Microfluidic Biodiesel Production from Used Cooking Oil

Group 20: Fuel^2
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Introduction

Goal: Produce biodiesel from waste cooking oil (WCO)

- Cheaper feedstock
- Avoids competition for food
- WCO has solid and free fatty acid (FFA) contaminants

The biodiesel will be sold for $2.41/gal

- $22M in profit, 23% profit margins

Current processes treat low-FFA feeds with base catalysis in a batch process

- Batch = Slow
- FFA + Base = Soap

Fuel^2 has designed a continuous process

- Acid catalysis pretreatment
- Microreactors

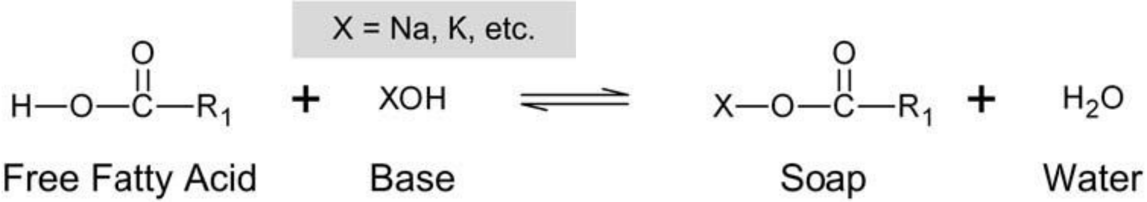
Biodiesel from low-price feedstocks

Make high quality biodiesel (ASTM standards) using low quality (high FFA) feedstocks

Price: 32.5¢/lb
%FFAs: <1%

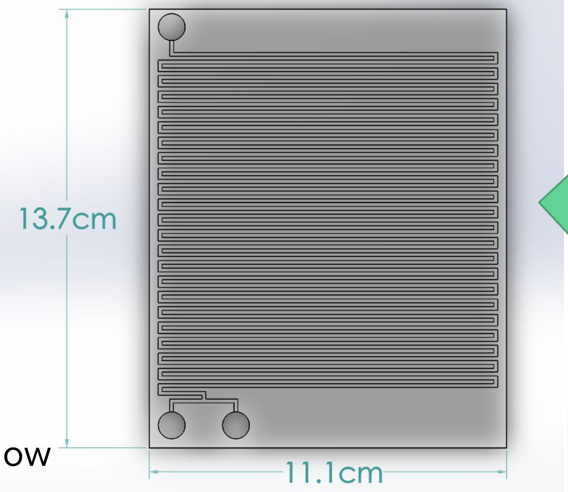
Price: 22¢/lb
%FFAs: 1-10%

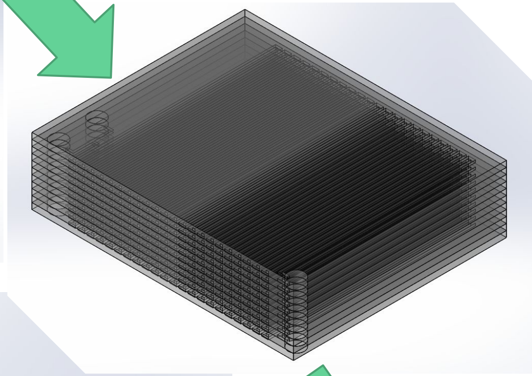
Problem:
Base catalyst makes soap with >2% FFAs

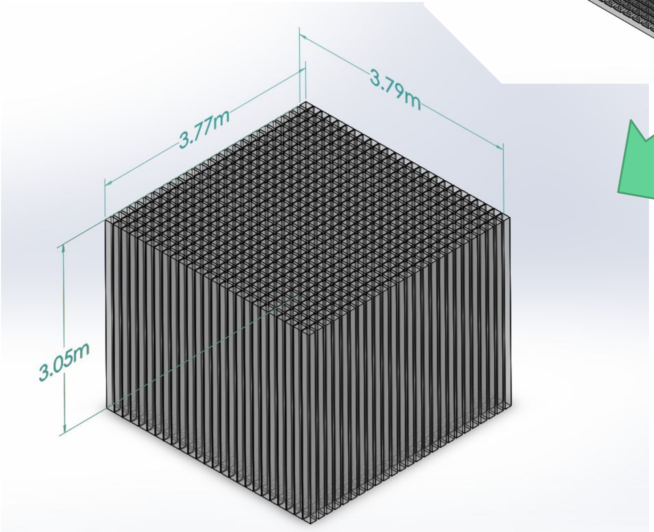


Why microreactors?

- Faster Kinetics
  - Efficient mixing and low diffusion distances
  - Transesterification is a relatively slow reaction
- Scalable
  - Many individual reactors can be multiplexed in parallel
- Safety
  - Little risk of runaway reactions or loss of control
- Cost
  - Easily and effectively assembled out of polycarbonate

