Lignin to Adipic Acid

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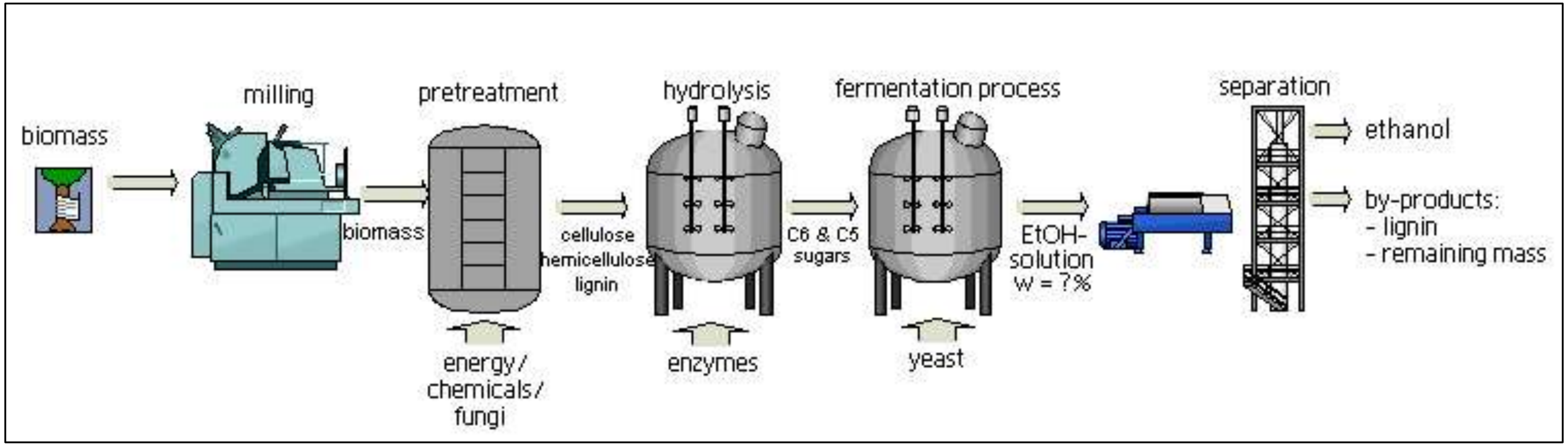
Introduction

- Second-generation biofuels are made from lignocellulosic biomass, found in agricultural residues or waste (corn stover)

- Production of ethanol from lignocellulosic feedstock is expected to increase significantly over the next few years



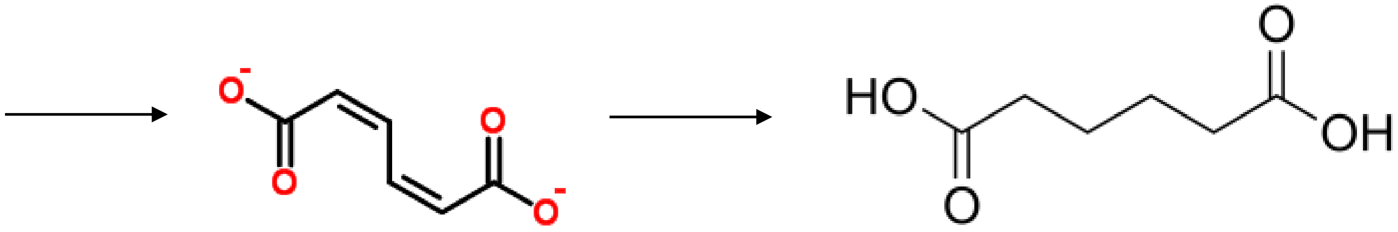
Introduction

- Lignin is a heterogeneous mixture of largely-aromatic polymers
  - Provides plant cell walls their structural strength, recalcitrance to biologic attack

- Economical projection estimates that feedstock lignin would be available at a price of half of its fuel value

- NREL:

Corn stover-derived lignin



Introduction

- NREL has further developed the technology
  - Process limited by contact area per volume of broth
  - Reported value of roughly 20 g/L in 2015 to 160 g/L in 2016
  - Removal of a phenol monooxygenase

