Glycerol to 1,3-Propanediol Through Anaerobic Fermentation.

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Project Definition

- Plan and design a plant that makes about 50 million lb/year of 1,3-Propanediol (1,3-PDO) through Glycerol fermentation.

Glycerol 1,3-Propanediol

Methods of Production

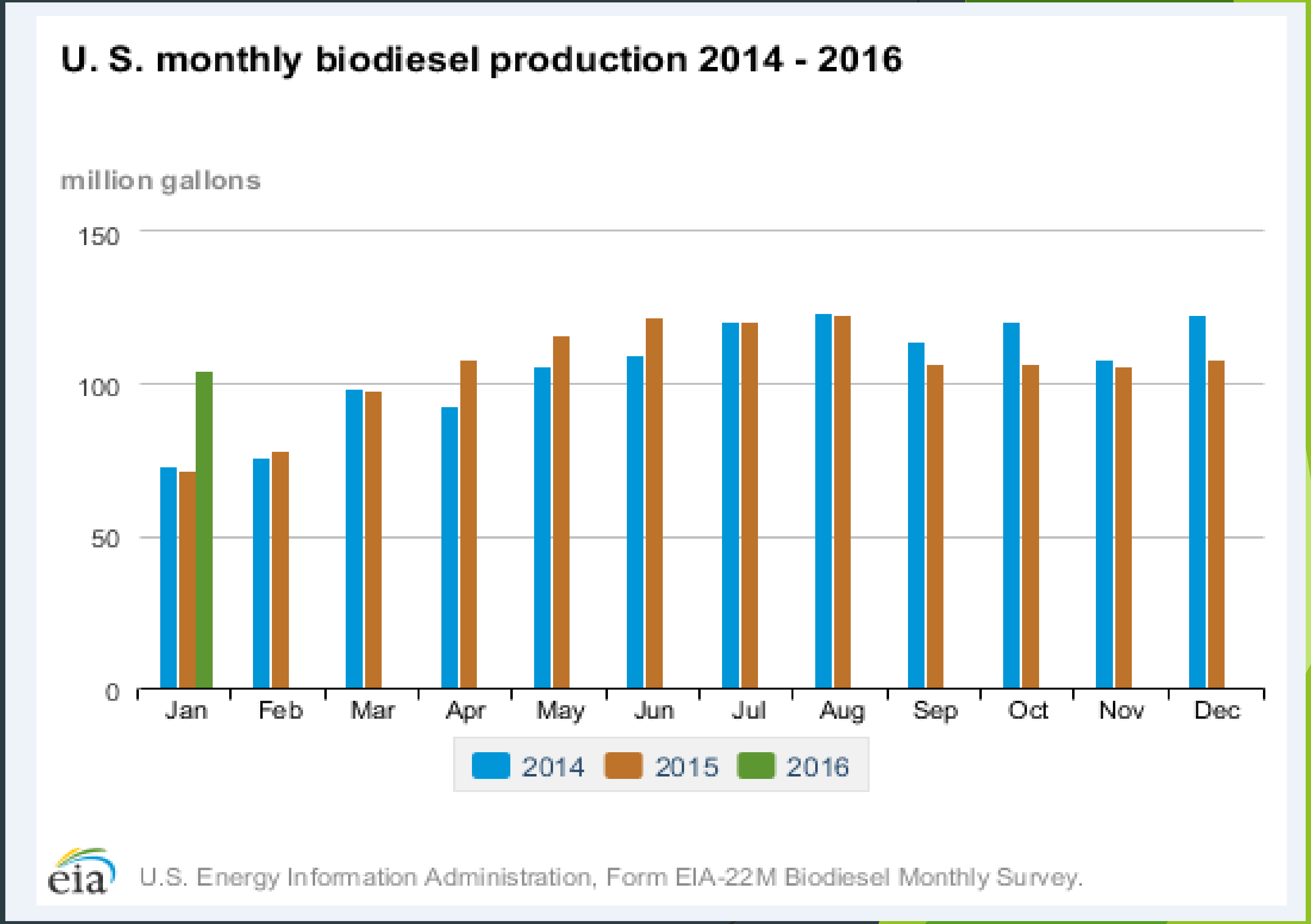
- Petroleum derivative catalyst approach
  - Most common method
  - Intermediates are products of petroleum industry
- Direct catalyst approach
  - Using a Platinum Zirconium catalyst converts Glycerol to 1,3-PDO
- Glucose fermentation
  - Converts Glucose to 1,3-PDO using microorganisms
- Glycerol fermentation
  - Converts Glycerol to 1,3-PDO using microorganisms

Why Glycerol Fermentation

- Avoid intermediate steps
- Avoid using petroleum derivatives
- No expensive catalyst
- Reduce complexity

Contemporary issues

- Our feedstock is a byproduct of biofuel processes
- The amount of biofuels produced in America is rising
- With an increase of biofuels come a increase in byproducts.



http://www.eia.gov/biofuels/biodiesel/production/

Environmental Impact

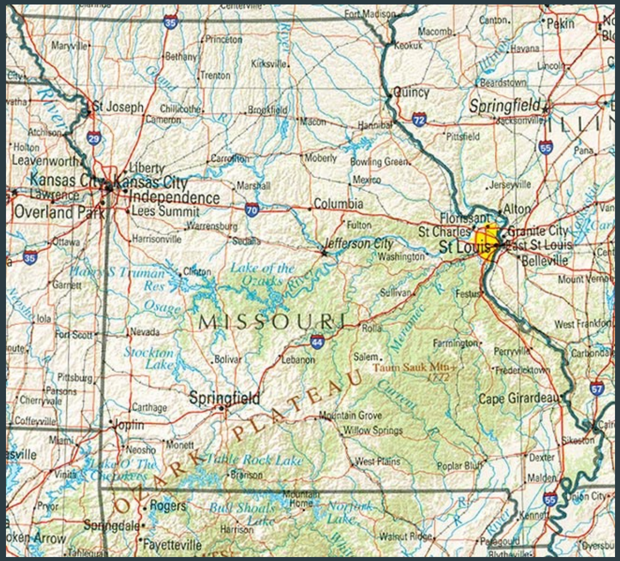
- Hazardous Pollutants
  - Very minimal
- Water
  - 18,000 lb/year
  - Very low concentration of pollutants
- CO, NOx, SOx and VOC
  - Most of these pollutants are produced by our Natural gas boilers
- Greenhouse Gases
  - Produced by natural gas boilers

