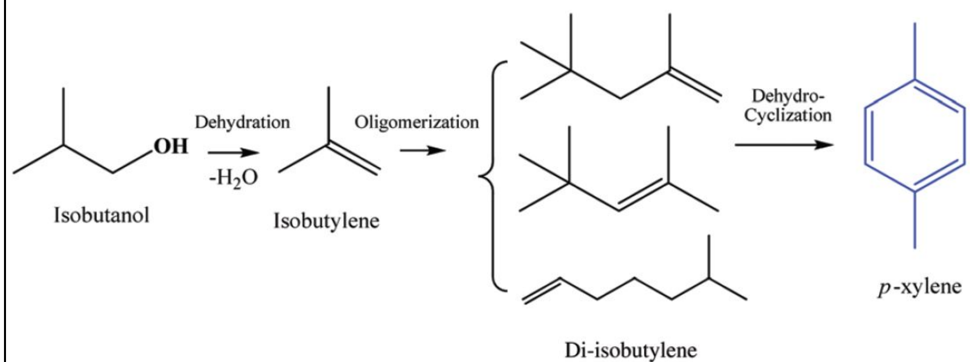
Green Routes: Isobutanol and HMF Routes

HMF pathway (CCEI)†



- Estimated p-xylene cost of $3,962/mt††
- Large capital cost from expensive Cu-Ru/C catalyst
- Catalyst replacement is also majority of operating cost
- Large solvent usage (THF, n-heptane)

Isobutanol pathway (GEVO)†



- Estimated p-xylene cost of $3,481/mt††
- Majority of operating cost from raw material (starch) price(46%)
- Valuable side products (o-xylene, benzene,etc)
- Petroleum based p-xylene is at $1630/mt

†Reaction pathways taken from Pang et.al. Synthesis of ethylene glycol and terephthalic from biomass for producing PET. *Green Chem.* **2016**,*18*, 342.

†† Z. Lin; V. Nikolakis; M. Ierapetritou, *Ind. Eng. Chem. Res.*, **2014**, *53*, 10688-10699.

Isobutanol and HMF Routes: Promise of Isobutanol

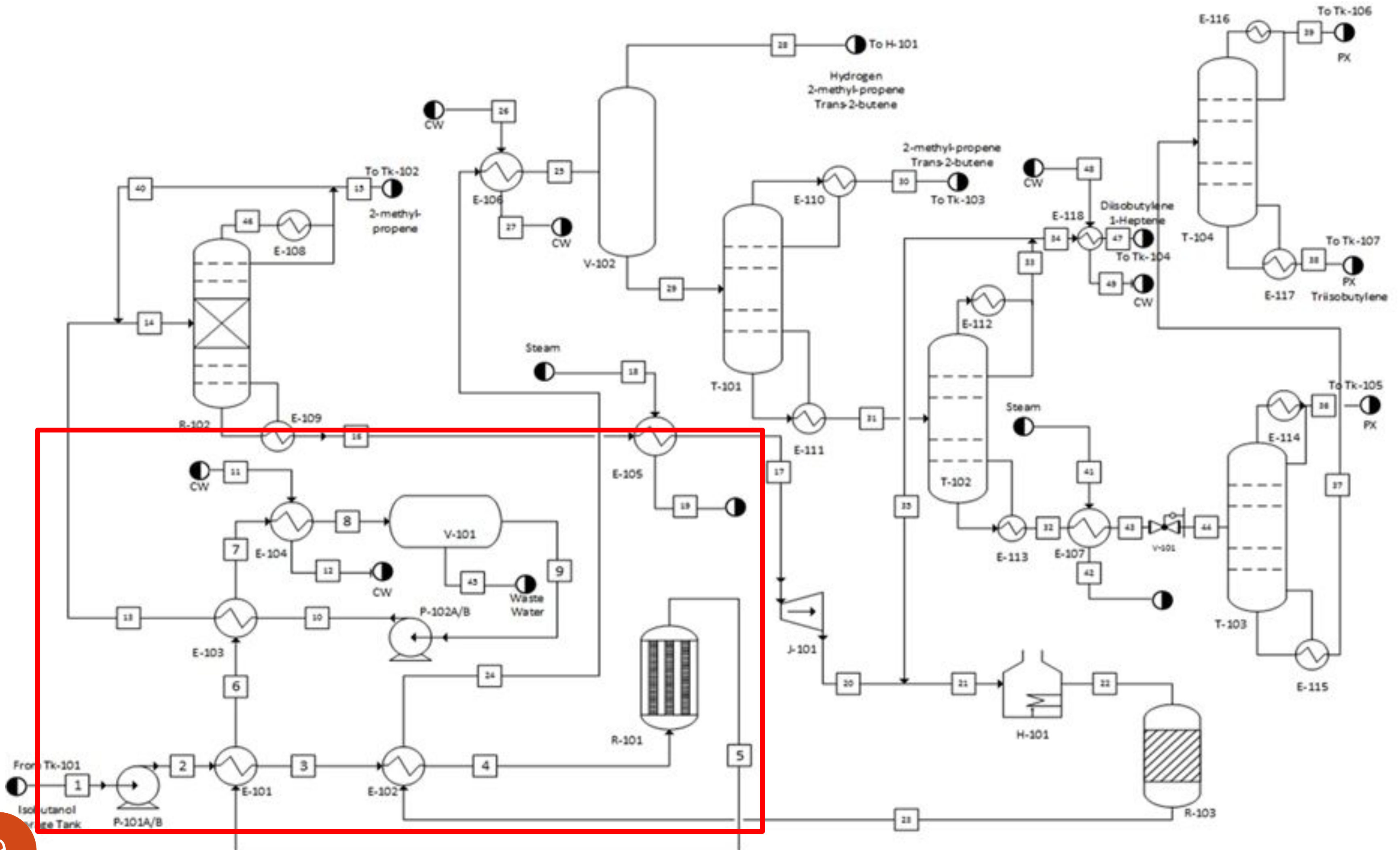
- Heavy research into its production already underway- Isobutanol has similar octane rating and energy density as gasoline.†
- Main challenge is effective bio-based production of isobutanol
- World's first renewable HMF facility (2013) – 20 tons/year.††
- GEVO isobutanol plant projected to produce 400 million gallons/year (~1.2 million metric tons/year).†††
- World oil production: 3.4×10^{10} barrels/year (4.7 billion metric tons/year)††††

† Advanced Motor Fuels. http://www.iea-amf.org/content/fuel_information/butanol/properties
†† First Industrial Production For Renewable 5-HMF https://chemicalparks.eu/news/2014-2-3-first-industrial-production-for-renewable-5-hmf
††† Second-Generation Biofuel: Isobutanol Producing Biocatalyst https://www.epa.gov/sites/production/files/2015-06/documents/gevo010711.pdf
†††† International Energy Statistics 2014 https://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=5&pid=53&aid=1