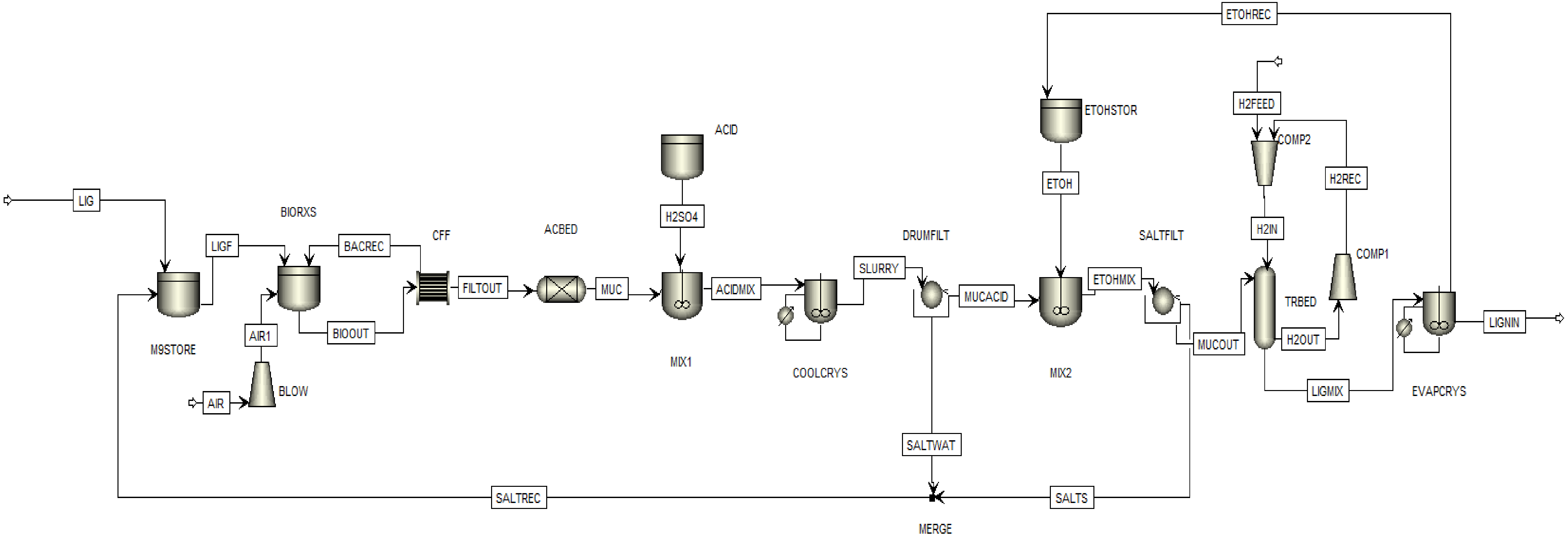
- Alternatively, adipic acid can be synthesized from the conventional petrochemical process
  - High cost of the raw material (cyclohexane)
  - Environmental impact (CO_2 and NOx gas emissions)

Scope

- Whether NREL's process will be a competitor in industry in the near future

- To determine this, an industrial process must be designed based on lab. scale procedures and results
  - Analyze industrial unit operations to determine technical feasibility
  - Analyze economics and sensitivities to determine economic feasibility