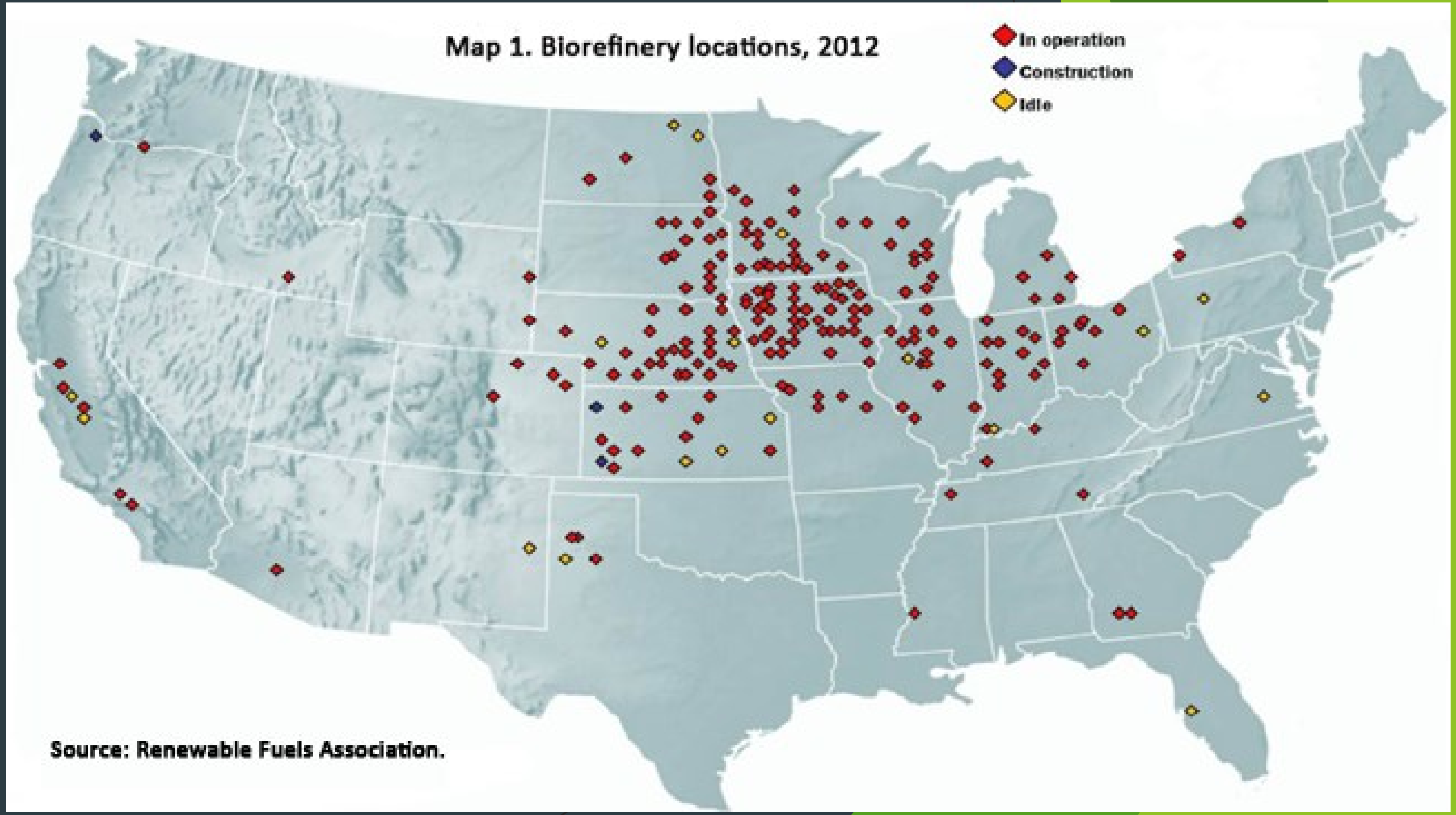
Market

- 1,3-PDO is used in the development of
  - Polytrimethylene Terephthalate
  - Polyurethane
  - Cosmetics
  - Cleaning materials
  - Antifreeze
  - And more

Plant Location

- Midwest of the United States
  - Proximity to biodiesel plants, and therefore access to primary feed (glycerol)
  - Northern Missouri, between Kansas City and St. Joseph
- New Plant Location
  - No one biodiesel plant will produce enough glycerol
  - Take feeds from multiple plants in the area





Process Overview

- Feeds: glycerol, Isobutyl Aldehyde (IBA), nutrients, water
- Product/By-products: 1,3-PDO, acetic acid, formic acid, lactic acid, succinic acid, ethanol, CO_2, H_2, water, biomass
- Sizing
  - Based on a primary feed, glycerol, flowrate of 100 MMlb/yr
- Recycles
  - No recycle needed for glycerol or nutrients
  - Large water recycled needed
  - IBA recycle