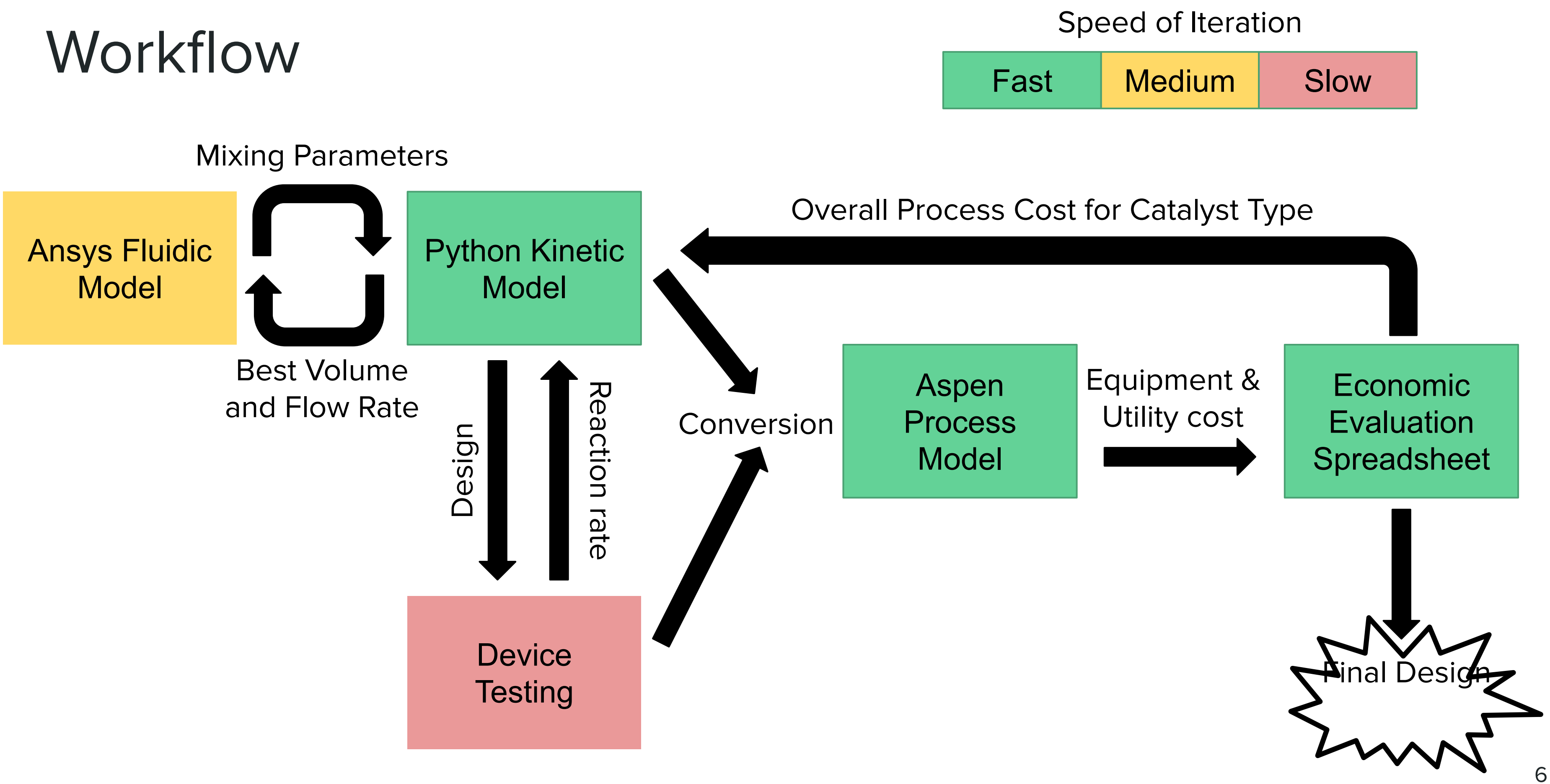




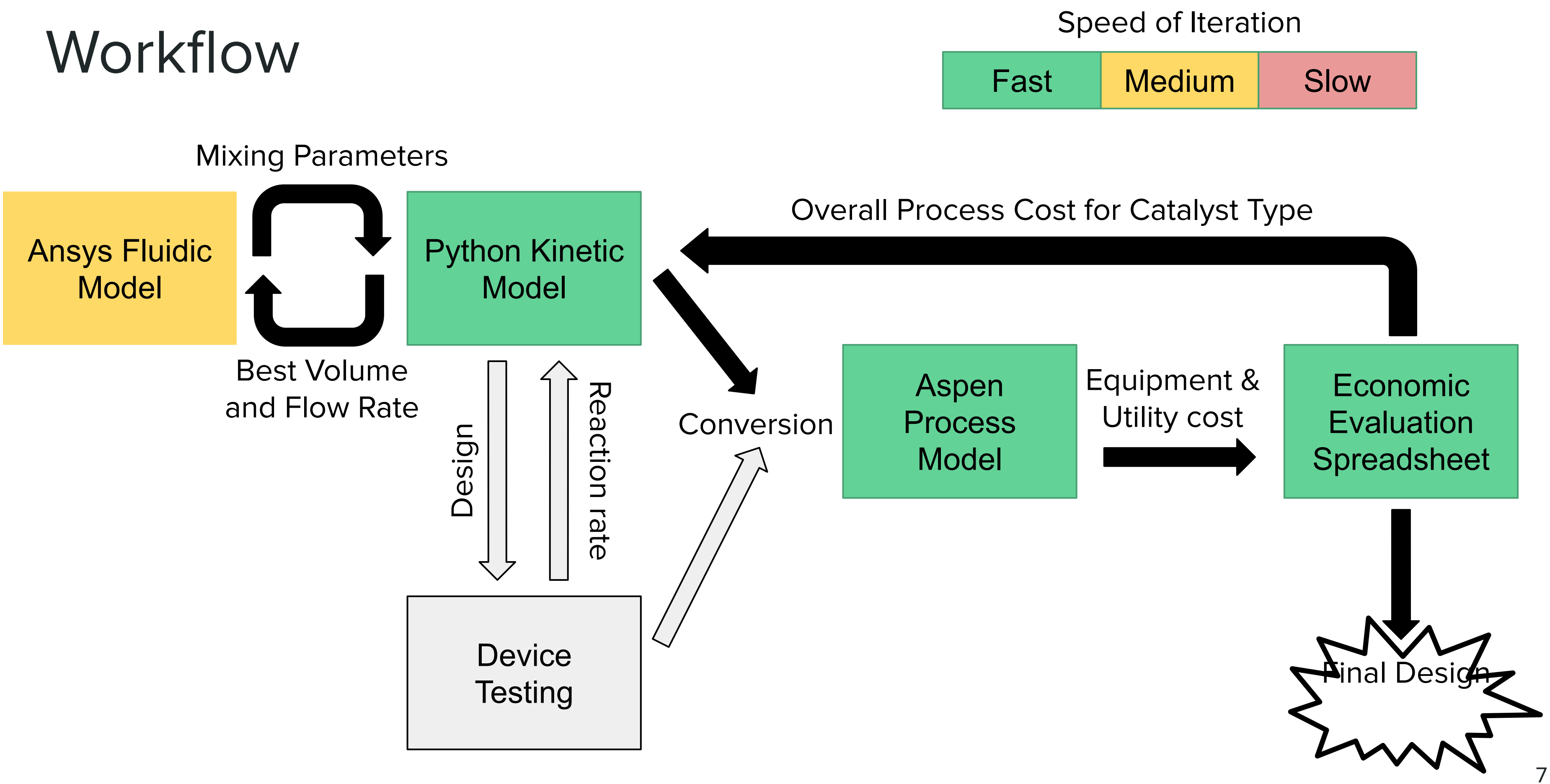


Experiments and Simulation

Workflow


Speed of Iteration
Fast
Medium
Slow
Mixing Parameters
Ansys Fluidic Model
Python Kinetic Model
Best Volume and Flow Rate
Design
Reaction rate
Device Testing
Overall Process Cost for Catalyst Type
Conversion
Aspen Process Model
Equipment & Utility cost
Economic Evaluation Spreadsheet
Final Design

Workflow



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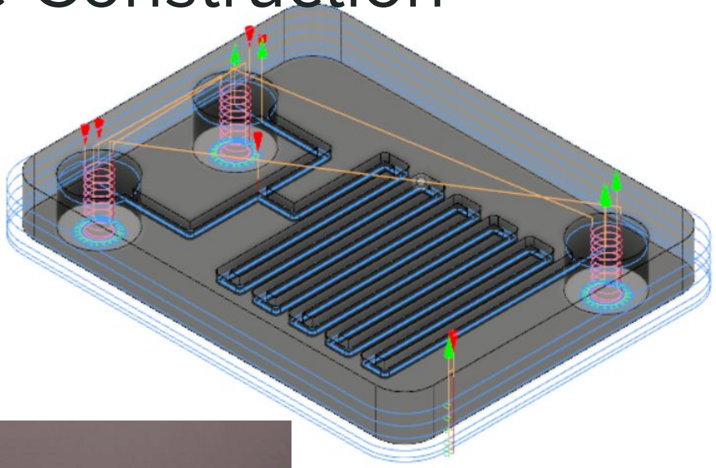
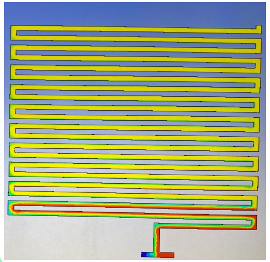
Experimental: Microreactor Device Construction

- Polycarbonate is CNC milled to have the desired channel geometry
- Milled part with channels is solvent welded to a cover plate
- Threads are tapped to accept fluid fittings
- Syringe Pump controls flow



Computational Fluid Dynamic Modeling



- Ansys Fluent
    - 2D Model

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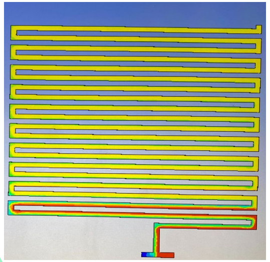

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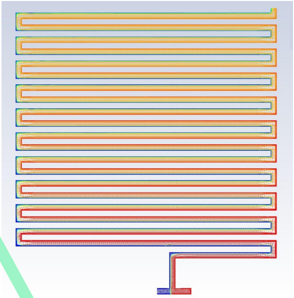

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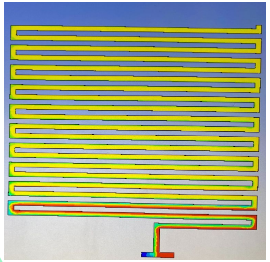

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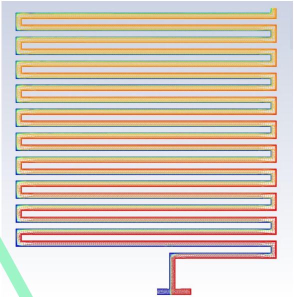
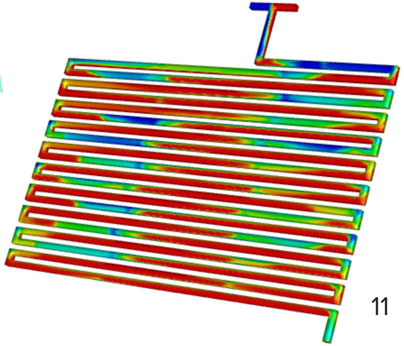
  - 3D Model
    - Shown 3D flow patterns
    - Full reactor model couldn't converge from Academic Fluent license mesh size limitations





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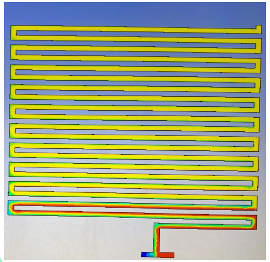

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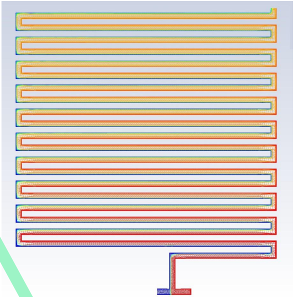
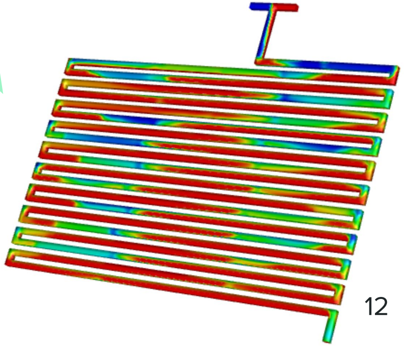
- Comsol CFD
  - Parameterized 3D Model
    - Simulations using 250+ GB of RAM run on supercomputer