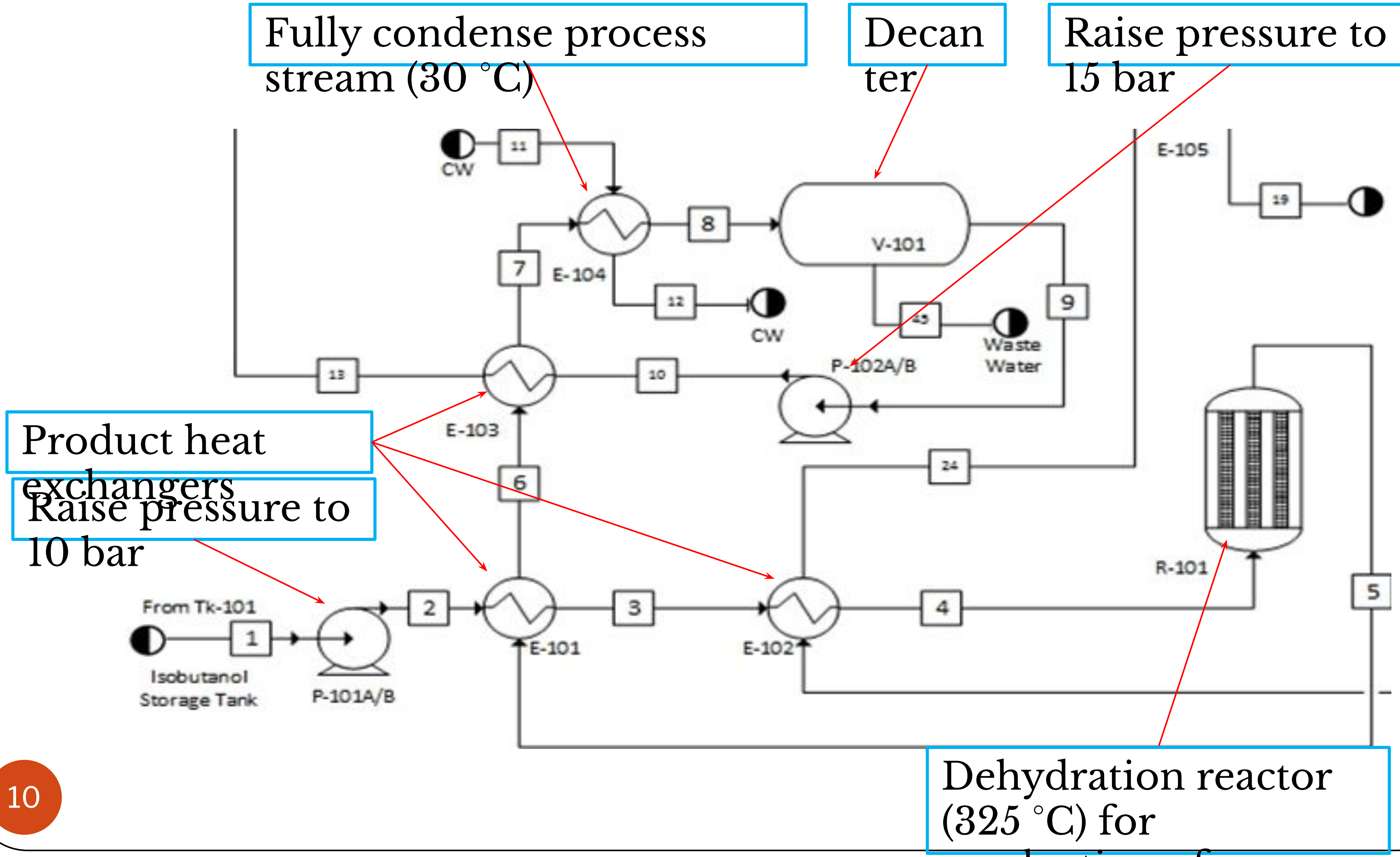
Isobutanol to P-xylene Process

- Feed rate of 150 million kg/year (17123 kg/hr) of isobutanol
  - Chosen to be on same order of magnitude as 5% of current NA PETE production
  - Use 30% mole fraction isobutanol
    - 26839 kg/hr flow rate of isobutanol-water mixture
- Shell and tube heat exchangers with floating tube sheet heads
- Most equipment made from carbon steel
  - Copper or titanium used when hydrogen present
  - Stainless steel for fired heater
- Pressure drop in system dealt with by oversizing pumps
  - System insensitive in general to local pressure increases
  - Over pressurize system to account for pressure drop
- Produces 99.5 % and 99.7 % purity p-xylene

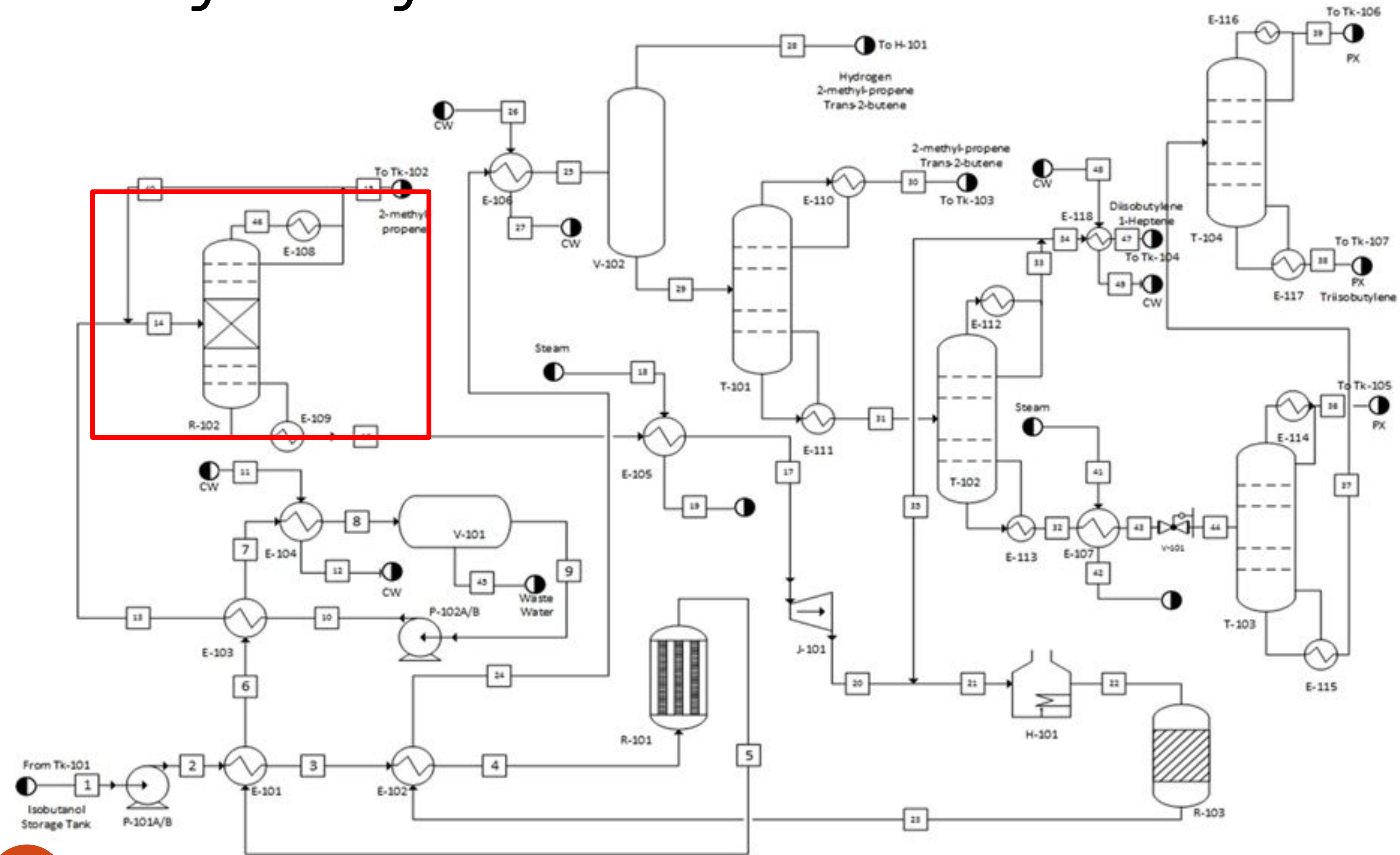
PFD Overview



PFD Part 1 - Dehydration



PFD Part 2 – Oligomerization and Dehydrocyclization



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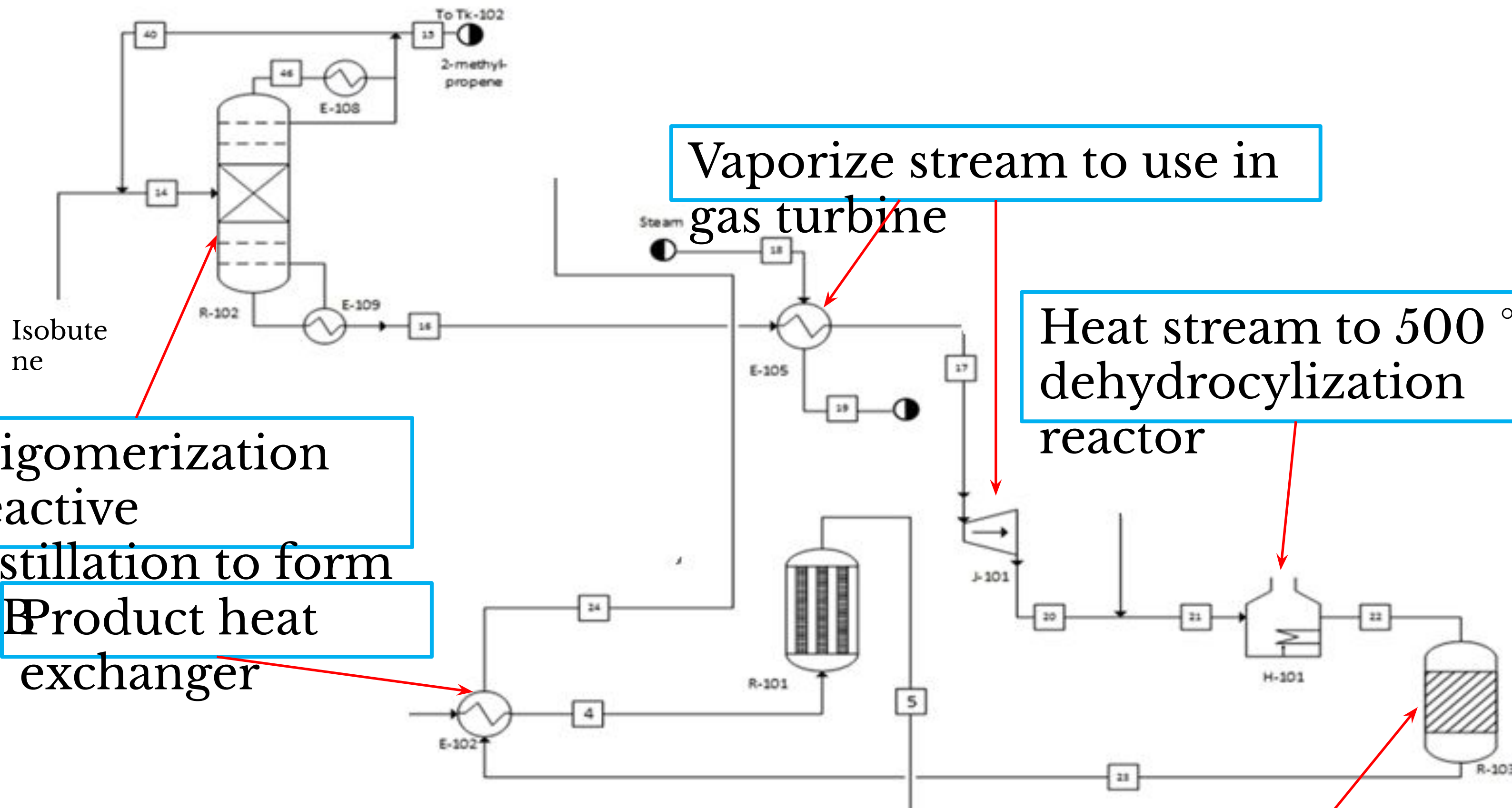