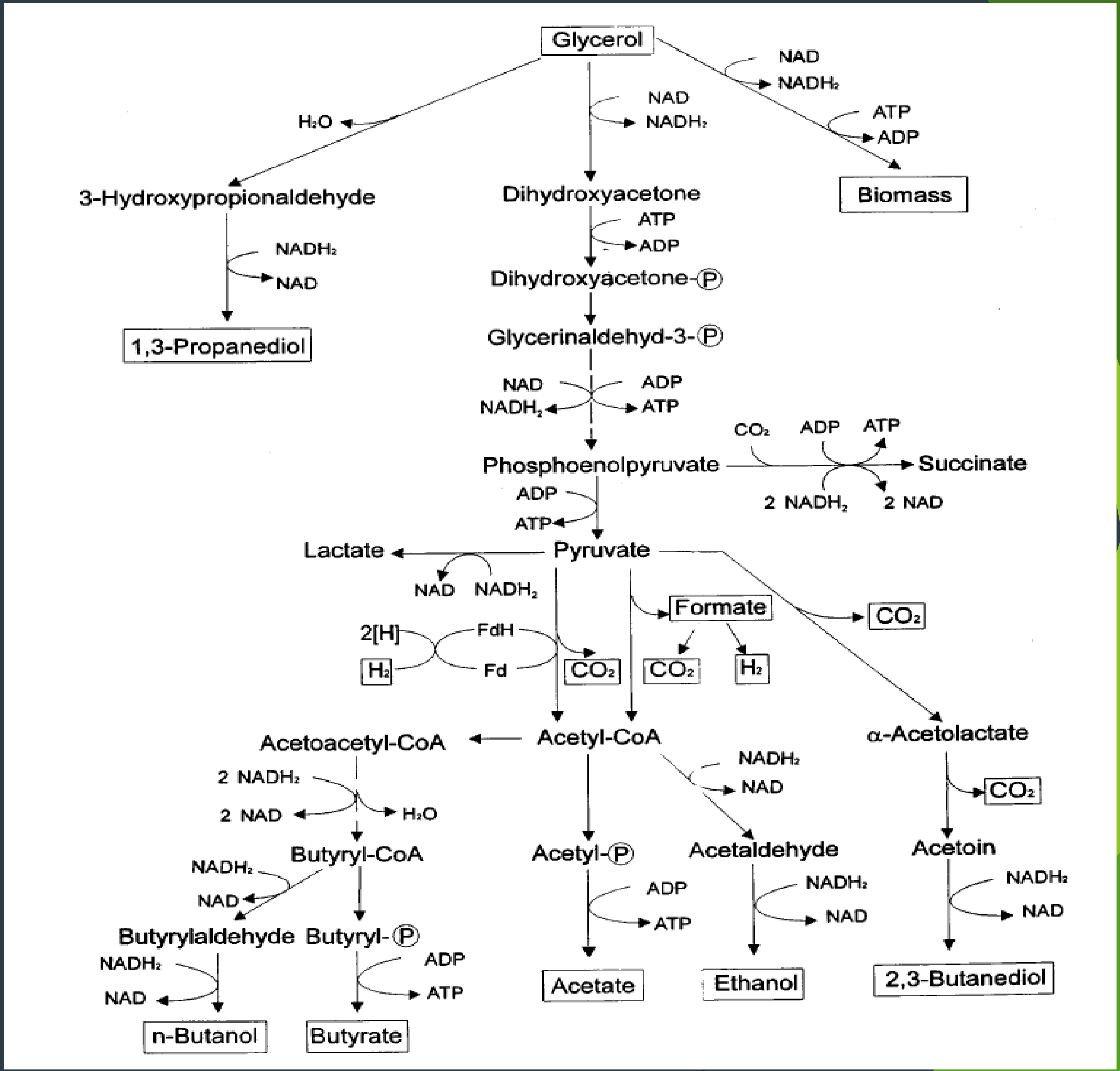
Feed and Product Flowrates (MMlb/yr)

Compound	Feed Flowrate	Product/Purge Flowrate	Product Purity
1,3-PDO	-	51.02	0.999
Glycerol	100.00	-	-
K_2HPO_4	19.08	-	-
KH_2PO_4	14.99	-	-
$(NH_4)_2SO_4$	10.00	-	-
$MgSO_4$-$7H_2O$	2.00	-	-
$CaCl_2$-$2H_2O$	0.50	-	-
$CoCl_2$-$6H_2O$	0.02	-	-
Acetic Acid	-	13.26	0.999
Formic Acid	-	8.82	0.970
Lactic Acid	-	3.68	0.999
Ethanol (Not Sold)	-	0.76	0.815
Succinic Acid	-	2.44	0.999
CO_2	-	6.81	-
H_2	-	0.33	-
Water	1.57	6.67	-
Biomass	-	51.60	-
IBA	2.55	9.46	-

Primary Reaction Overview

- Reactions
  - 1st: Glycerol → 0.65 1,3-PDO + 0.22 Acetic Acid + 0.20 Formic Acid + 0.04 Lactic Acid + 0.03 Ethanol + 0.02 Succinic Acid + 0.15 CO_2 + 0.16 H_2 + 0.33 Water
  - 2nd: Glycerol + 2.0175 K_2HPO_4 + 2.0295 KH_2PO_4 + 1.3941 $(NH_4)_5SO_4$ + 0.1495 $MgSO_4$-$7H_2O$ + 0.06263 $CaCl_2$-$2H_2O$ + 0.001548 $CoCl_2$-$6H_2O$ → Biomass + 1.181048 H_2O
  - Yield selectivity is 95:5 in favor of the first reaction
  - Catalyst equivalent = *K. pneumoniae*
  - 48 hour residence time, achieve 100% conversion of glycerol
- 15 Parallel batch reactors

Biological Pathways



Secondary Separation Reaction Overview

- In order to facilitate a liquid-liquid two phase separation, a reversible acetylation reaction is carried out using IBA, which forms a pseudo-product with 1,3-PDO.
- The reaction is reversed using a reactive distillation tower.
- IBA is separated out and recycled. Some IBA is lost, so there is a minor feed of IBA in order to maintain the necessary amount