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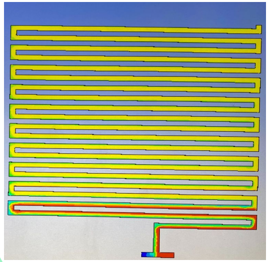
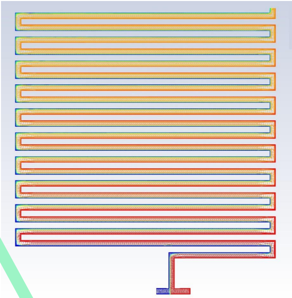
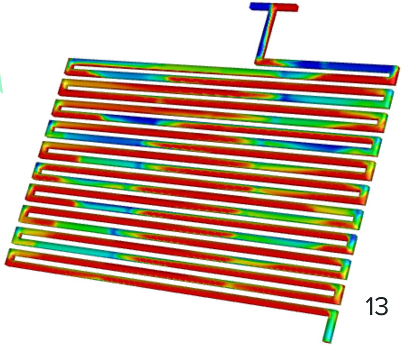


- Ansys Fluent
    - Laminar Flow Model
    - Mixture Multiphase Model
    - Steady State Simulation



- Comsol CFD
    - Laminar Flow Model
    - Phase Field Multiphase Model
    - Sudo-Transient Simulation



CFD Phase Interaction Parameters

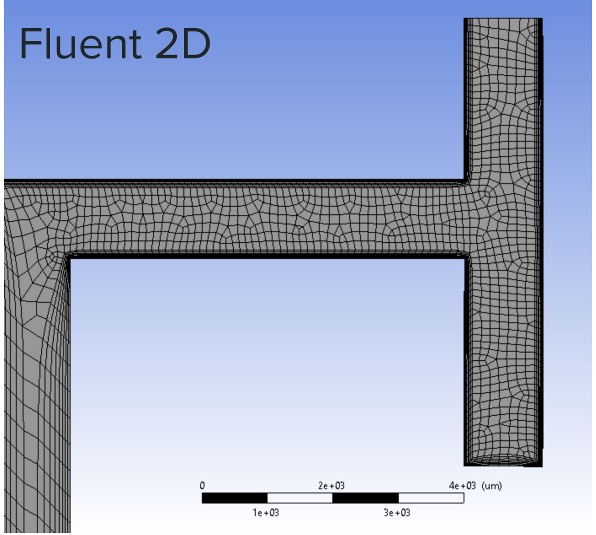
- Diffusivity for a methanol-canola oil system
  - $$D_{12} = 7.4 * 10^{-12} \frac{T\sqrt{xM_2}}{\eta_2 {V_1}^{0.6}}$$ [1]

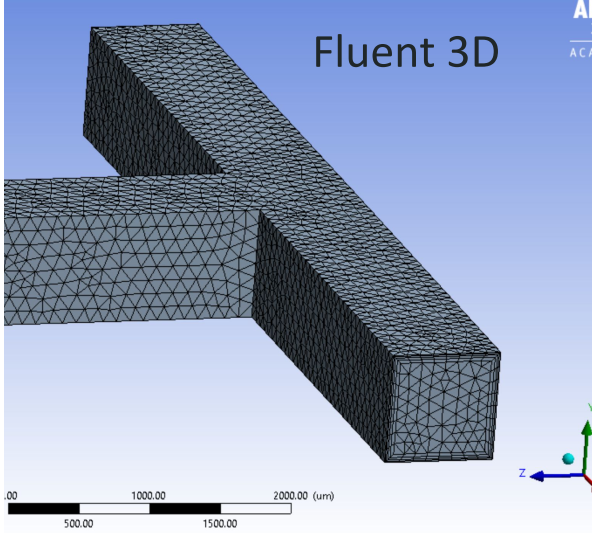
    - Used as a user-defined scalar diffusivity
    - Oil: 0.148 m^2/s
    - Methanol: 0.125 m^2/s
- Interfacial tension
  - Oil:methanol – 0.618 mN/m [2]

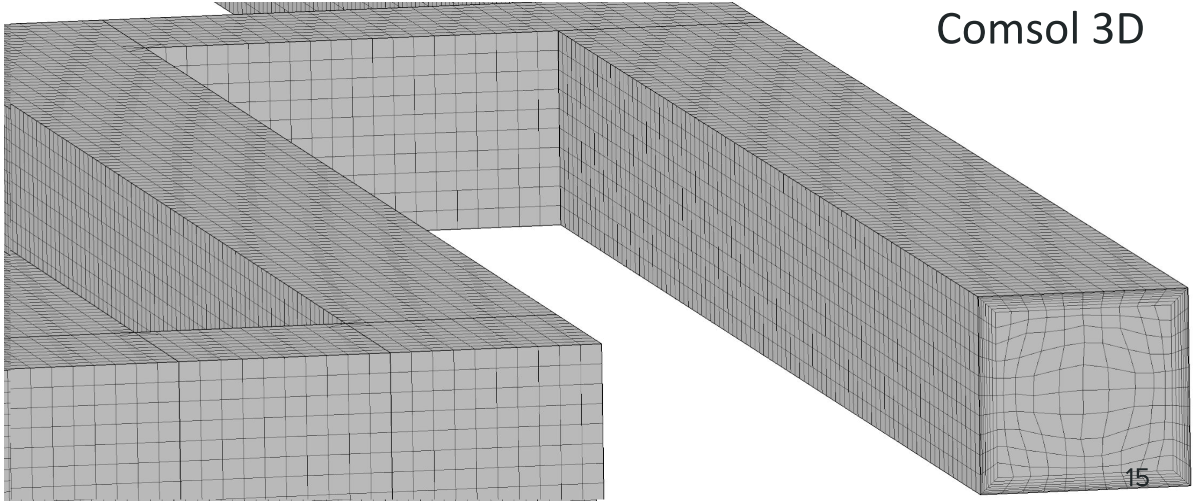
[1] K. Pal, "Investigations of transesterification of canola oil with methanol and ethanol for a new efficient method of biodiesel production," *Electronic Thesis and Dissertation Repository*, Nov. 2011.
[2] G. Sanaiotti, Silva César A. S. Da, A. G. Parreira, Tótola Marcos R., A. J. A. Meirelles, and E. A. C. Batista, "Densities, Viscosities, Interfacial Tensions, and Liquid−Liquid Equilibrium Data for Systems Composed of Soybean Oil Commercial Linoleic Acid Ethanol Water at 298.2 K," *Journal of Chemical & Engineering Data*, vol. 55, no. 11, pp. 5237–5245, Nov. 2010.

CFD Meshes and Mesh Sensitivity Analysis

- Fluent 2D
  - 400,000 computational cells
  - Average quality: 0.6
- Fluent 3D
  - 450,000 cells
  - Average quality: 0.3
- Comsol
  - 1.62 million cells
  - Average quality: 0.73
- Comsol (Refined)
  - 2.54 million cells
  - Average quality: 0.84