Vaporize stream to use in gas turbine

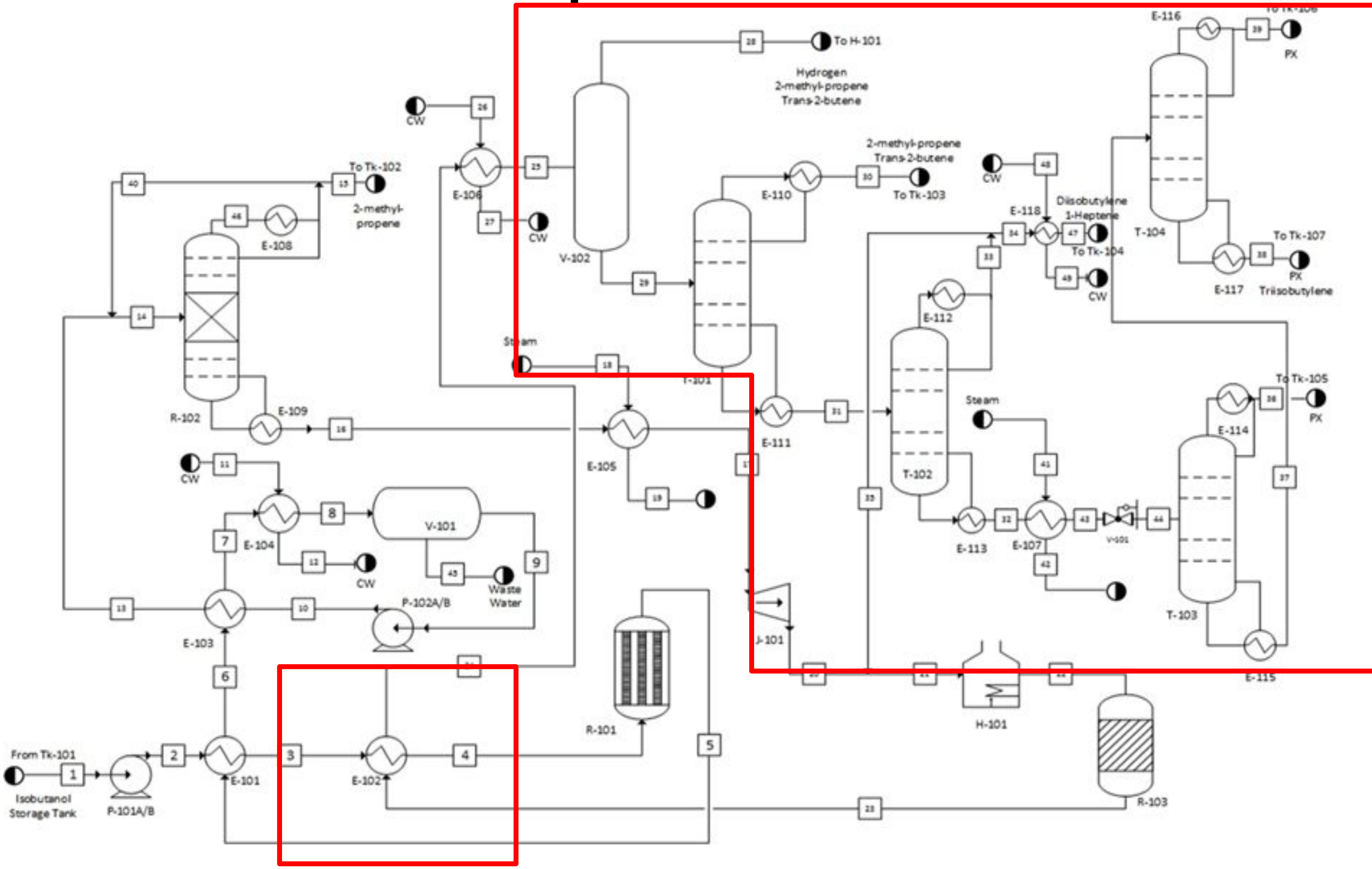
Heat stream to 500 °C for dehydrocylization reactor