Process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COMP2
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ACID
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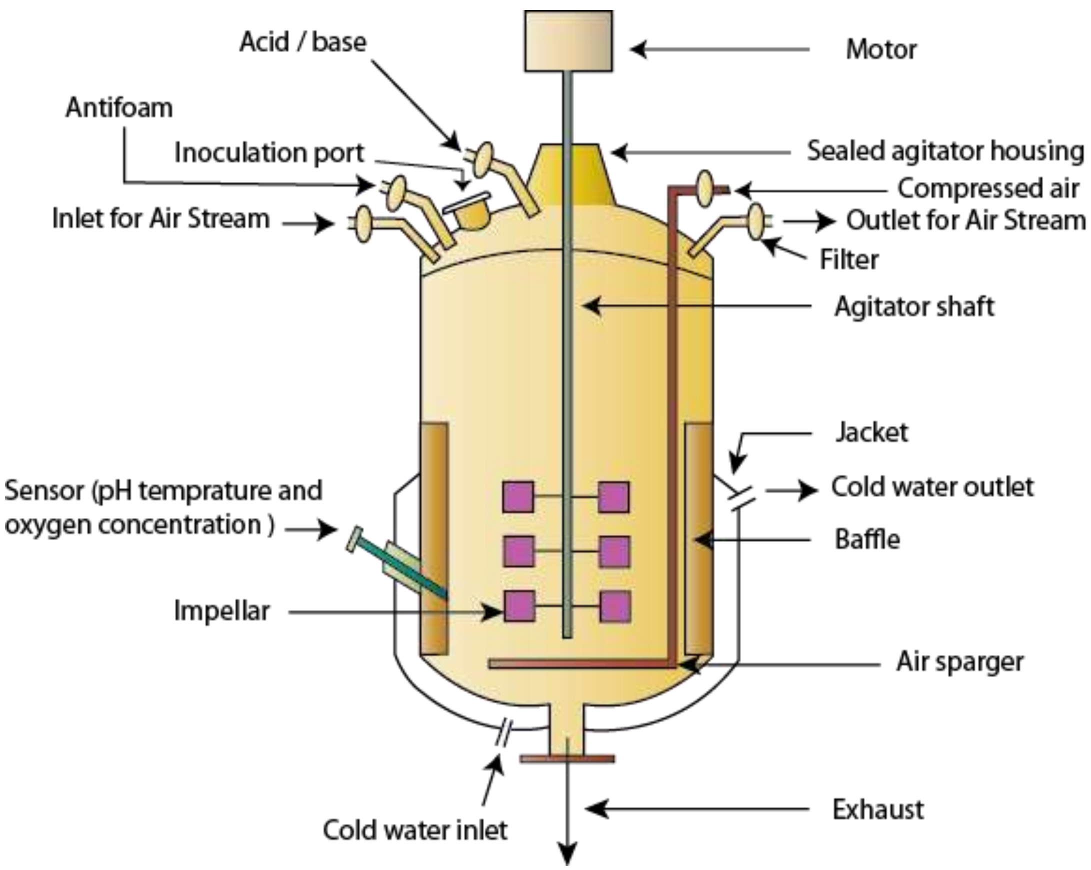
BACREC
CFF
ACBED
DRUMFILT
SALTFILT
SLURRY
ETOHMIX
TRBED
FILTOUT
MUC
ACIDMIX
MUCACID
LIGNIN
AIR1
BIOOUT
MUCOUT
H2OUT
M9STORE
MIX1
COOLCRYS
MIX2
LIGMIX
EVAPCRYS
AIR
BLOW
SALTWAT
SALTREC
SALTS
MERGE

Process – Bioreactor

- Relies on the engineered bacteria (160 g/L), in an M9 minimal medium to mix with lignin and react for 72 hrs
- Temperature 30 ^{o}C
- pH 7
- Filtered air will be constantly fed
- Impeller to provide suspension with baffles to prevent vortices



Process – Bioreactor

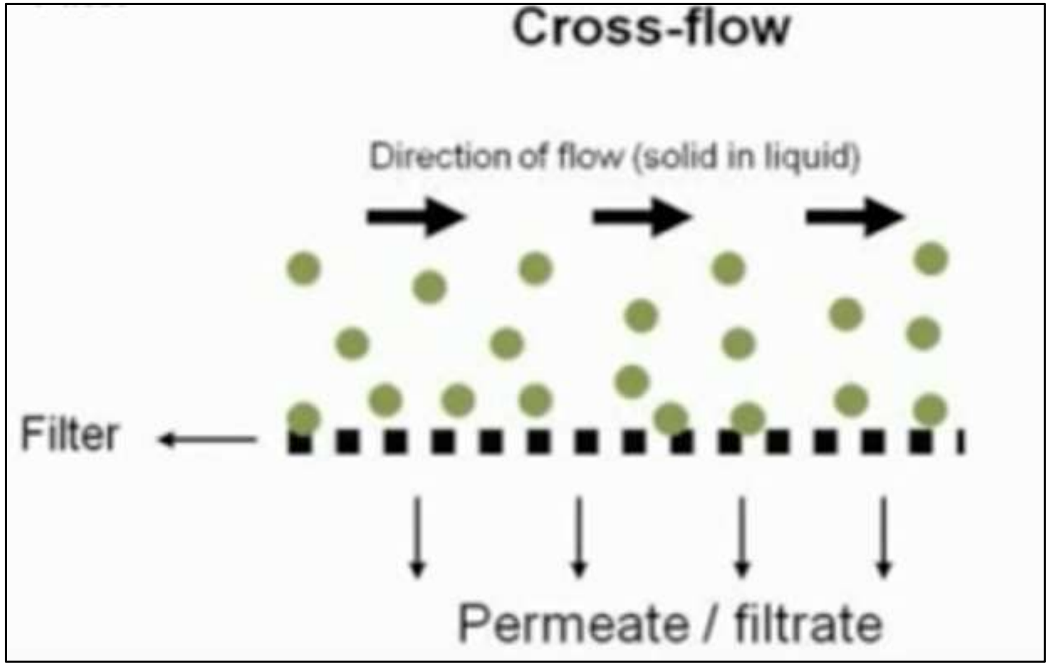
- The current design is based on three batch bioreactors, all identical, with operating schedules staggered (24 hours)