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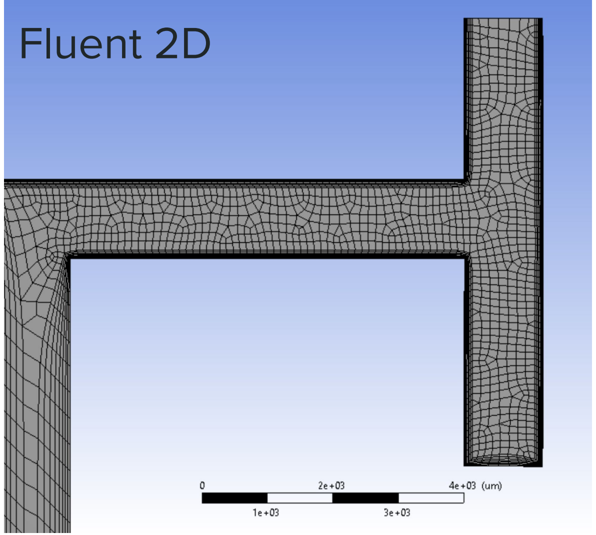
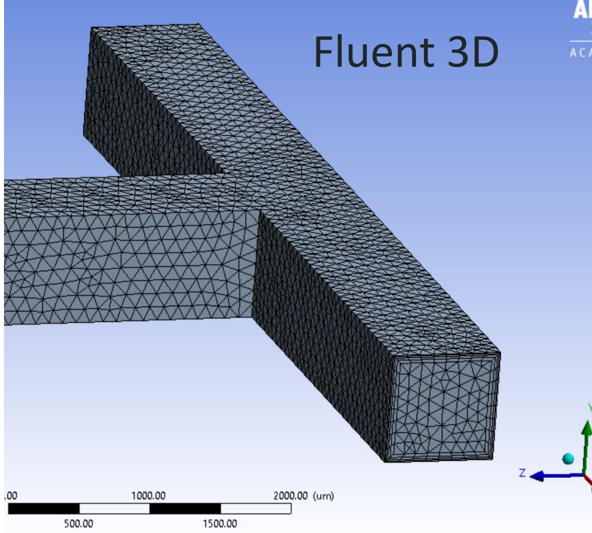
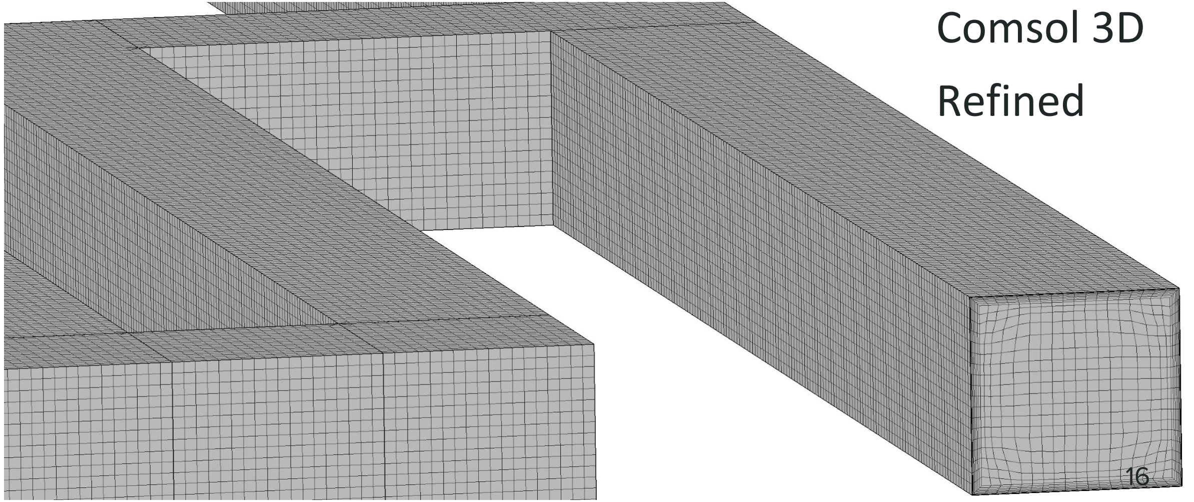
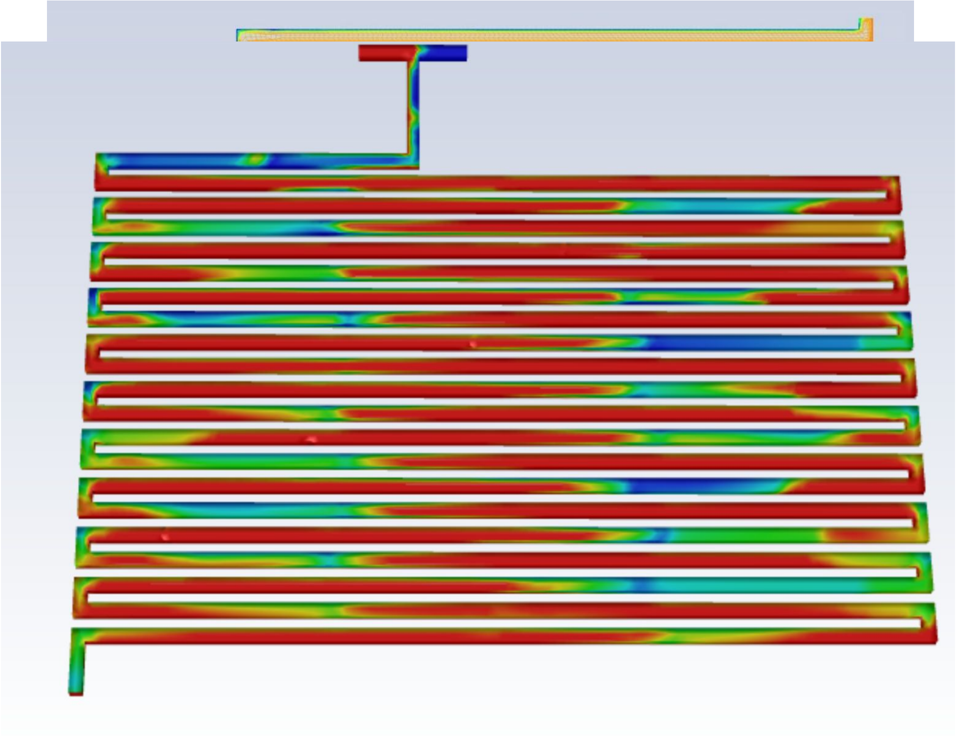






CFD Flow Simulation Results

- Biphasic Flow Pattern
    - Seen in both 2D and 3D models



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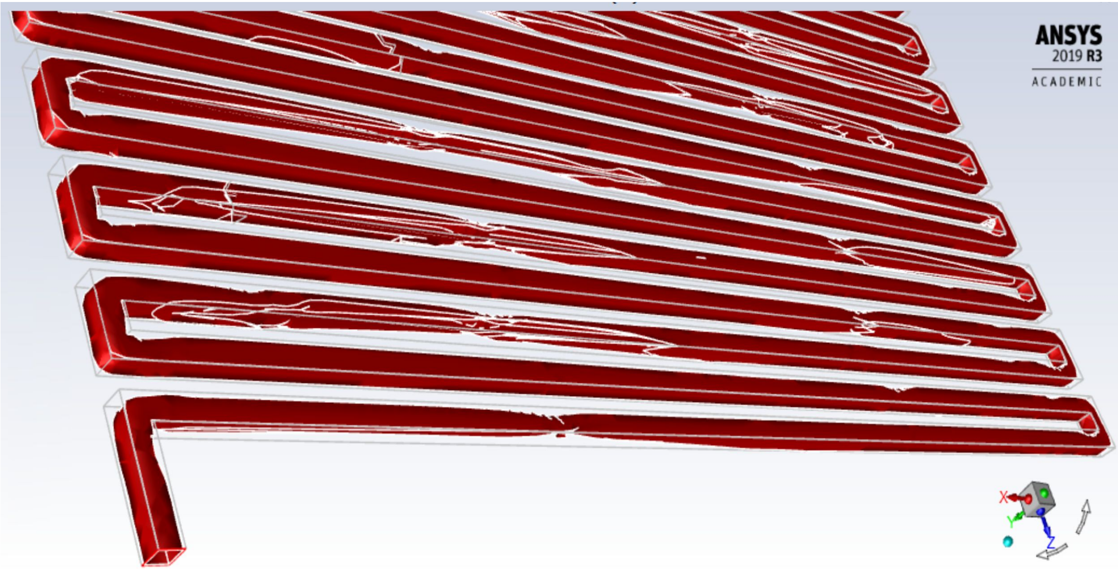
- Potential Annular Flow



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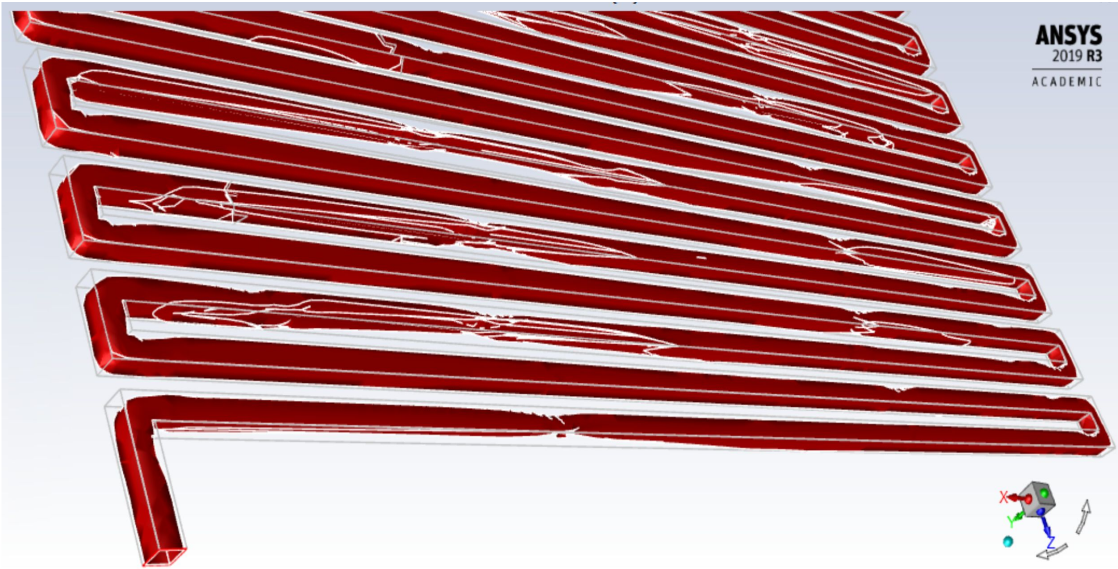
  - Resulted in interfacial area concentration of ~2500 m^2/m^3