Oligomerization Reactive Distillation to form DIB

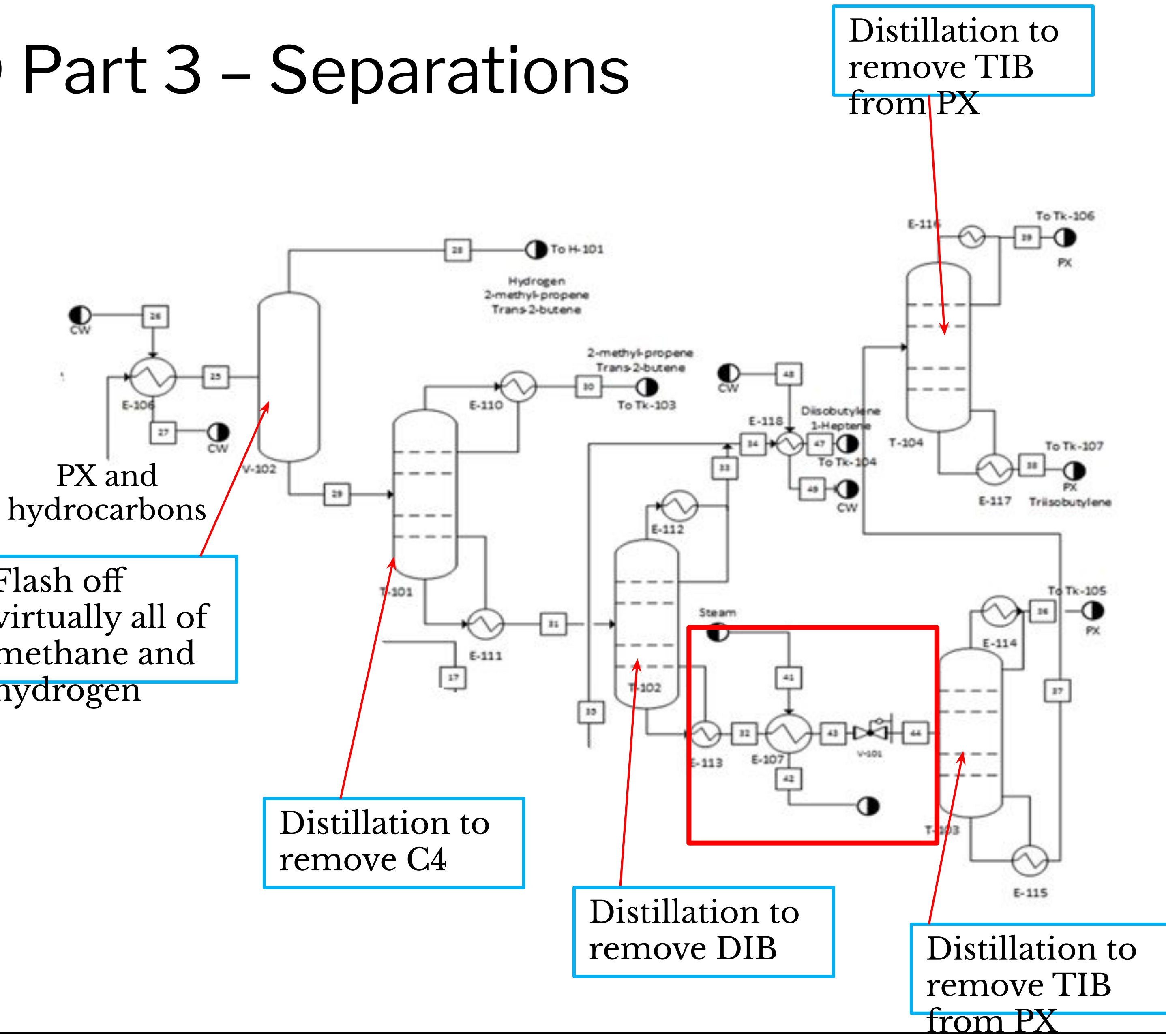
Product heat exchanger

Dehydrocyclization reactor for formation of PX

PFD Part 3 – Separations



PFD Part 3 – Separations

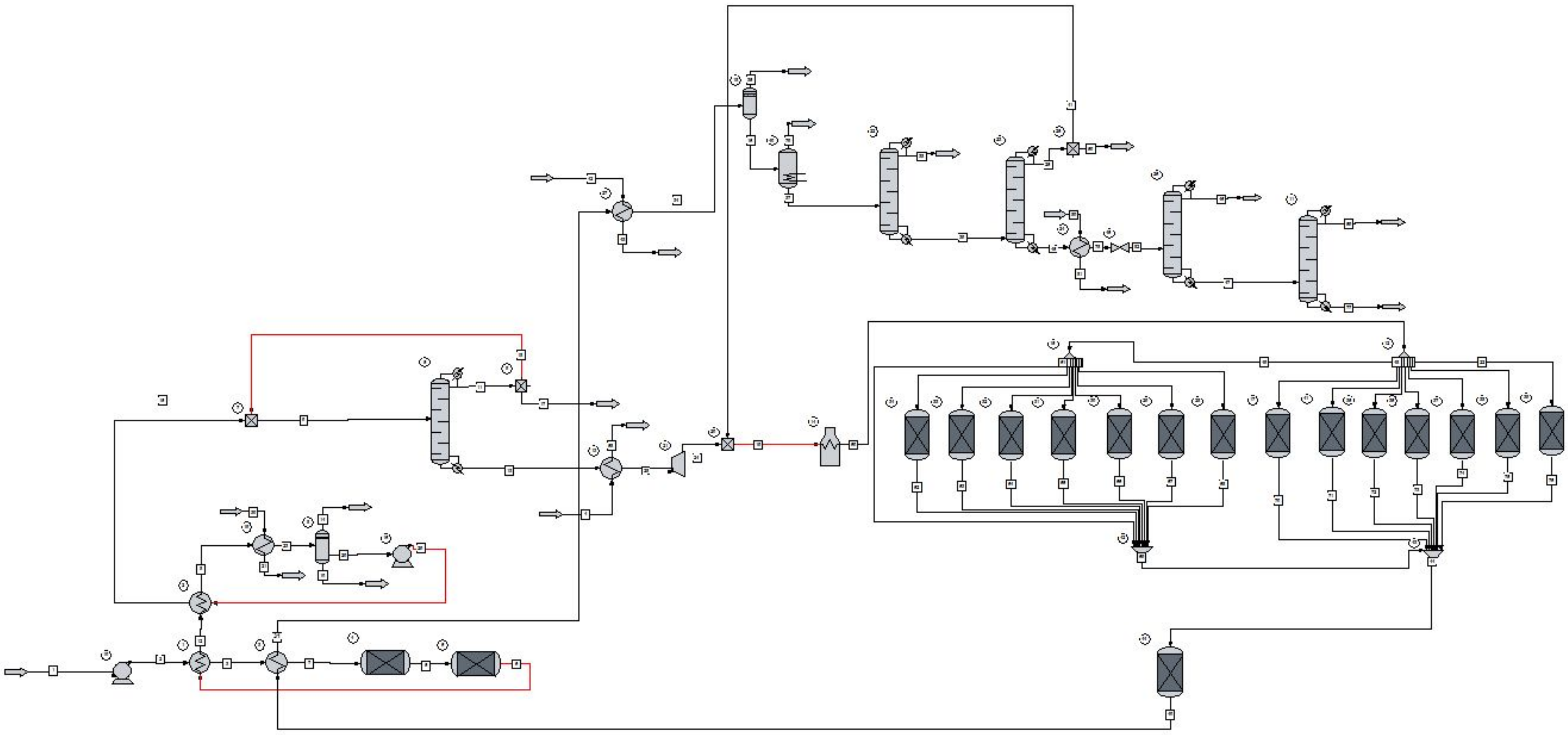


Simulation Overview

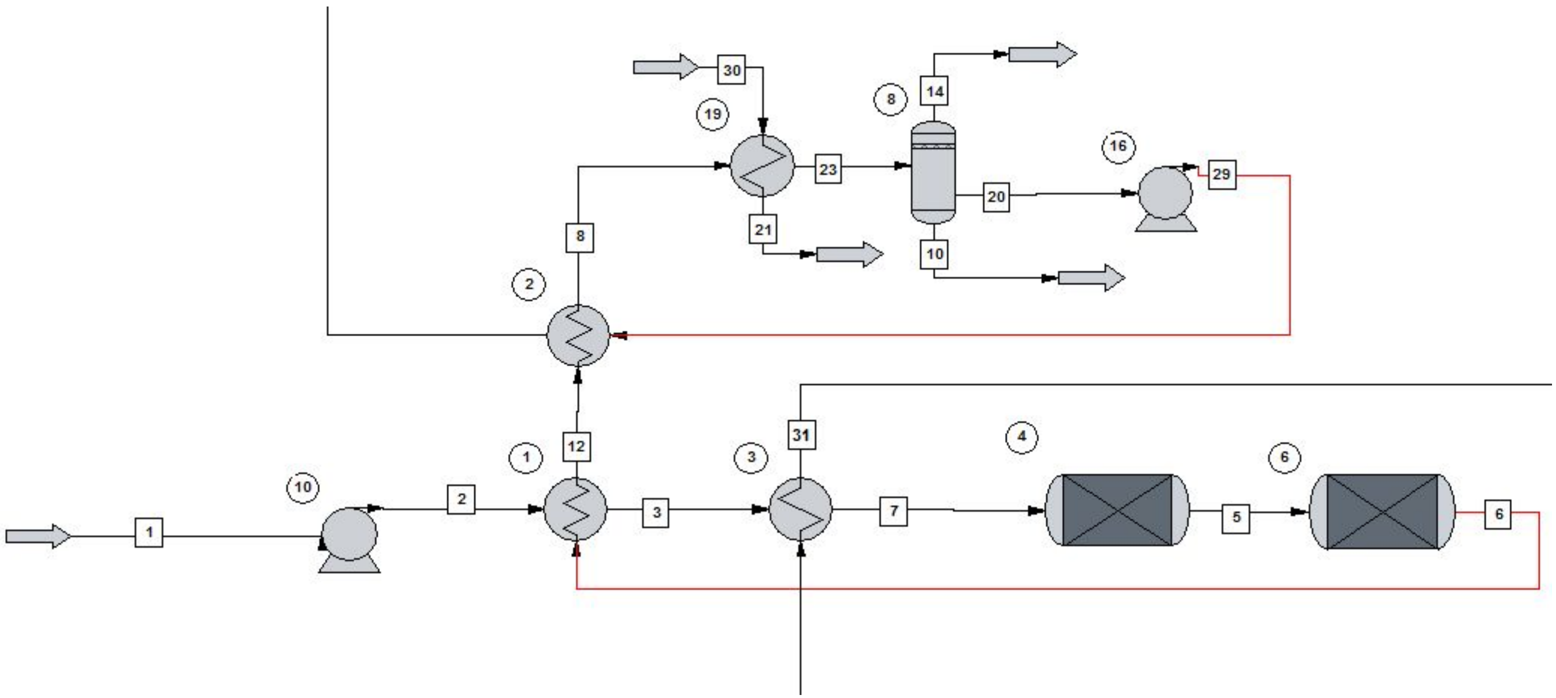
- Single simulation to detect process wide effects of changes
- Pieces result in recycle streams not matching in terms of mass balances
- Sections ran individually for convergence before including recycle streams, then combined until entire simulation converged
- Multiple thermodynamic models used, local models applied where needed; selected based on D*on't Gamble with Physical Properties for Simulation*†

†Carlson, E. *Don't Gamble with Physical Properties for Simulation*. Chemical Engineering Progress. 1996.

Simulation Overview



First Reaction

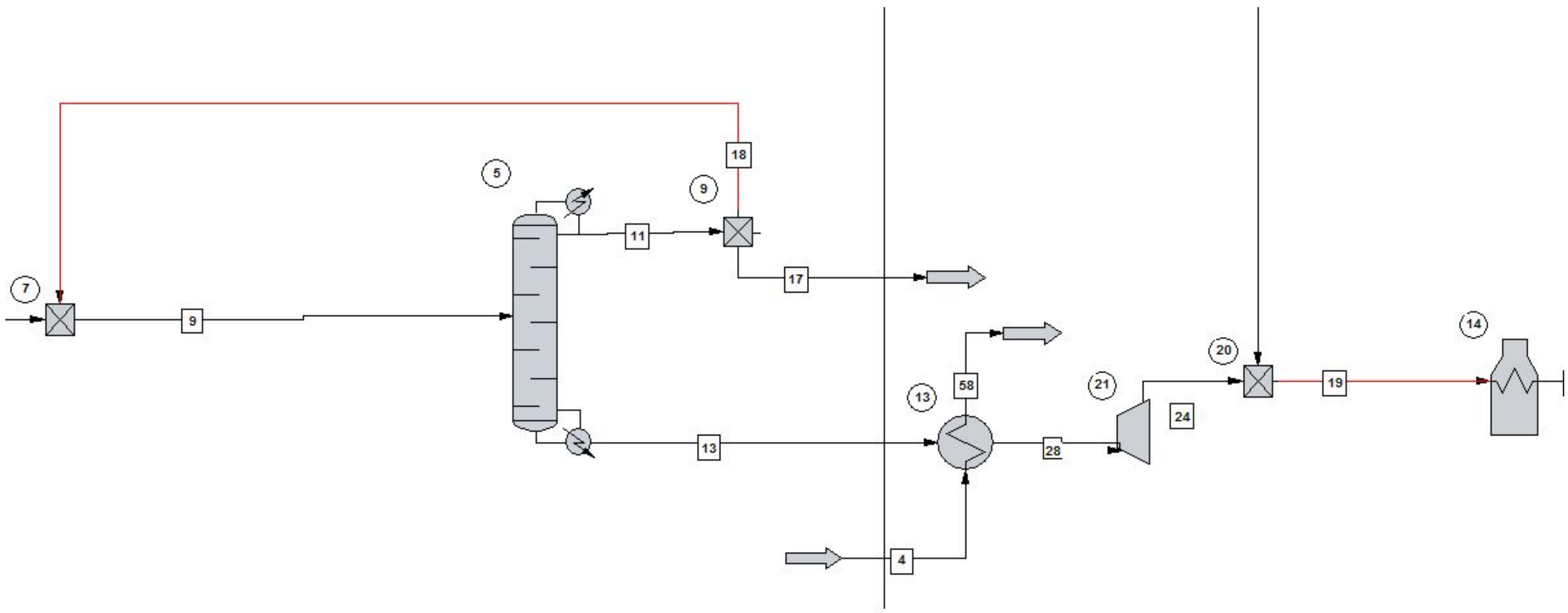


First Reaction

- Done with two reactors as kinetics for butene side product could not be found
- Paper studying kinetics of isobutanol dehydration†
  - Conversion of isobutanol was 99% & Selectivity was 95%
  - Our conversion was 97% with 95% selectivity
- Major side products linear butenes, collectively represented by trans-2-butene