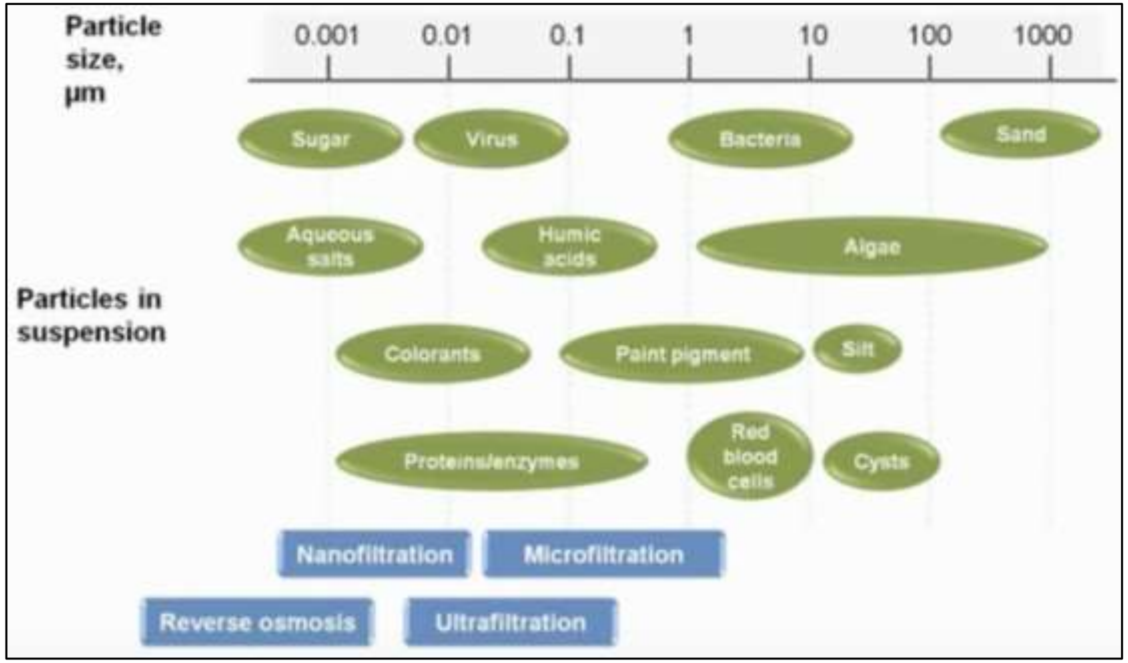
- Allowed for the sizing of the rest of the units for processing 21.4 ton of lignin every day, using a continuous design, based on each unit operation time requirements

- Another important consideration is the sterilization of lignin to ensure no contamination in the bioreactor

Process – Cross-flow Filter

- Accomplishes the separation of the engineered bacteria from solution by filtering parallel to the direction of the flow
- Assumes no significant amount of solids after biological conversion