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- Biphasic Flow Pattern
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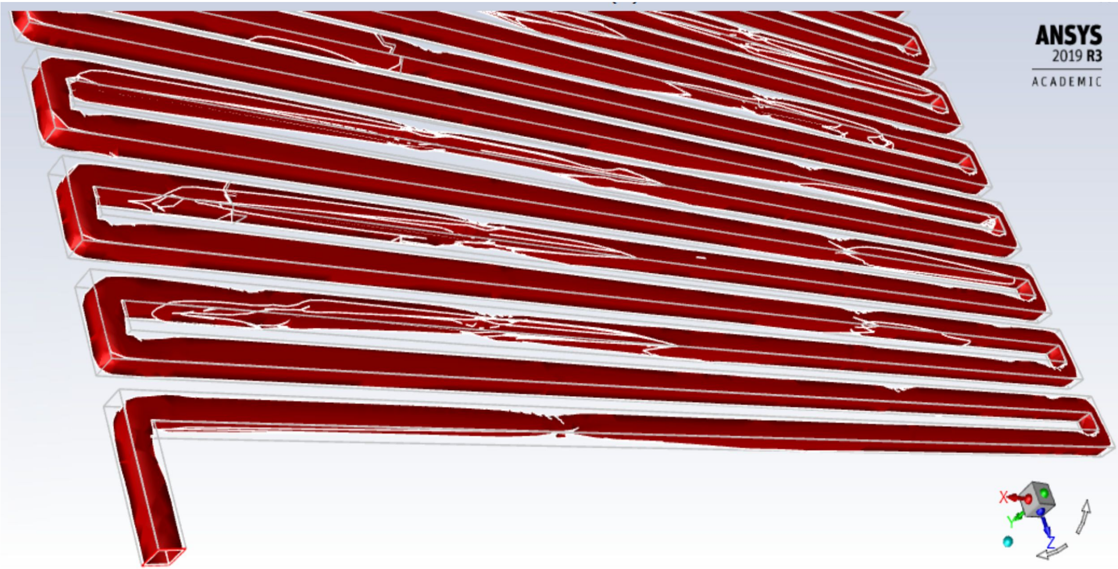
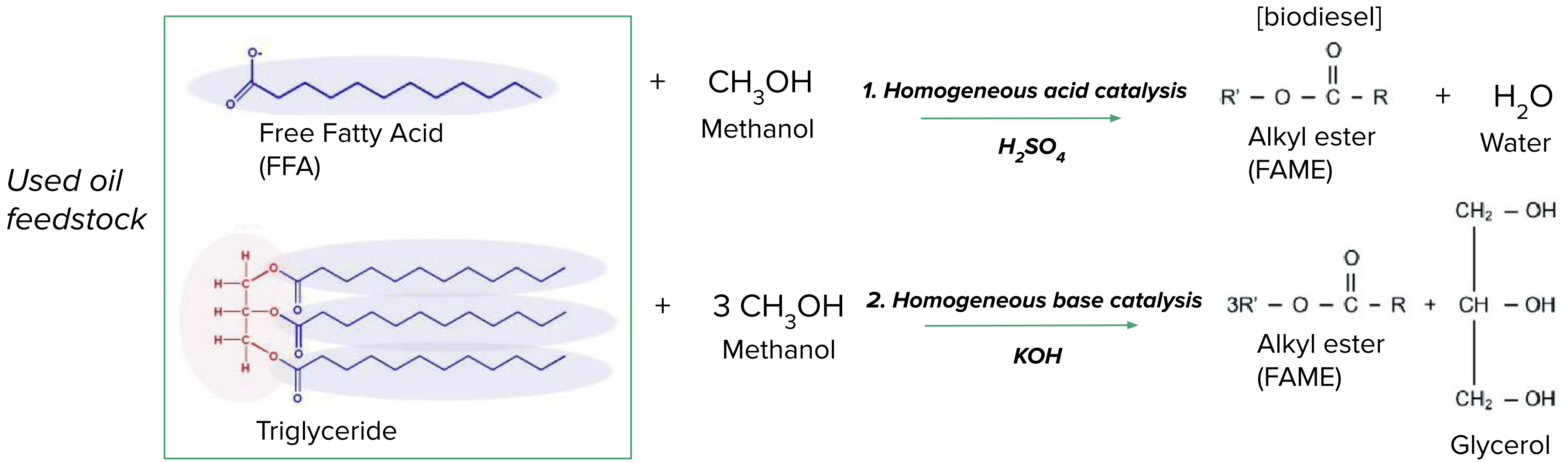
- Potential Annular Flow
  - Resulted in interfacial area concentration of ~2500 m^2/m^3
    - Residuals were not below 10^{-3} so solution did not reach steady state yet.



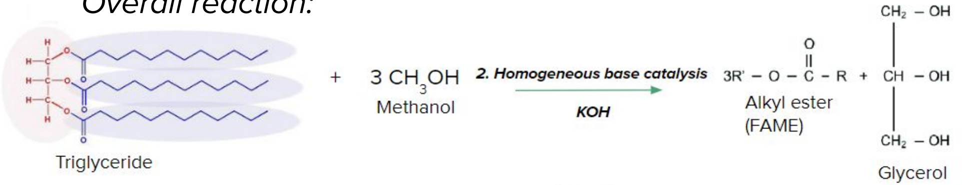
Acid Pre-treatment / Base-catalyzed Transesterification

- *Goal:* Robust catalyst for use with high Free Fatty Acid (FFA) feedstock
    - H_2SO_4: converts FFAs to FAME, but slow
    - KOH alone: fast but sensitive to FFAs ➔ makes soap
- *Goal:* Catalyst with fast kinetics
- *Goal:* Inexpensive catalyst



Kinetics of Transesterification

Overall reaction:



TG $MeOH$ Cat $FAME$ G

Reaction steps:

$$TG + MeOH \rightleftharpoons DG + FAME$$

$$DG + MeOH \rightleftharpoons MG + FAME$$

$$MG + MeOH \rightleftharpoons G + FAME$$

Diglyceride and monoglyceride reaction intermediates

Reaction kinetics:

$$r_1 = k_1[TG]_A[MeOH][Cat] - k_{1r}[DG]_A[FAME][Cat]$$

$$r_2 = k_2[DG]_A[MeOH][Cat] - k_{2r}[MG]_A[FAME][Cat]$$

$$r_3 = k_3[MG]_A[MeOH][Cat] - k_{3r}[G][FAME][Cat]$$

Mass transfer kinetics between oil and alcohol phases:

$$r_{mTG} = k_{LTG}a([TG]_O - [TG]_A)$$

$$r_{mDG} = k_{LDG}a([DG]_O - [DG]_A)$$

$$r_{mMG} = k_{LMG}a([MG]_O - [MG]_A)$$

	Microreactor Reaction Conditions from Literature [1]	**Our Reaction Conditions in Microreactor**
Oil	Sunflower	Varied feedstock
Alcohol	EtOH	MeOH
Alcohol to Oil (Molar) Ratio	6:1	6:1
Catalyst	EtONa	KOH
Catalyst loading	1 wt%	1 wt%
Temperature	65°C	60-65°C
Channel width	500 µm	1200 µm

Rate constants for reaction with comparable conditions found in literature

[1] R. Richard, S. Thiebaud-Roux, L.E. Prat, "Modelling the kinetics of transesterification of sunflower oil with ethanol in microreactors," *Chemical Engineering Science*, vol. 87, pp. 258-269, January 2013.

Optimization of Microreactors for Transesterification

Constraints: Microreactor throughput 18.9 L/s (45 MMGy target for FAME output)

Goals:

1. Maximize product (FAME) yield and purity
2. Minimize microreactors' footprint
3. Minimize pumping power requirement

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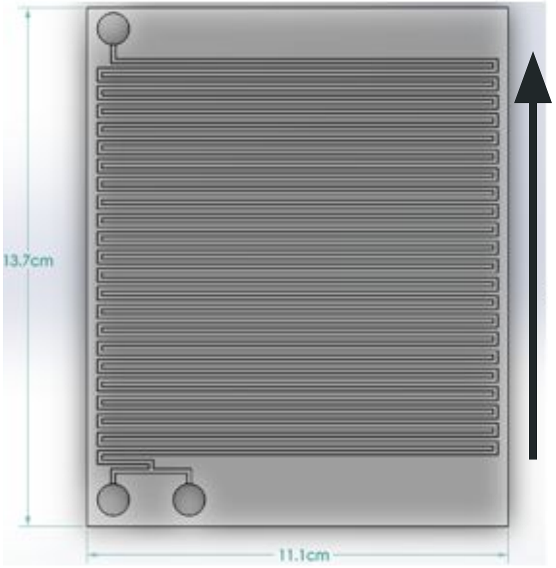
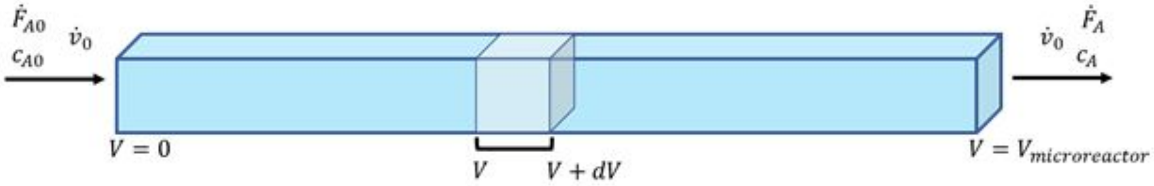