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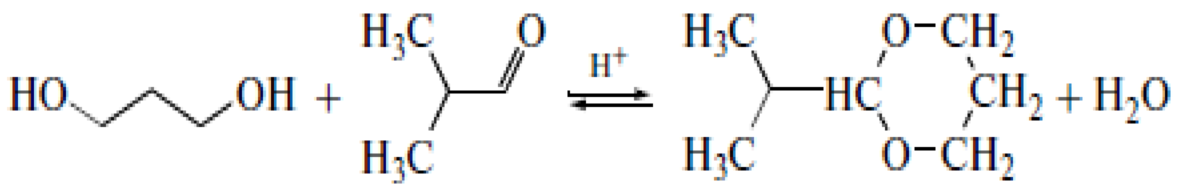
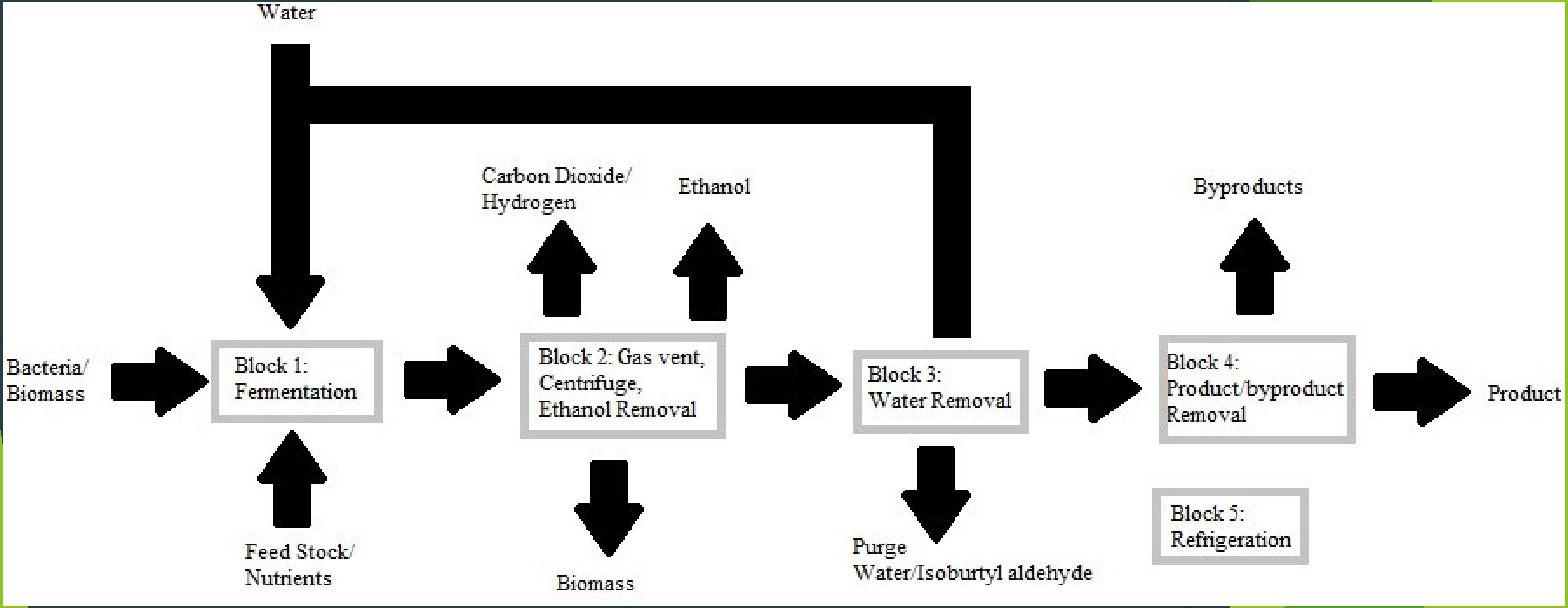
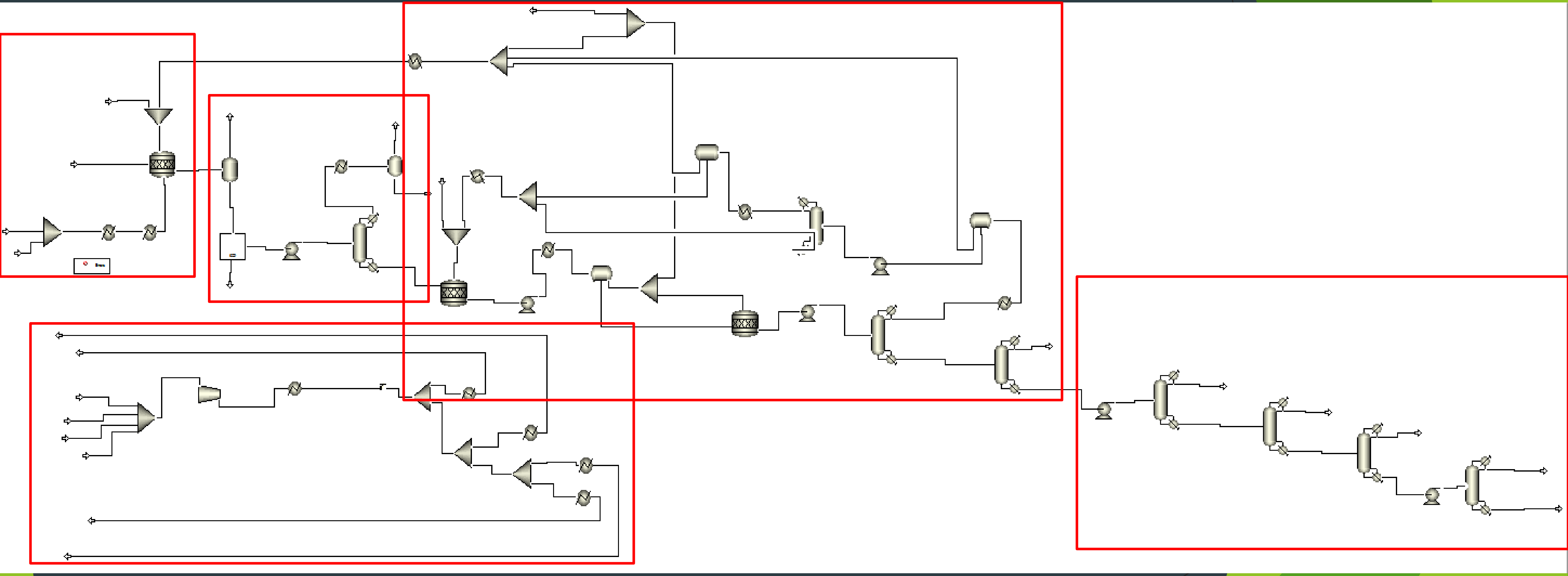


Fig. 1. Acetylation reaction of 1,3-propanediol with isobutyl aldehyde to 2-isopropyl-1,3-dioxane.