† Dehydration of isobutanol to isobutene in a slurry reactor (Technical Report) | SciTech Connect. http://www.osti.gov/scitech/biblio/171265

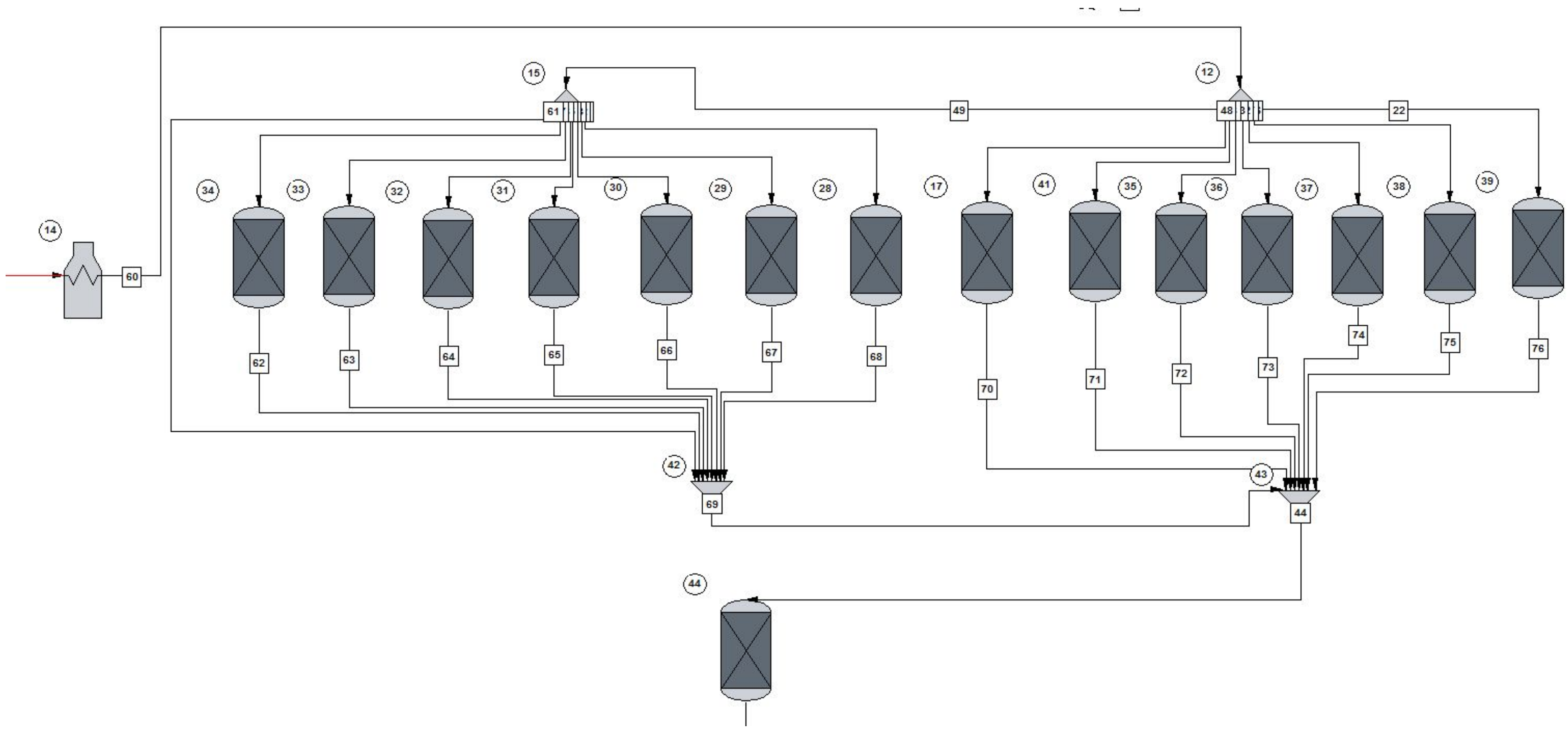
Second Reaction



Second Reaction

- SCDS column with reactive distillation option used with di-isobutylenes collectively represented by 1-di-isobutylene
- Reality, reactions involving formation of tert-butyl alcohol from water affecting rate of oligomerization and selectivity
  - IB + IB □ DIB
  - DIB + IB □ TIB
  - TIB + IB □ TEB
  - IB + H_2O □ TBA
  - TBA □ IB + H_2O
- Couldn't converge for complex kinetic equations, only two reactions specified

Third Reaction



Third Reaction

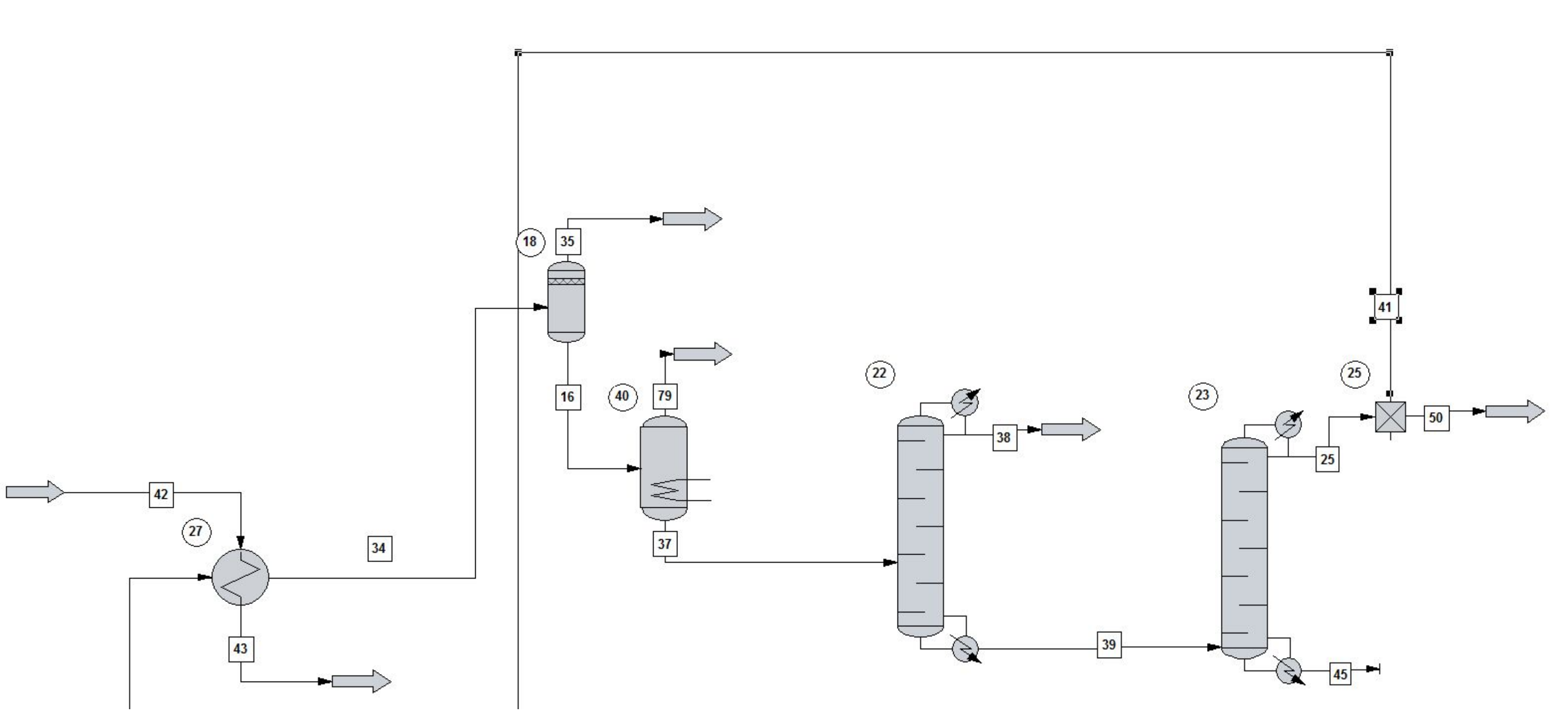
- Direct kinetics of dehydrocyclization for di-isobutylene (2,4,4-Trimethyl-1-Pentene) to p-xylene not available
- Similar kinetics for 2,4,4-Trimethyl-Pentane
- Rate expression simulated in kinetic reactor using user defined VBA expression

$$r = \frac{kP_A - k^{'}P_B P_{H_2}}{\left(\frac{P_A}{P_{H_2}^{0.5}} + \frac{A_1 P_B}{P_{H_2}^{0.5}} + A_2 P_{H_2}^{0.5} + A_3 P_A \left(\frac{A_4}{P_{H2}}\right)^{0.5(n+1)}\right)^{2m}}$$