🠉 microreactor channel length 🠉 microreactor volume

- Higher FAME yield/purity attainable
- Higher construction cost with larger footprint



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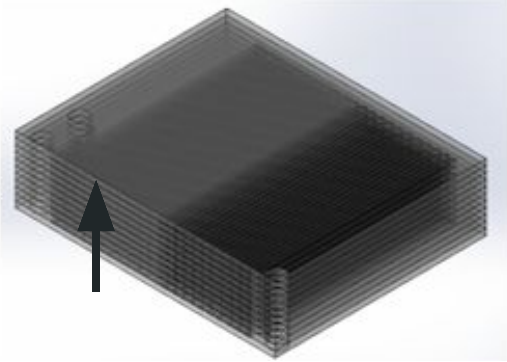

↑ # of microreactor chips ↓ flow rate through individual microreactor channels

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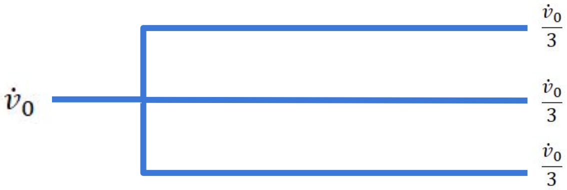

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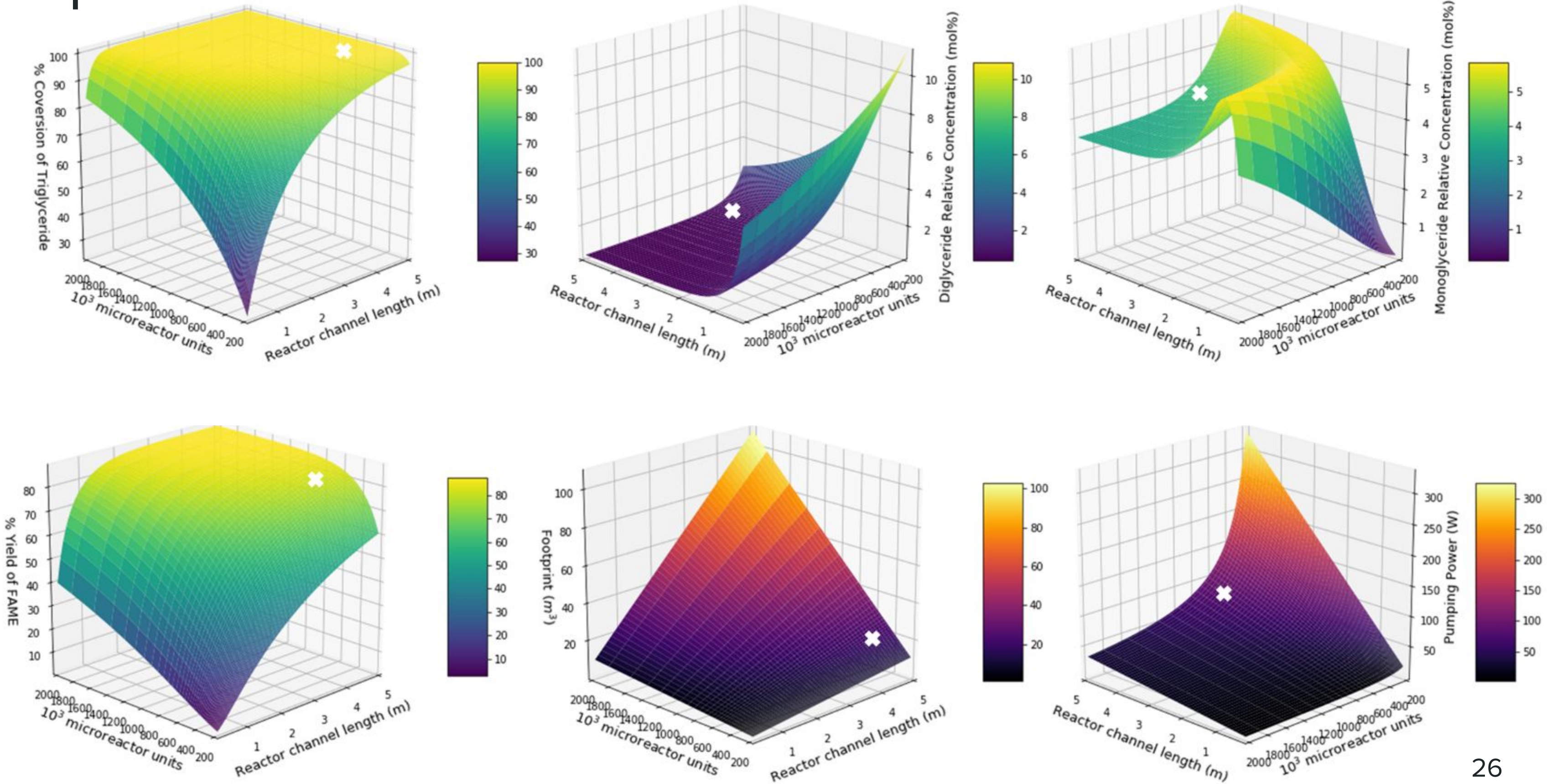

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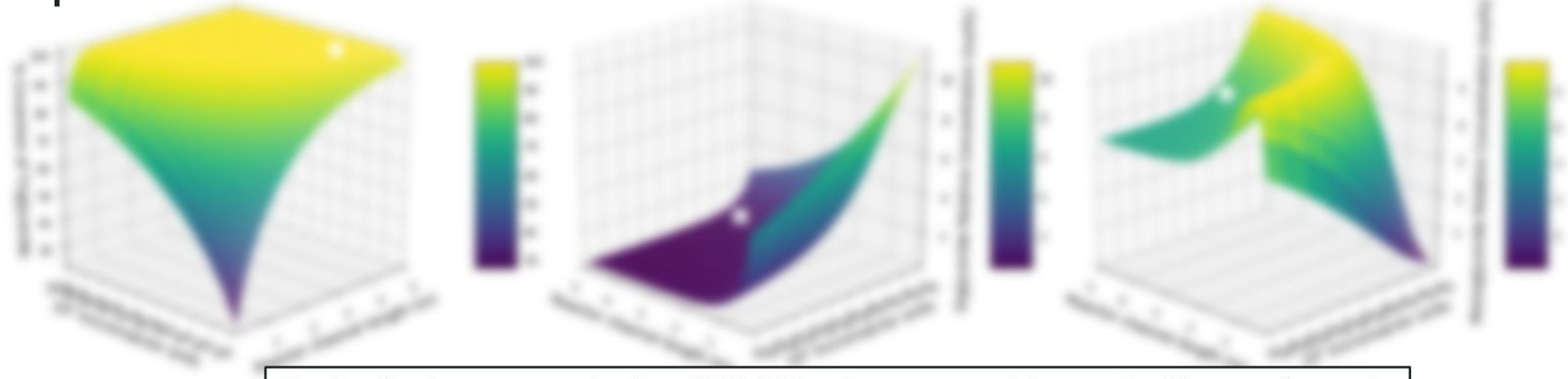
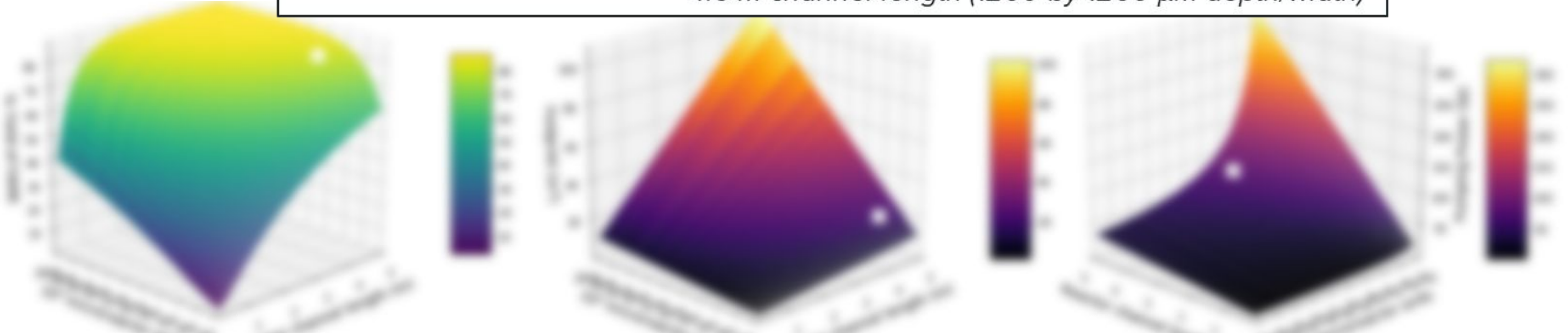


Optimal microreactor design: *600,000 microreactor chips each with one channel*
4.6 m channel length (1200 by 1200 μm depth/width)