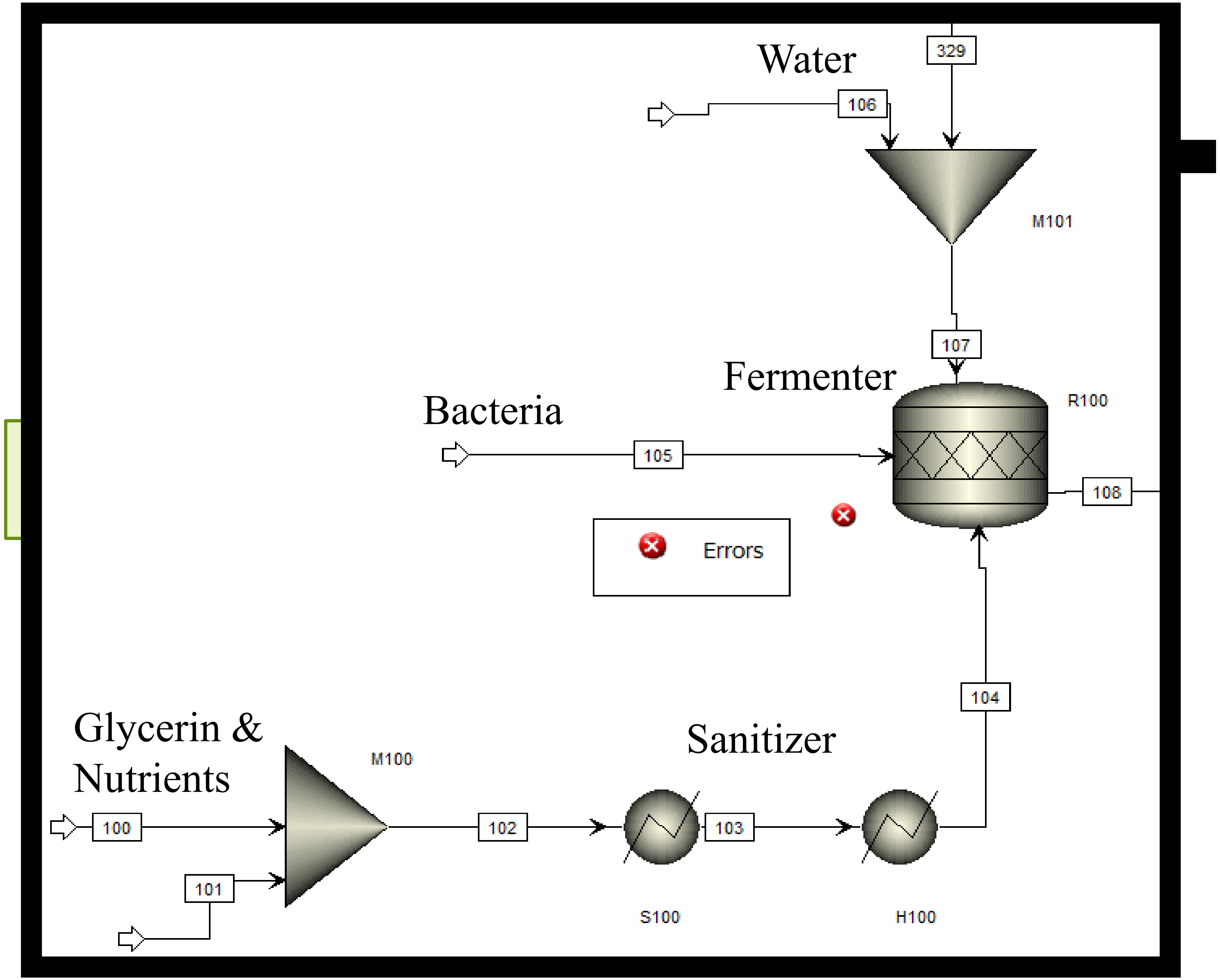


Water
Carbon Dioxide/
Hydrogen
Ethanol
Byproducts
Bacteria/
Biomass
Block 1:
Fermentation
Block 2: Gas vent,
Centrifuge,
Ethanol Removal
Block 3:
Water Removal
Block 4:
Product/byproduct
Removal
Product
Block 5:
Refrigeration
Feed Stock/
Nutrients
Biomass
Purge
Water/Isoburtyl aldehyde