Third Reaction

- Harsh conditions caused many side products due to cracking, infeasible to simulate all kinetics
- 14 parallel stoichiometric reactors used to form side products before entering main reactor
- Streams from all reactors combined into kinetic reactor with rate law
- After optimizing and sizing kinetic reactor replaced with stoichiometric

Recycle & Side Product Separation



Recycle & Side Product Separation

- Component separator used after flash to remove H_2 & CH_4 as there is virtually none left after flash
- ChemCAD attempts to lower temp of stream below 0°C to condense this small amount of H_2 & CH_4 causing convergence problems and greatly skewing duties

Optimization

- Sensitivity studies ran on equipment comparing variables usually to amount of a component in product stream
  - Amount of desired product out of reactor
  - How much of component left after separation
- Values chosen to get best conversion or separation before there was greatly diminished returns

Economic Analysis: Capital Costs

- Equipment Sizing + CAPCOST
- 2015 CEPCI of 537
- Grass Roots
  - 15 % for contingency cos
  - 3 % for fees
- Land cost of $450,000
- Location: North American Midwest

Grassland biome†

† What is a grassland biome? Web. (accessed May 8, 2016). ask.com

Equipment Sizing: Heat Exchanger

- Shell and tube heat exchanger
- Parameters required to be sized:
  - Area of heat exchanger

http://www.indothermindustries.com/product%209.html

Equipment Sizing: Flash Tank

Parameters required for sizing:

- Density of vapor stream
- Density of liquid stream
- Mass flow rate of vapor stream
- Mass flow rate of liquid stream

Equipment Sizing: Decanter

Parameters required for sizing:

- Density of heavy phase stream
- Density of light phase stream
- Volumetric flow rate of heavy phase stream
- Kinetic viscosity of mixed stream

Equipment Sizing: Distillation Column

<u>Parameters required for sizing:</u>

- Density of heavy phase stream
- Density of light phase stream
- Mass flow rate of vapor stream
- Mass flow rate of liquid stream
- Kinetic viscosity of entering stream
- Number of trays

Equipment Sizing: Reactors

- R-101: multi-tubular packed bed reactor
  - Similar to a shell and tube heat exchanger but has catalyst
  - Heat duty of the reactor (6169 MJ/hr) → minimum heat exchanging area
  - Heat exchanging area
    - Assumption: heat transfer coefficient: 300W/m^{2}K; heating agent: in at 360 °C, out at 330 °C
  - Estimate number of tubes for given radius and length
    - Determine number of tubes for optimized reactor volume then determine surface area of those tubes
- R-102: reactive distillation reactor
  - Sized like distillation column with additional cost of catalyst

Equipment Sizing: Reactor 103

Fixed Bed Column

- Mass of catalyst using → Volume of catalyst
- Assume cylindrical shaped reactor
- Total pressure drop of the reactor is limited to 10% of inlet pressure
- Pressure drop per length calculated (Ergun Equation)
- Pressure drop → Length of the reactor
- Length of the reactor & Radius → volume of the reactor
- Compare volume of the reactor to volume of the catalyst

Economic Analysis: Cost of Manufacturing

- Operator cost
  - $N_{OL} = \left(6.29 + 31.7P^2 + 0.23N_{np}\right)^{0.5}$
    - $P = 0$, $N_{np} = 16$, $N_{OL} = 3.16$
  - 4 active operators per shift
    - 18 operators on payroll
    - Illinois annual median wage for operator is $55,690
- Utility cost – used default costs in CAPCOST
  - Heater utility cost was neglected due to sufficient fuel being provided from hydrocarbons produced in process (1.03×10^5 MJ/h)

Economic Analysis: Cost of Manufacturing

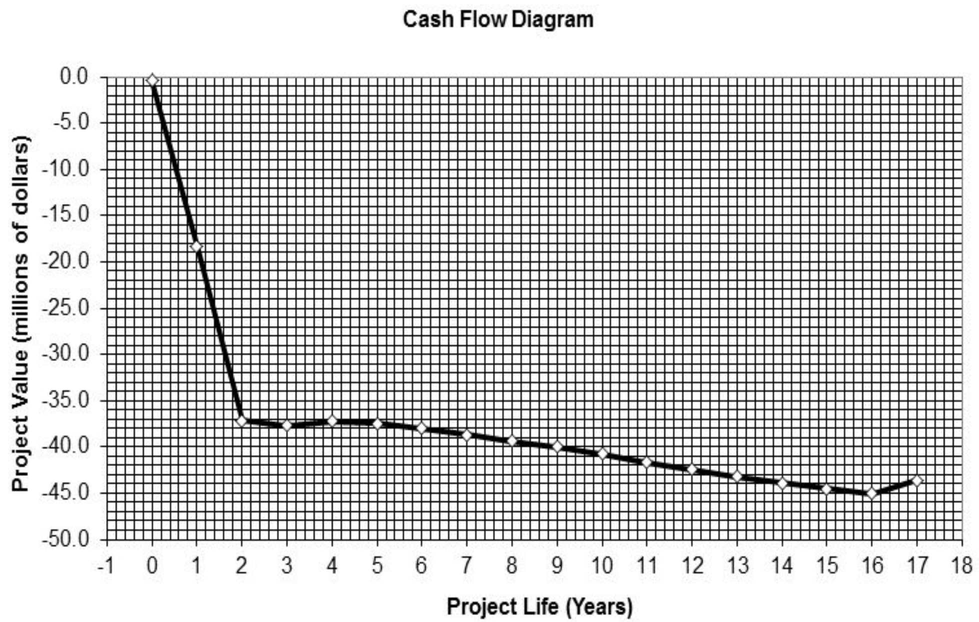
- Chemical Pricing from ICIS, GEVO, etc
  - Catalyst prices used were laboratory prices

Chemical	2006 Price ($/kg)	Projected 2016 Price ($/kg)	Source
Isobutanol	-	1.15-$1.48	GEVO
Terepthalic Acid	0.925	1.066	ICIS
P-xylene	1.43	1.53	ICIS
Ni-Al_2O_3 (1% by mass Ni loading)	-	4272	RiogenInc
γ-alumina	-	15.60	AdvancedMaterials
Platinum on Carbon	-	9890	RiogenInc
Isobutylene	0.70	0.752	ICIS
Di-isobutylene	-	1.25	Zauba

Economic Analysis:Profitability

- Additional Assumptions:
  - 10 % discount rate
  - 18% hurdle rate
  - 7 year MACRS depreciation
  - 8500 hours of operation a year
  - 15 year project lifetime (not including construction)
  - No salvage
  - Assume half of catalyst replaced each year
- Two scenarios evaluated: selling PX or TPA as a product

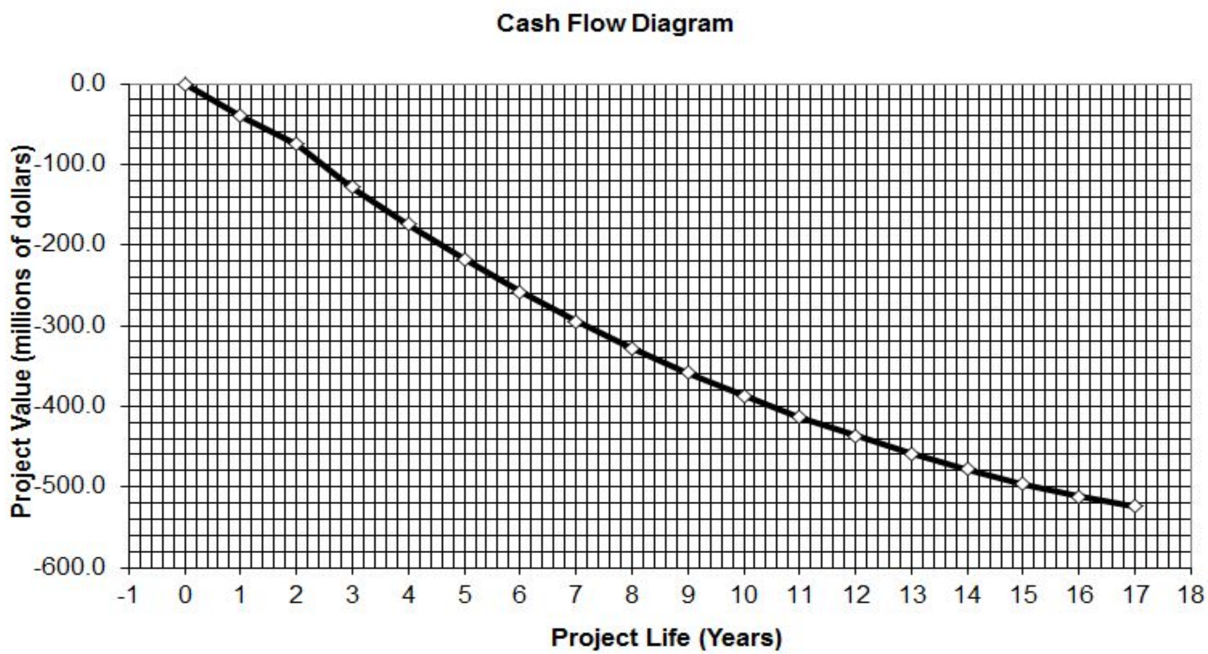
Economic Analysis: Profitability



- Selling PX as Product
  - NPV of -$52.3 million
  - Undefined payback period
- Increase at end is CAPCOST factoring in cost of land and capital costs