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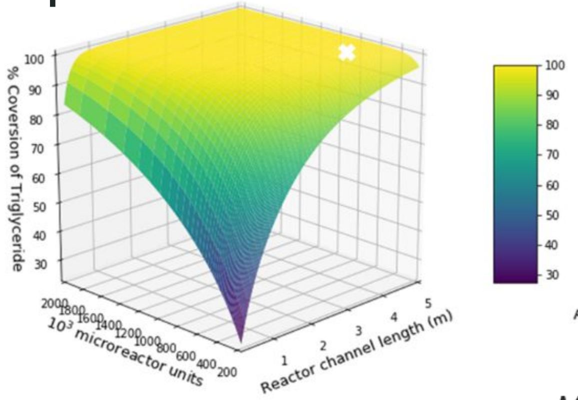

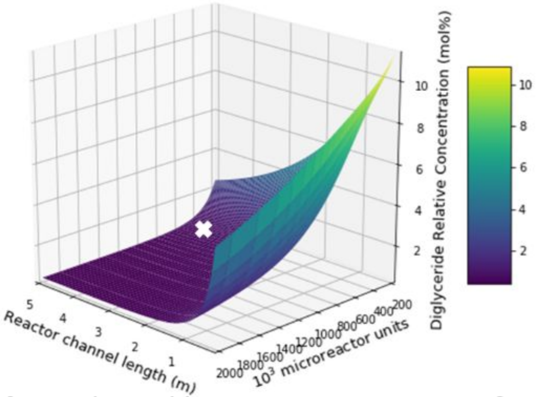

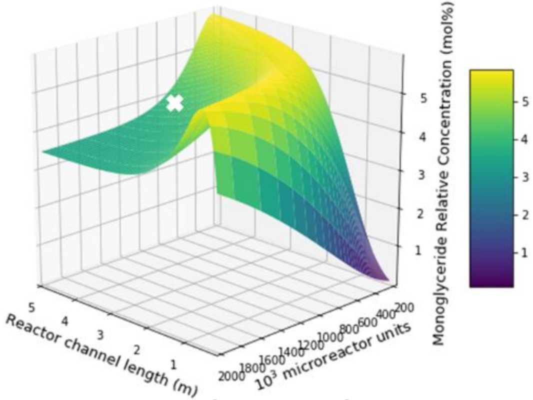

Minimal equilibrium concentration of reaction intermediates and reactants result in high purity product and reduce load on separation unit operations

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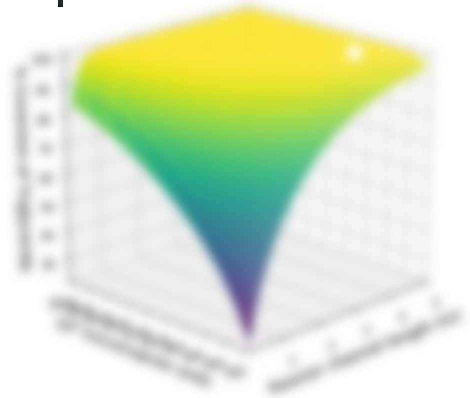
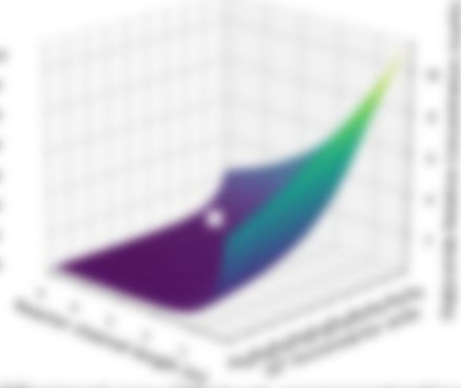
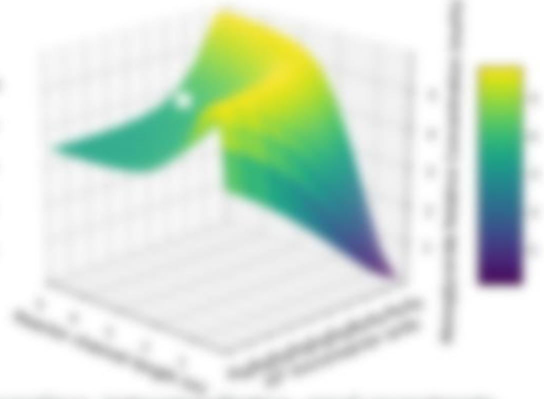
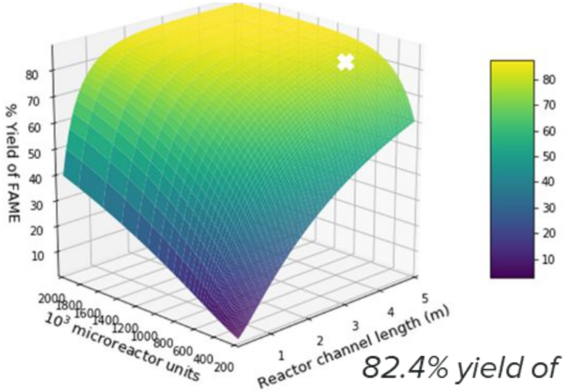
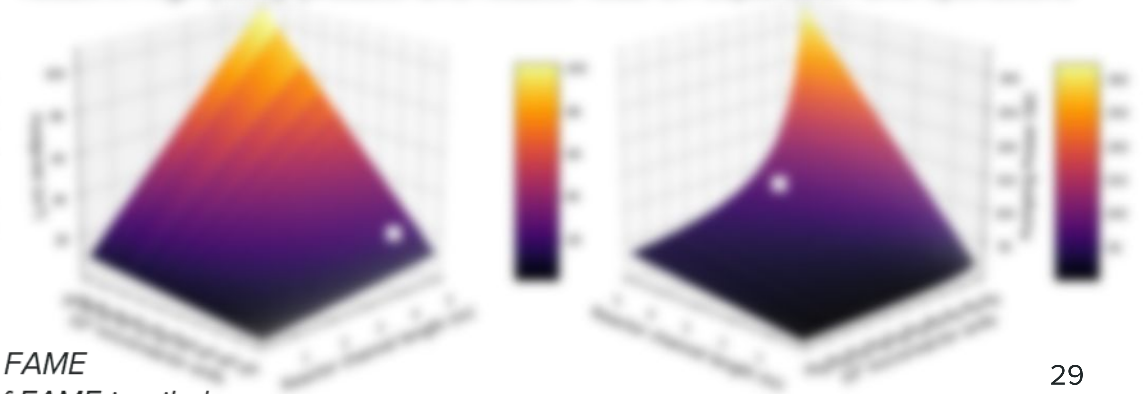








82.4% yield of FAME
85.2% purity of FAME in oil phase



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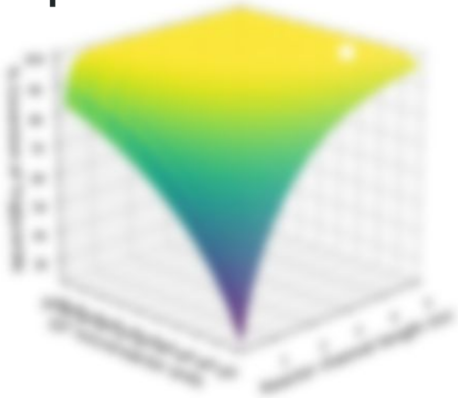
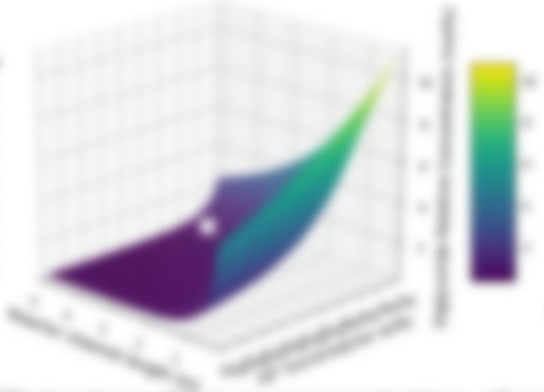
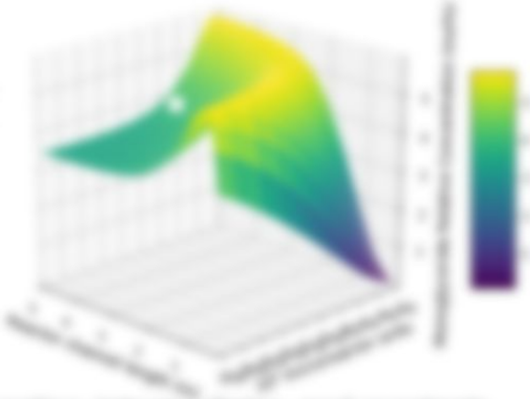
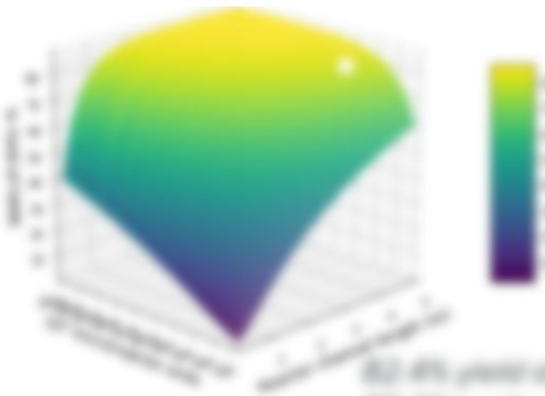
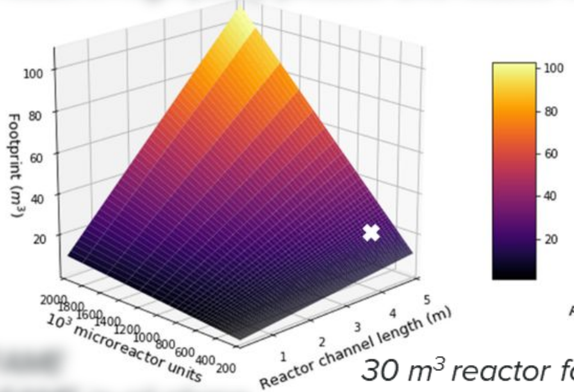
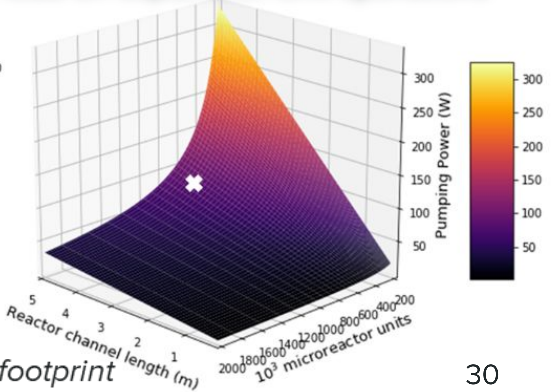