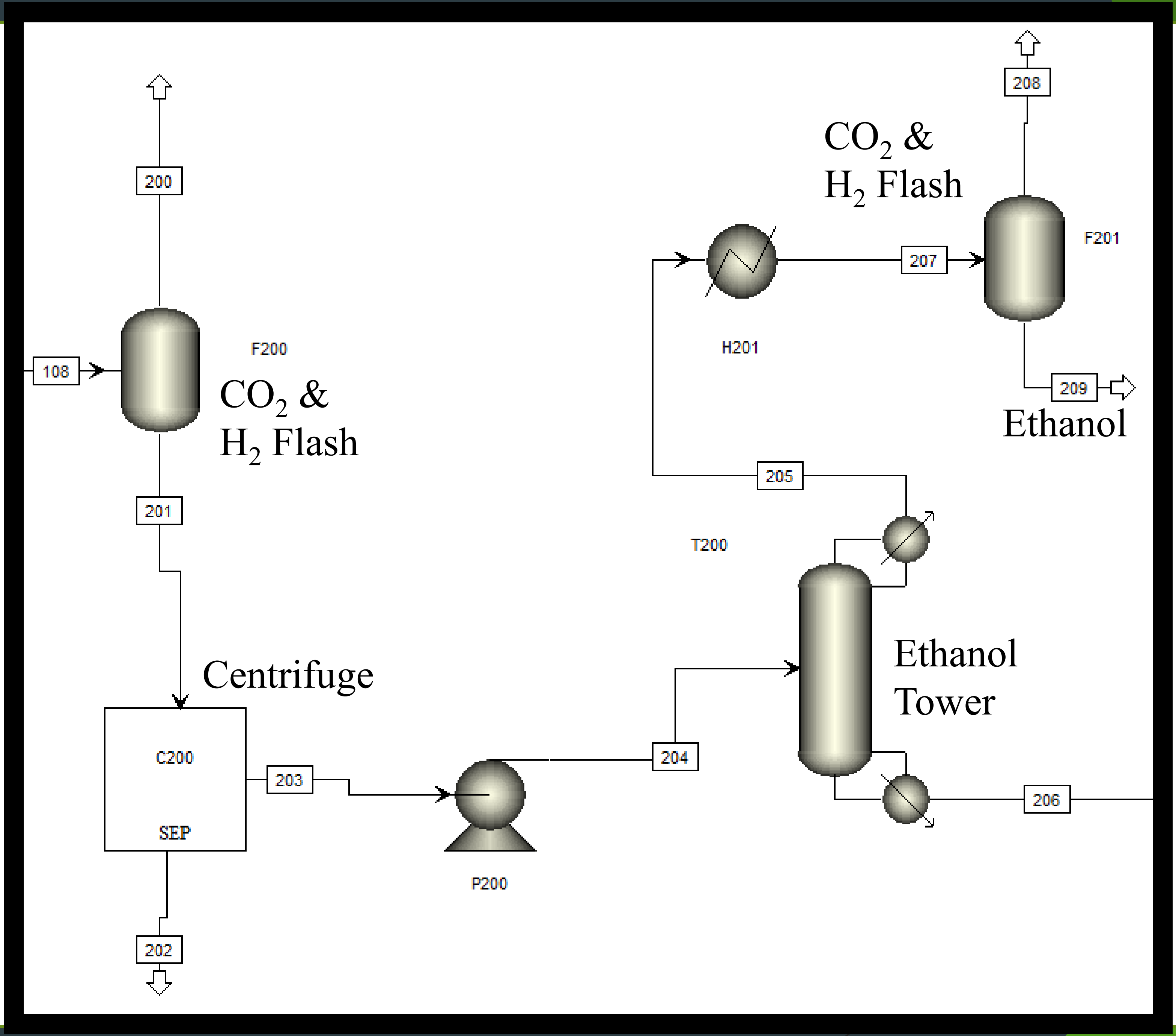


Reaction

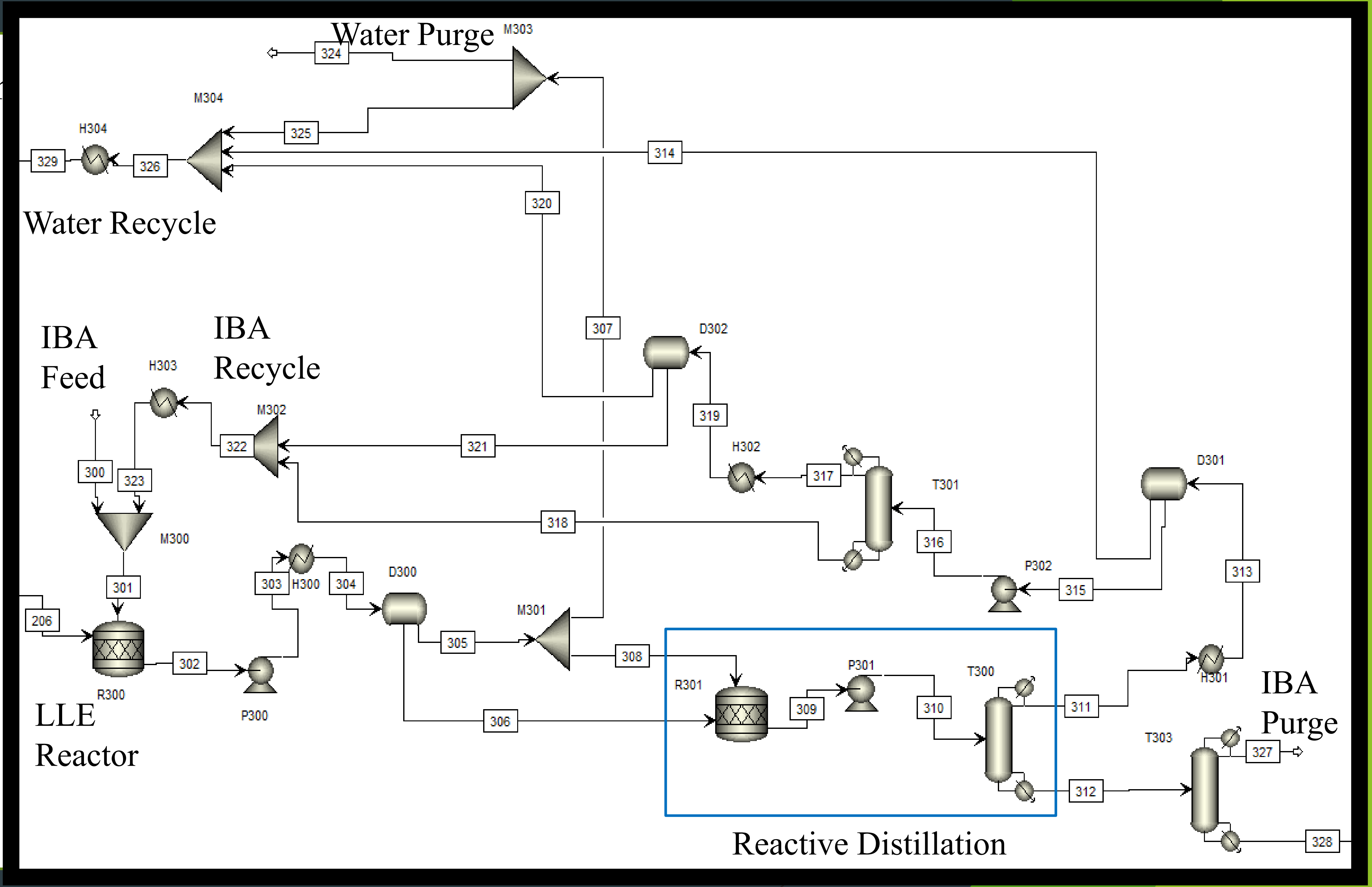
Bacteria



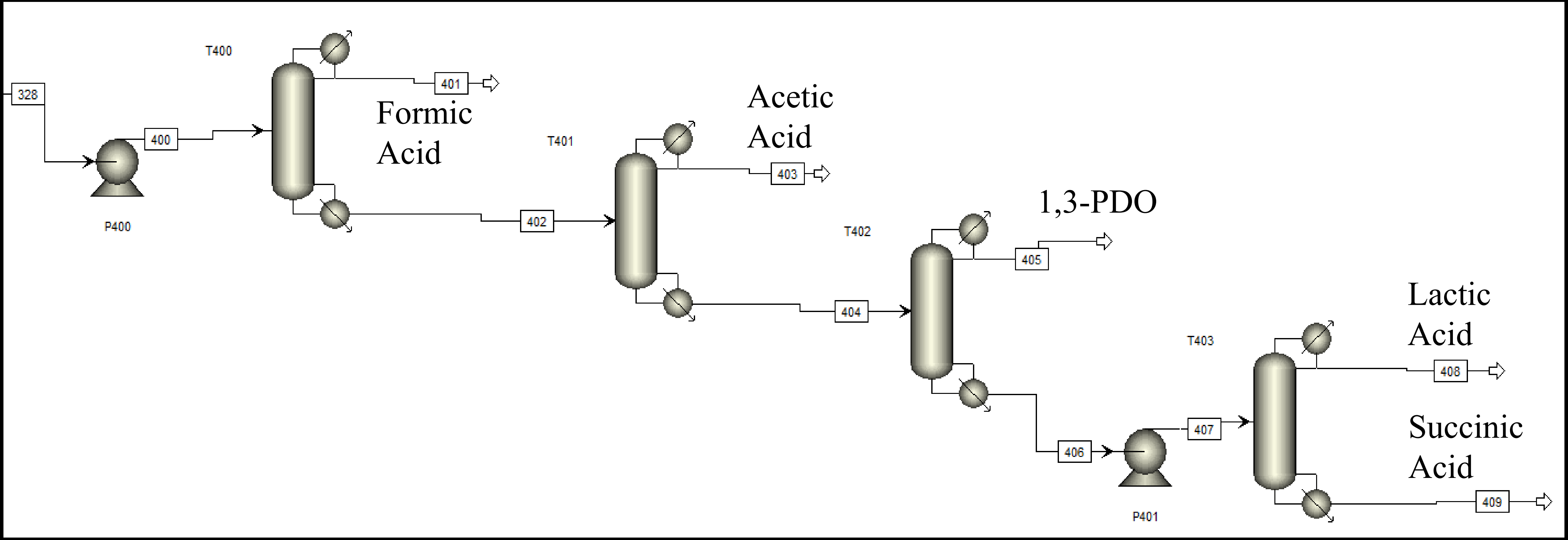
Removal of Biomass CO_2, H_2, and Ethanol