Economic Analysis: Profitability

- Selling TPA as product
- Used Capital cost and COM without PX from Team 5 ($61.7 and $89 million respectively)
  - Scaled their costs to the ratio of their PX feed rate and our PX production rate (FCI and COM adjusted to $40 and $58.3 million respectively
  - NPV (
  - Unde



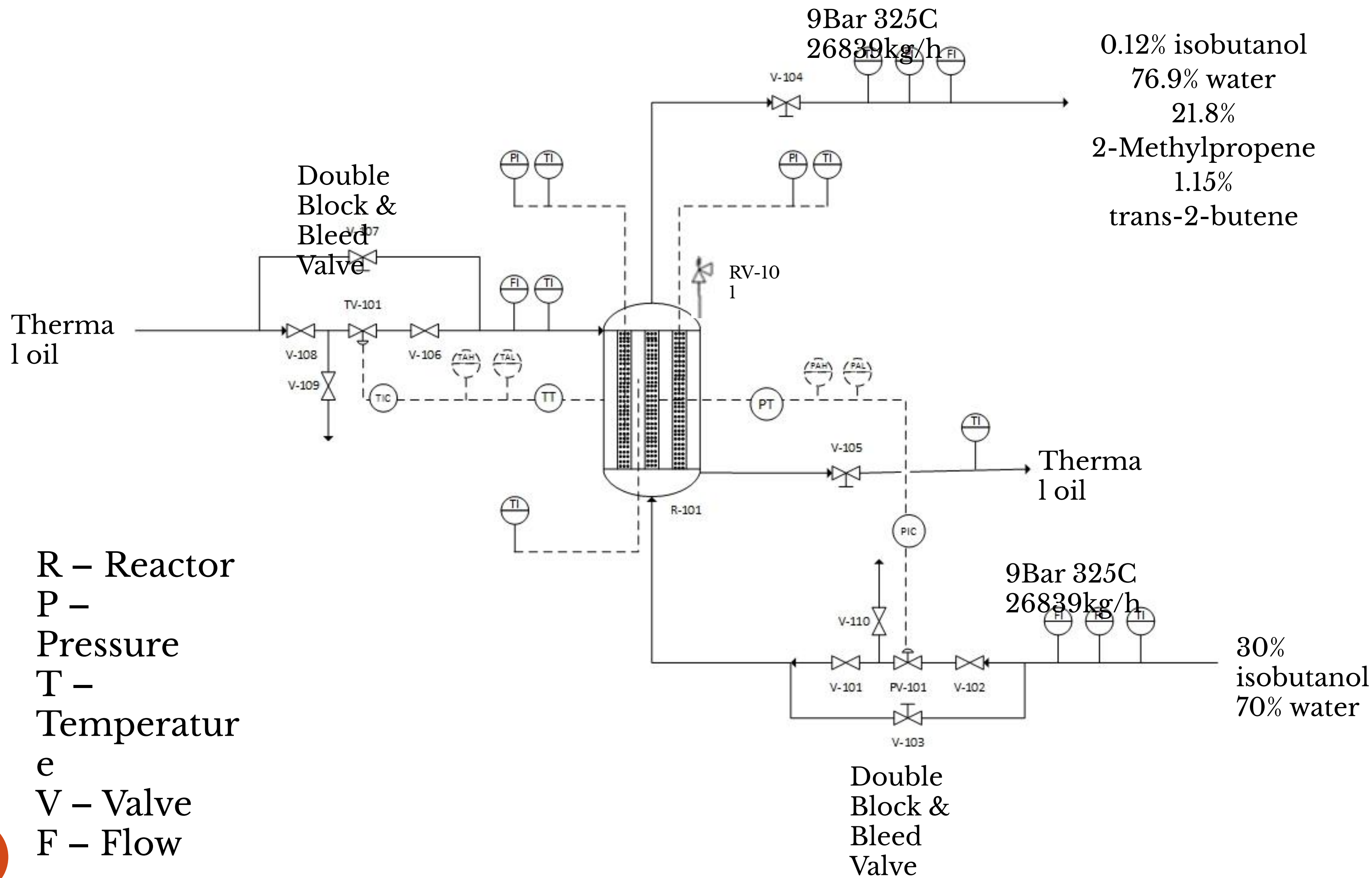
Profit Conditions

- As is, process not generating profit
- Two scenarios investigated, increase in price of p-xylene and the decrease in price of impure isobutanol used
- Prices were changed until the projected value on the cash flow diagram evened out to 0 at end of 17 years
  - Above $1.77 per kg of p-xylene (was $1.53)
  - Below $0.37 per kg of isobutanol (was $0.44)

Environmental, Health, and Safety Concerns

- All reagents are flammable
  - Need to be stored in appropriate, cool, well-ventilated area
- Chemicals not corrosive
- Some chemicals (e.g. p-xylene) are hazardous to aquatic environment
- Waste water must be disposed of appropriately
  - Required compliance with federal, state, and local environmental regulations

Piping and Instrumental Diagram R-101



R – Reactor
P – Pressure
T – Temperature
V – Valve
F – Flow

Sustainability

- Environmentally friendly as raw material generated from bio sources, greatly reduces impact of TPA process
- Image better received by public as being green seen as responsible and is becoming more popular
- Prepared for petroleum raw material running out or politically difficult to obtain
- Becomes profitable as technology to reduce raw material price develops or as current price of oil increases
- Differentiates commodity product by being green

Concluding Remarks***

Supplementary Slides

CAPCOST Default Utility Pricing

	Cost ($/GJ)
Common Utilities	
Electricity (110V - 440V)	16.8
Cooling Water (30°C to 45°C)	0.354
Refrigerated Water (15°C to 25°C)	4.43
Steam from Boilers	
Low Pressure (5 barg, 160°C)	13.28
Medium Pressure (10 barg, 184°C)	14.19
High Pressure (45 barg, 260°C)	17.7
Fuels	
Fuel Oil (no. 2)	14.2
Natural Gas	11.1
Coal (FOB mine mouth)	1.72

	Cost ($/GJ)
Common Utilities	
Thermal Systems	
Moderately High (up to 330°C)	12.33
High (up to 400°C)	13
Very High (up to 600°C)	13.88
Refrigeration	
Moderately Low (5° C)	4.43
Low (-20°C)	7.89
Very low (-50°C)	13.11
	Cost ($/tonne)
Waste Disposal (solid and liquid)	
Non-Hazardous	36
Hazardous	200