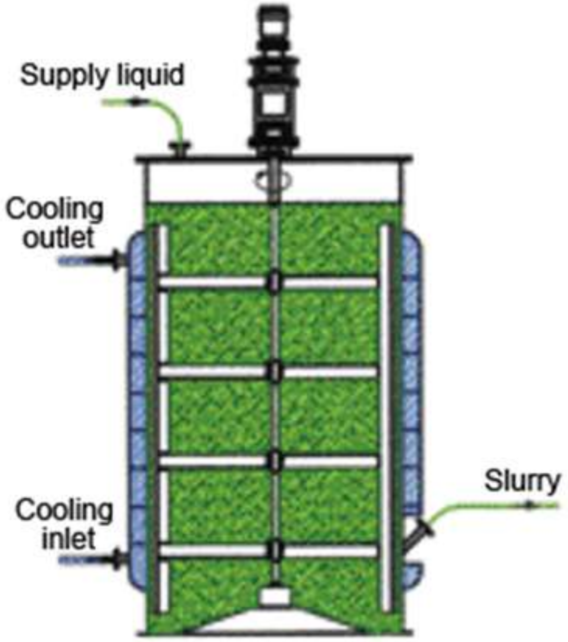
Process – Activated Carbon Packed Bed

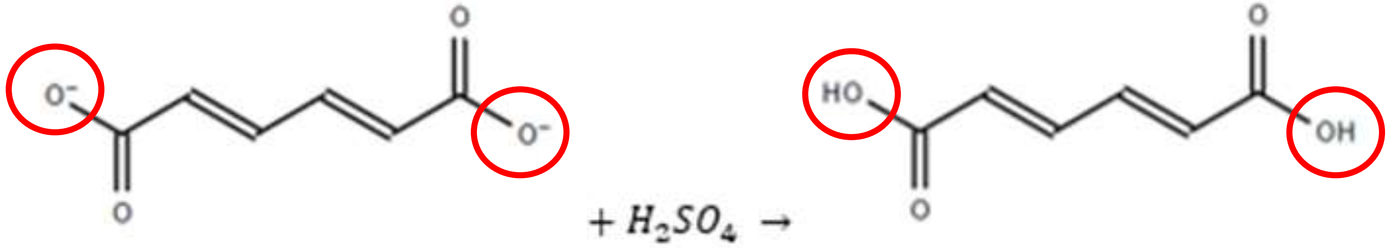
- Adsorption of unwanted aromatics present in muconate stream
- 10 g activated carbon per L of bioreactor effluent
- Residence time of 1 hour, negligible muconate loss
- Upon exhaustion, carbon will be sent offsite for regeneration
  - Determined with UV absorption sensors
  - Rotation of two activated carbon packed bed columns to keep continuous
  - May be more economical to regenerate carbon onsite

Process – Acid Unit Operations

- Mixing Tank
  - pH 2
  - Cooling jacket

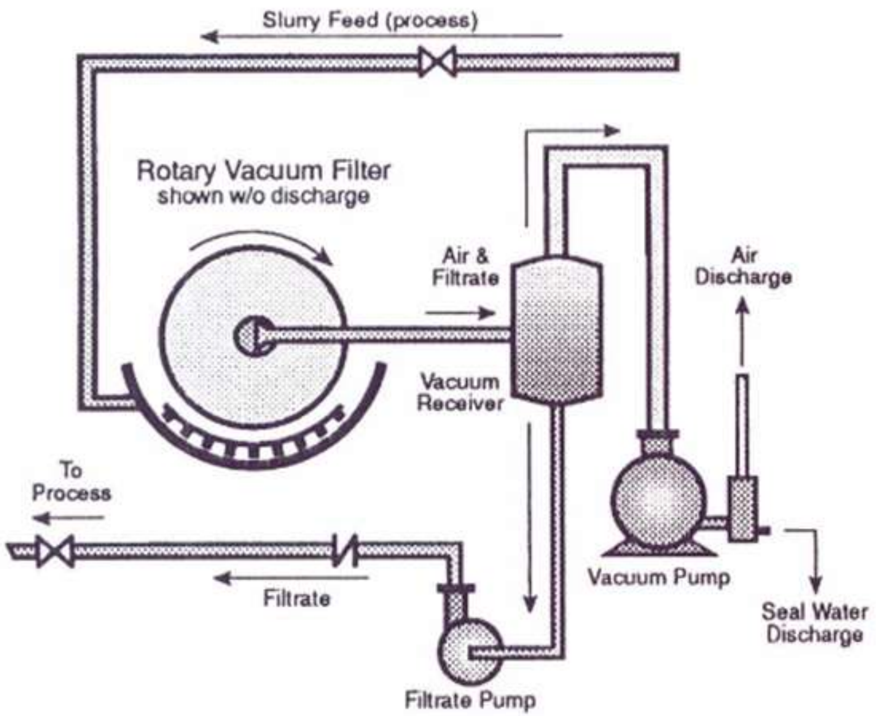
- Scraping, cooling crystallizer
  - 5°C