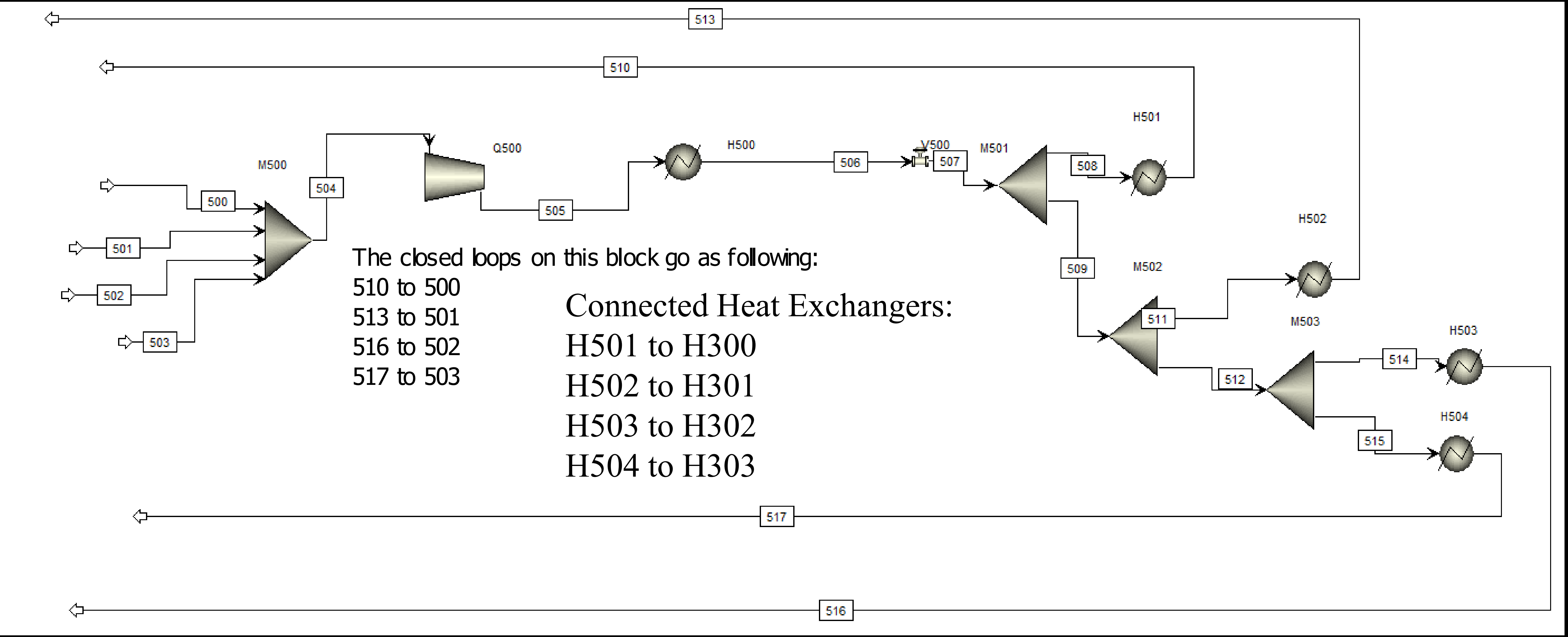
Separation of Water



Separation of Product & Byproducts



Refrigeration Unit (Propane 25psia)



The closed loops on this block go as following:

510 to 500
513 to 501
516 to 502
517 to 503

Connected Heat Exchangers:

H501 to H300
H502 to H301
H503 to H302
H504 to H303

Design Alternatives

- Different Bacteria Species
  - Citrobacter freundii
  - Enterobacter agglomerans
  - Clostridium butyricum
  - → Klebsiella pneumoniae
    - Highest Overall Conversion Rate
- Separation Process
  - Multiple Distillation Towers
    - Too much Energy & Capital
  - → Liquid-Liquid Separation

Equipment Cost Summary

- Heat Exchangers - $20,000
- Compressors -$700,000
- Vessels - $200,000
- Reactors - $2,400,000
- Towers - $2,900,000
- Centrifuge - $1,700,000
- FCI - $13,000,000

Economics

- Product
  - 1,3-PDO - $1.80/lb
- By-Products
  - Acetic Acid - $0.25/lb
  - Formic Acid - $0.19/lb
  - Lactic Acid - $0.50/lb
  - Succinic Acid - $0.90/lb