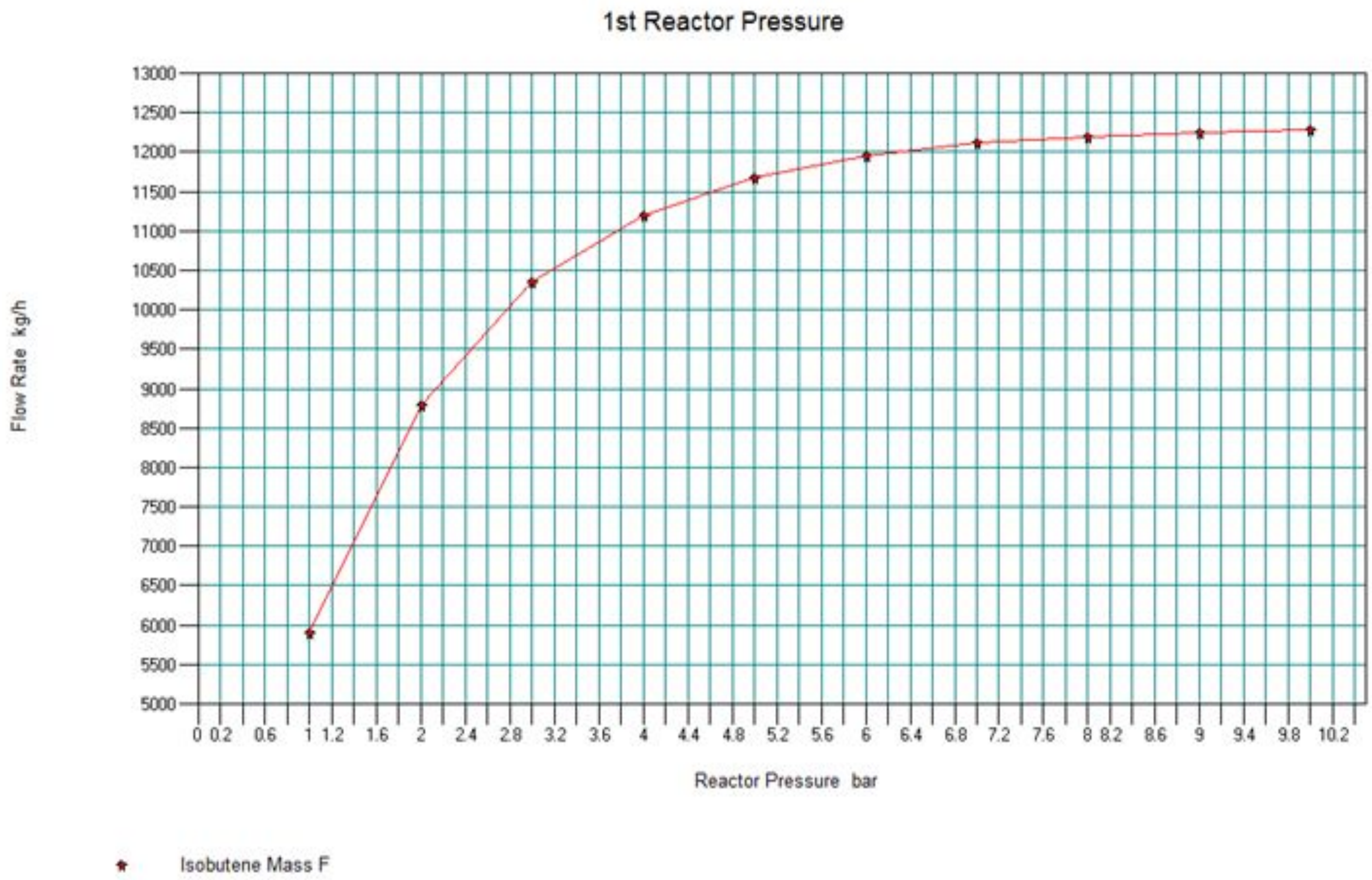
Heat obtained from stream sent to H-101

Chemicals	Heat of Combustion (MJ/kg)	Flow Rate (kg/h)
Isobutanol	33	4.85
P-xylene	40.8	21.7
Toluene	41	4.02
Methane	50	7.35
Propene	48.9	27.2
2-Methyl-1-butene	47.5	4.66
2-Methy-1-pentene	44.8	2.04
1-heptene	47.4	35.2
2-Methyl propene	48.1	535
Trans-2-butene	45.1	149.4
1-Diisobutylene	44	113.4
Hydrogen	142	423.2
2,3-dimethyl-1-hexene	45 *estimated	8.28

$$\text{Heat} = \sum (heat\ of\ combustion * Flow\ Rate)$$

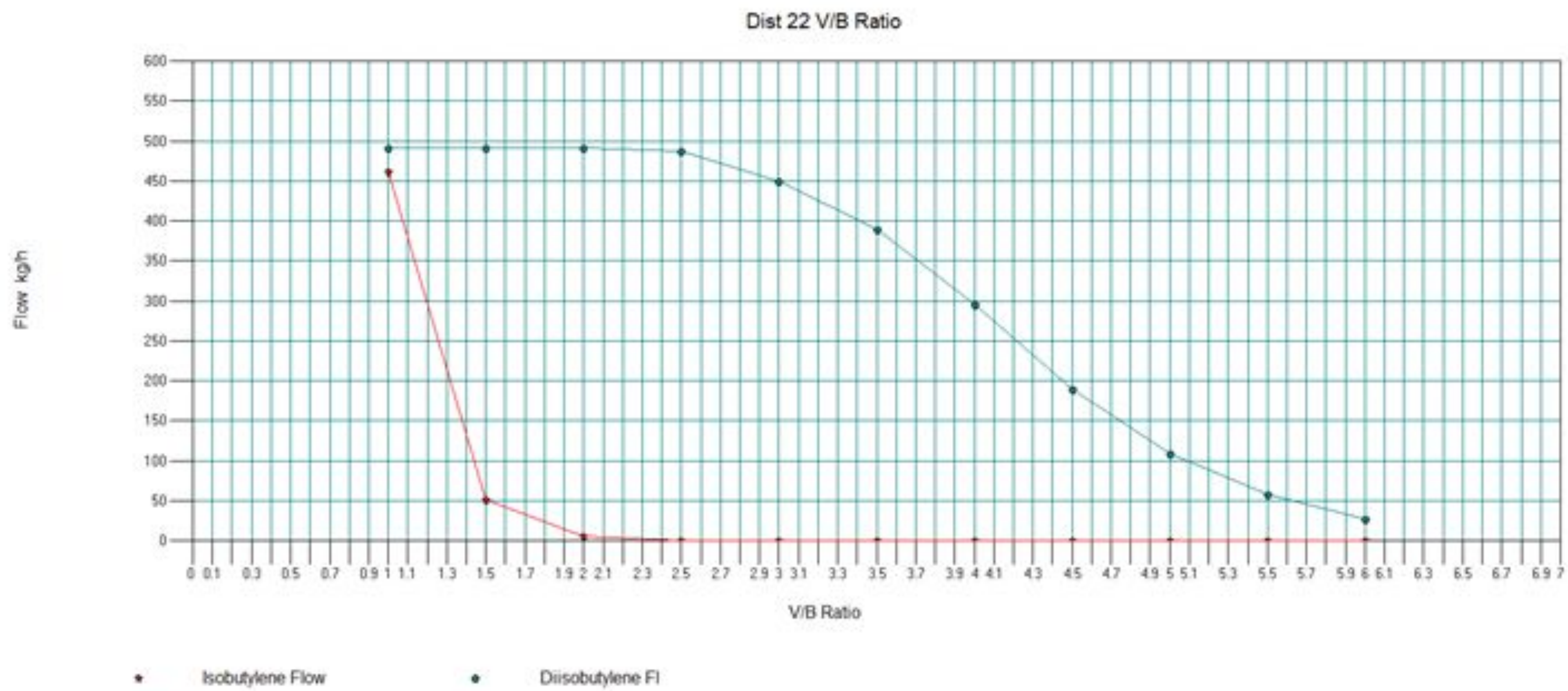
Heat≈1.03*105MJ/h

Sample Optimization: R-101 Pressure



First Reactor plots of volume, temperature, and pressure

Sample Optimization: T-101 V/B Ratio



First distillation column plots of the number of stages, the feed stage location, the reflux ratio, and the V/B ratio compared to the isobutylene and di-isobutylene in the bottoms

Supplementary: Flash tank sizing

- Flash Tank
- $A_c = 5 \times \frac{N_{vapor} MW_{vapor}}{u_{perm}(3600)\rho_{vapor}} = 5 \times \frac{M_{vapor}}{u_{perm}(3600)\rho_{vapor}}$
- $u_{perm} = K_{drum}\sqrt{\frac{\rho_{liquid} - \rho_{vapor}}{\rho_{vapor}}}$ (Souders-Brown Equation)
- $K_{drum} = 1.25e^{A + B\ln F_{LV} + C(\ln F_{LV})^2 + D(\ln F_{LV})^3 + E(\ln F_{LV})^4}$
- $F_{LV} = \frac{M_{liquid}}{M_{vapor}}\sqrt{\frac{\rho_{vapor}}{\rho_{liquid}}}$
- $D_{horizontal} = \sqrt{\frac{4A_c}{\pi}}$
- Rule of thumb: Height/Diameter 3~5

Supplementary: Decanter Sizing

- Decanter
  - $V_{decanter} = \tau_{holding} * v_{heavy}$
  - $\tau_{holding} = \frac{0.1(hr)}{60\ (\frac{hr}{\min})}\ [\frac{\mu}{(\rho_H/\rho_L)-1}]$
  - Rule of thumb: Height/Diameter 3.5~5

Supplementary: Equipment Sizing

- Distillation Column
- $D_c = \sqrt{\frac{4M_{vapor}}{\pi \rho_{vapor} u_f f_{flood} \left(1-\frac{A_d}{A}\right)}}$
- $u_f = k_{1,adjusted} \left(\frac{\rho_{liquid}-\rho_{vapor}}{\rho_{vapor}}\right)^{\frac{1}{2}}$
- $k_{1,adjusted} = k_1 \left[\frac{\sigma}{0.02}\right]^{0.2}$
- $k_1 \propto \frac{M_{liquid}}{M_{vapor}} \sqrt{\frac{\rho_{vapor}}{\rho_{liquid}}}$
- $h_{distillation} = N_{tray} * h_{tray} + h_{top} + h_{liquid} + h_{reboiler} + h_{skirt}$
- $h_{liquid} = \frac{\frac{M_{liquid}}{\rho_{liquid}} \times \frac{holding\ time}{60min}}{\pi \left(\frac{D_c}{2}\right)^2}$
- Rule of Thumb:
  - $f_{flood} = 0.8$
  - $\frac{A_d}{A}$ range from 0.1 to 0.2
  - Height of vapor engagement: larger than 4 ft
  - Height of reboiler return: larger than 3 ft
  - Height of skirt: 15 ft
  - Liquid holding up time: 5 min

Piping and Instrumental Diagram T-103