Process – Acid Unit Operations

- Rotary Drum Vacuum Filter
  - Muconic acid crystals
    - Purity: 97.71 $\pm$ 0.01%
  - Waste "salt" water stream
    - Assume 100% recycle
    - Regeneration to M9 salts

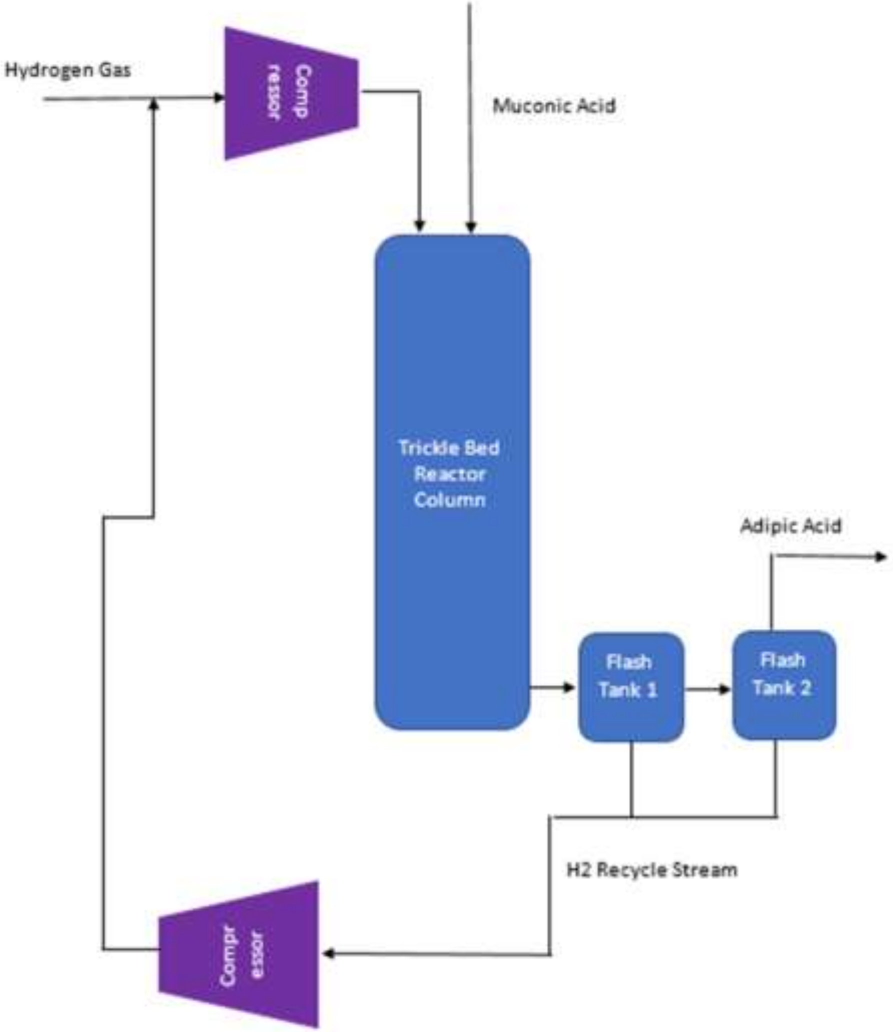


Process – CSTR, Filter, EtOH Storage

- Muconic acid and salts solution mixed in ethanol in a continuous stirred tank reactor
- Muconic acid will dissolve in EtOH, salts will not
  - 99.8% purity required for adipic acid
- Solution will then be separated in a mechanical filter

Process – Trickle Bed Reactor

- Converts muconic acid into adipic acid
- Two hydrogen compressors
  - Feed and recycle
- Filled with Pd/C catalyst
- 24 bar and 24°C