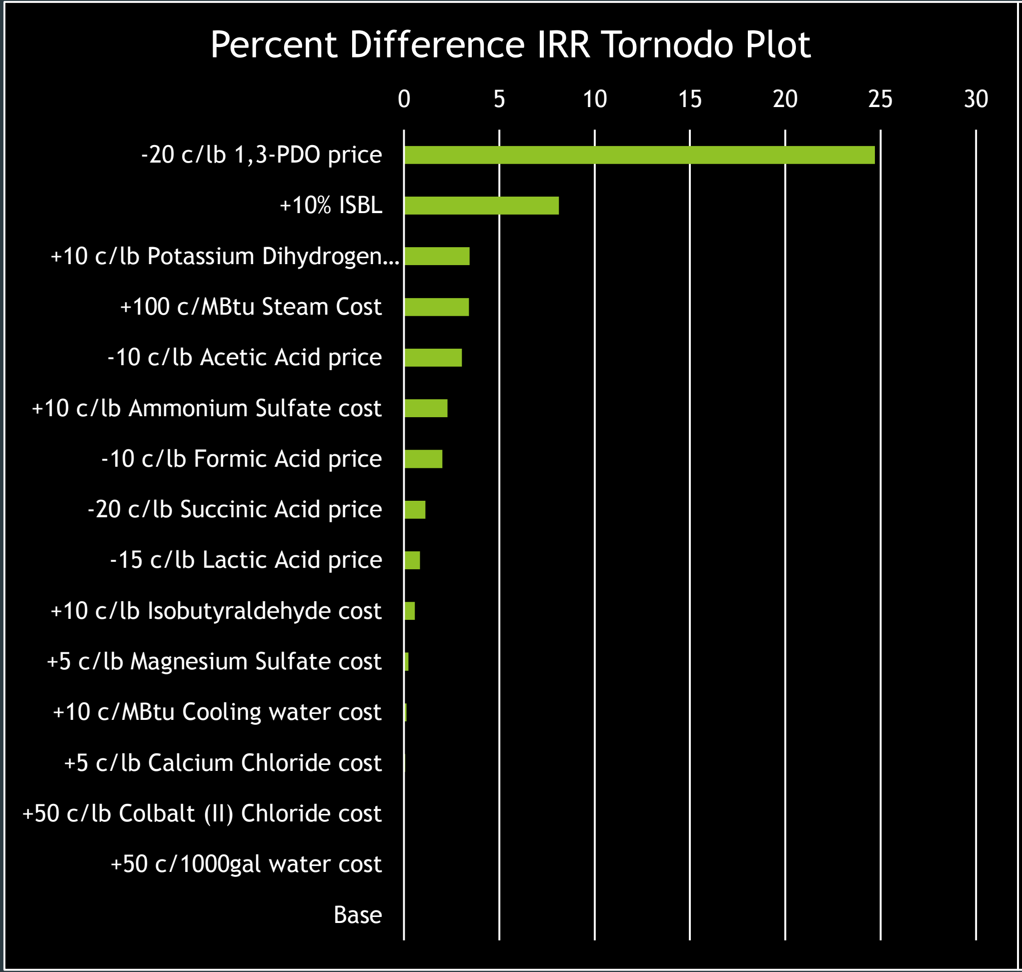
Economics

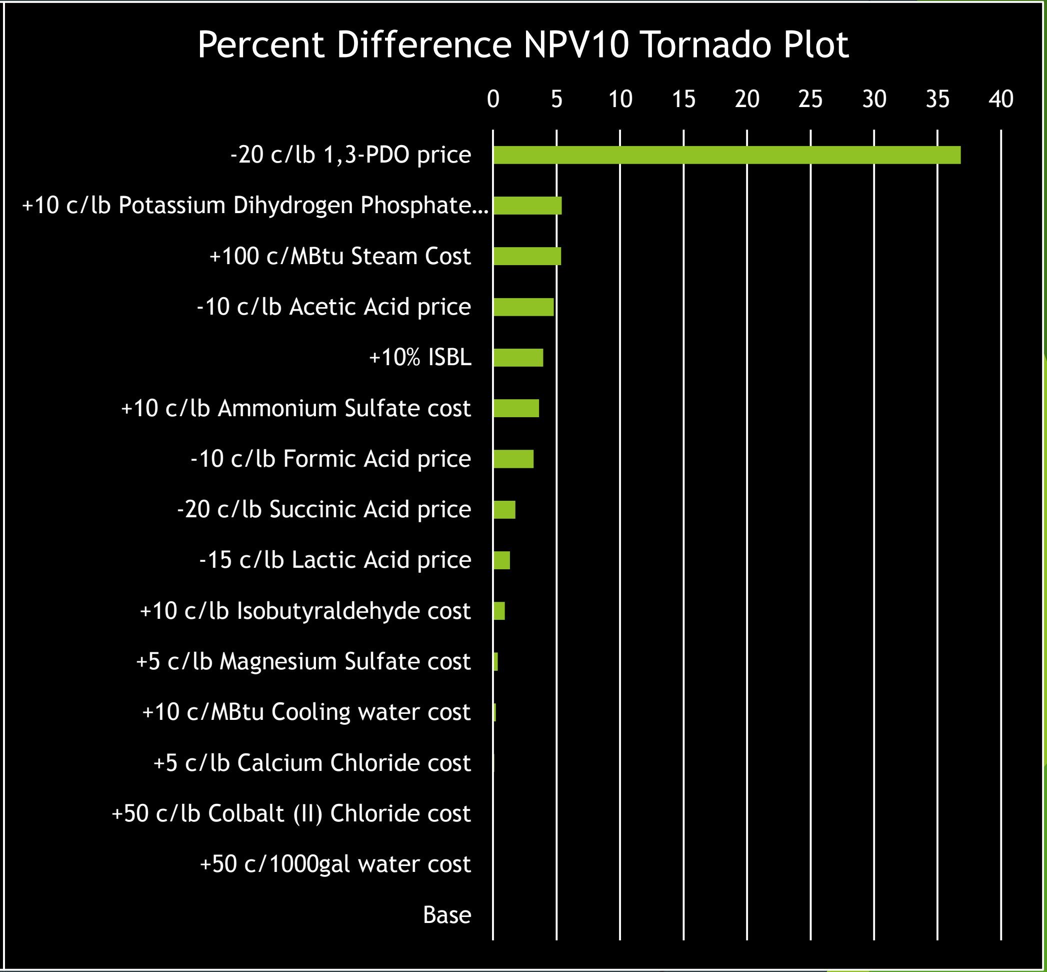
- Feeds
  - Glycerol – $0.31lb
  - Dipotassium Phosphate - $0.45/lb
  - Isobutyl aldehyde – $0.45/lb
  - Water $0.0002/lb
  - Potassium Dihydrogen Phosphate $0.58/lb
  - Ammonium Sulfate $0.13/lb
  - Calcium Chloride $0.08/lb
  - Cobalt (II) Chloride $4.35/lb
  - Magnesium Sulfate (Epsom salt) $0.05/lb

Economics, cont.

- TCI – \$23,000,000
- Revenue – \$93,000,000/yr
- Variable Costs – \$53,000,000/yr
- IRR – 48%
- NPV0 - \$405,000,000
- NPV10 – \$144,000,000

Sensitivities





Work Distribution

- Rex Bagley: Simulation
- Christian McWorkman: Economics
- Spencer Nelson: Physical Properties, Environmental Issues
- Graham Wallace: Reaction, Location

Future Work

- Further investigation of design alternatives
- Independent research
- Pricing Quotes
- Detailed analysis of individual unit operations
- Eventual completion of full scale plant

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Questions