Process – Evaporation Crystallizer

- Final unit operation to separate adipic acid from ethanol

- Utilizes large difference in boiling points to achieve separation
  - BP ethanol = 78 degrees C
  - BP adipic acid = 265 degrees C
  - Ethanol can be evaporated with no effect on adipic acid crystalline product

- Ethanol will be recycled assuming a 1% loss per year

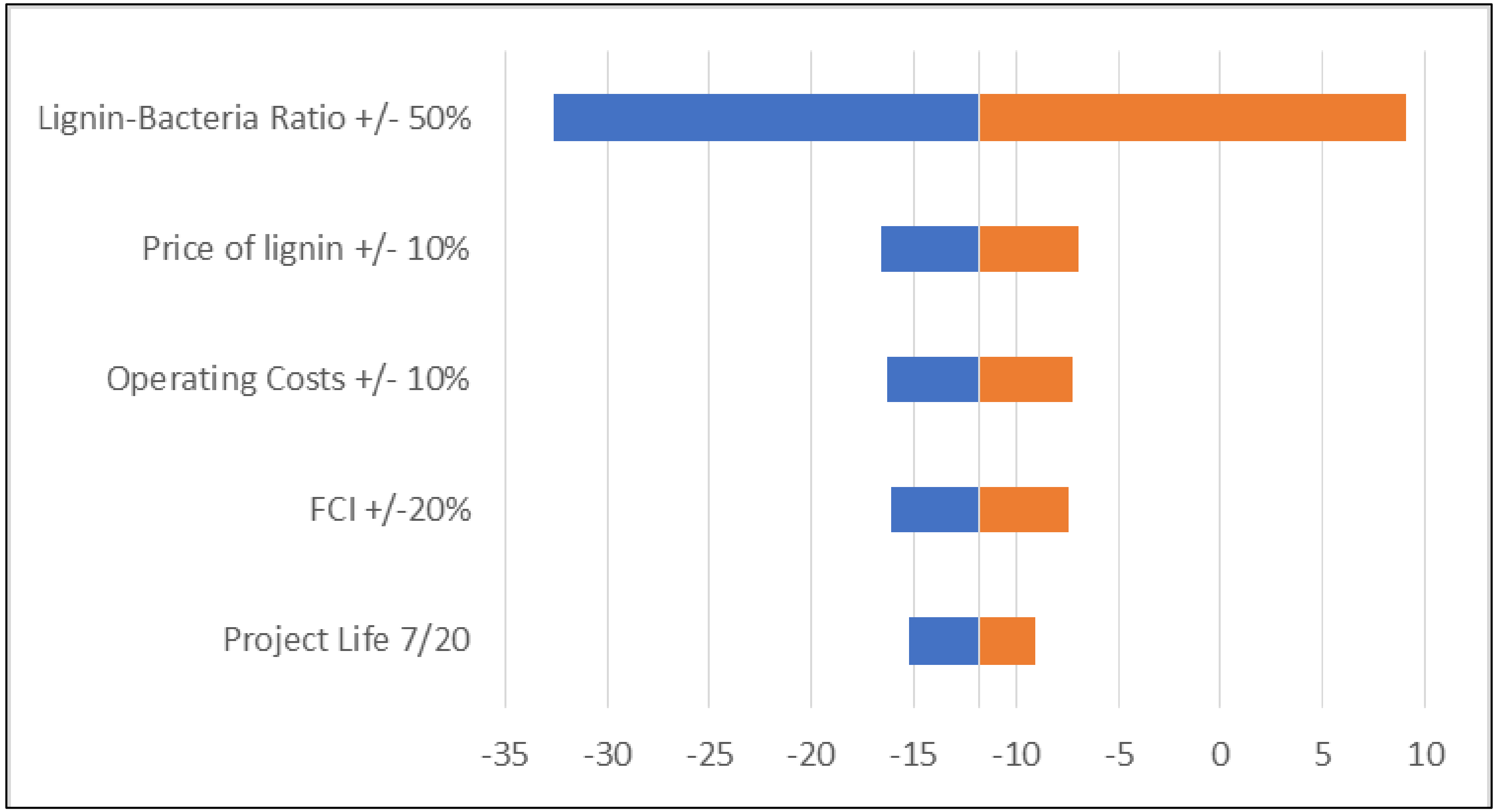
- NREL reports a 99.8% pure adipic acid product (required for production of nylon-6,6)

Economics

- Installed and delivered FCI: $15.9 million
  - Based on methods from P&T
- Fixed costs: $2.2 million per year
  - Labor, maintenance, utilities, etc
  - Licensing bacteria
- Variable costs: $4.8 million per year
  - Feedstocks and catalysts
  - M9 is 77% of this cost
- Revenue: $7.4 million per year

Economics and Sensitivities

- NPV0: -$11.8 million, NPV10: -$16.7 million, IRR: -11%



Future Work and Recommendations

- In order to make this process more economically attractive:
  - Continue to increase the lignin to bacteria ratio
  - The reaction time (72 hours) must decrease
  - Depends on the engineered bacteria, since other considerations such as biological reaction conditions have been studied and optimized

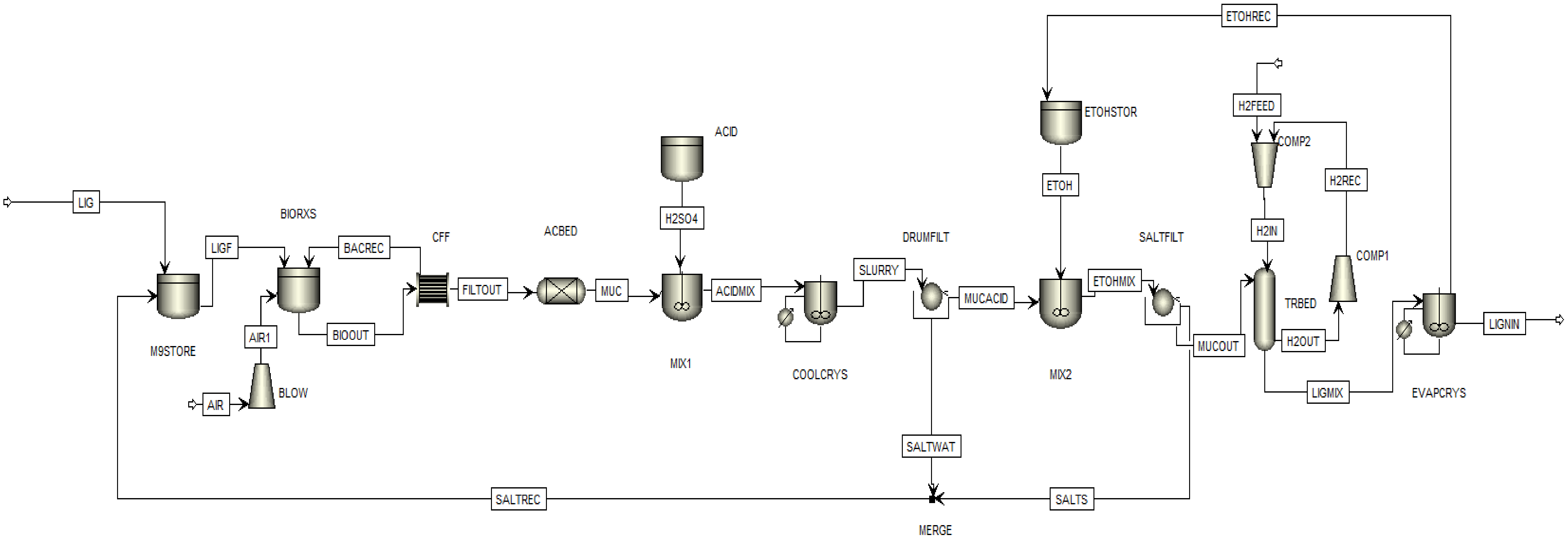
- If a profitable process can be achieved:
  - Look into purging of salt streams
  - What nutrients are actually necessary for lignin-bacteria system?
  - Indirect alternatives to increase the contact area between lignin and bacteria to facilitate higher conversion

Conclusions

- Currently, using lignin to produce adipic acid is not profitable

- If improvements are made to the engineered bacteria
  - Project economics would improve
  - Design alternatives could increase production

- Using lignin to produce adipic acid is attractive
  - Lignin is inexpensive
  - Environmentally friendly



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