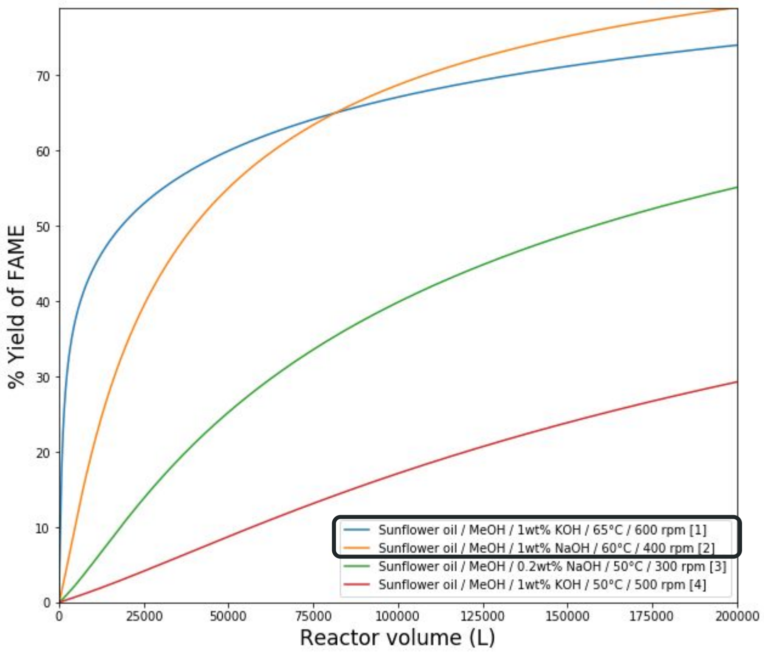


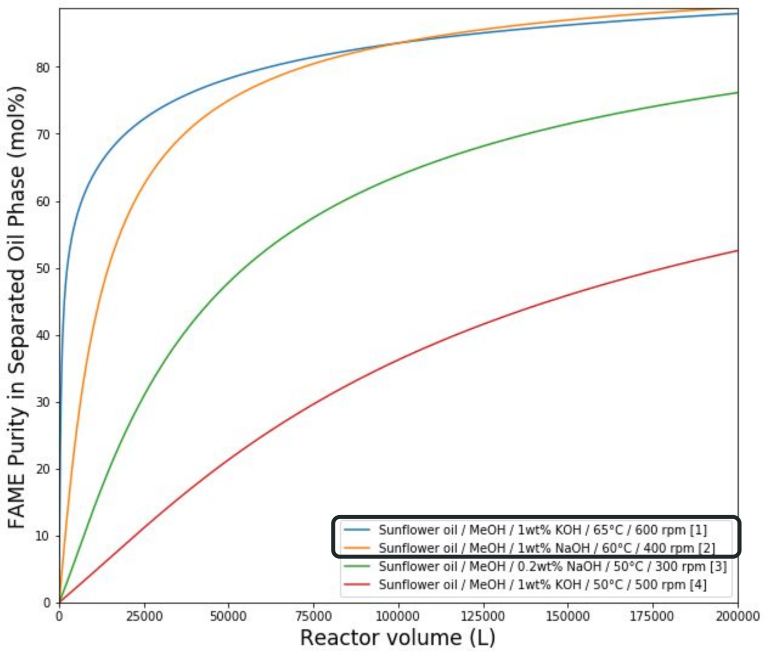




30 m^3 reactor footprint
Demonstrated scaling relationship for pumping power

Comparing with Conventional CSTR for Transesterification





*For ideal reaction conditions, a **200,000 L** CSTR is required to achieve comparable FAME yield/purity.*

[1] G. Vicente, M. Martinez, J. Aracil, A. Esteban, "Kinetics of sunflower oil methanolysis," *Industrial & Engineering Chemistry Research* vol. 44, no. 15, pp. 5447-5454, June 2005.
[2] M.E. Bambase, N. Nakamura, J. Tanaka, M. Matsumura, "Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters," *Journal Chemical Technology and Biotechnology,* vol. 82, no. 3, pp. 273–280, March 2007.
[3] H. Noureddini, D. Zhu, "Kinetics of transesterification of soybean oil," *Journal of the American Oil Chemists' Society,* vol. 74, pp. 1457-1463, November 1997.
[4] B. Klofutar, J. Golob, B. Likozar, C. Klofutar, E. Zagar, I. Poljansek, "The transesterification of rapeseed and waste sunflower oils: mass-transfer and kinetics in a laboratory batch reactor and in an industrial-scale reactor/ separator setup," *Bioresource Technology,* vol. 101, no. 10, pp. 3333-3344, January 2010.

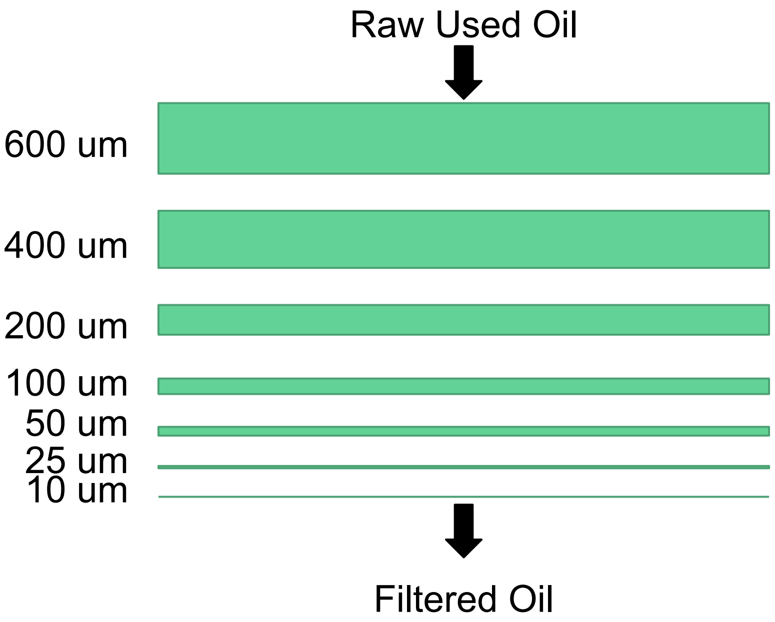
Process Design and Safety

Step 0: Extensive filtration of Used Cooking Oil

Used Cooking Oil comes laden with solids

- Risk plugging microreactors (1200 um)
- Risk damaging engines

Solids will be filtered through a series of filters with decreasing pore size.



Step 1:

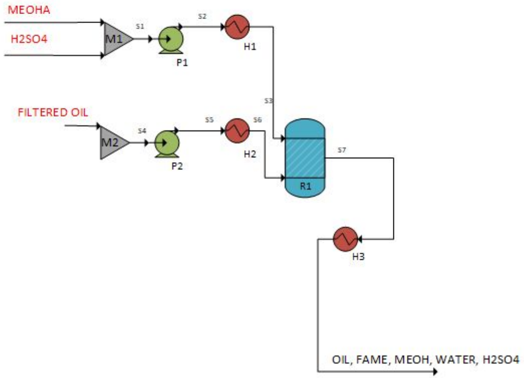
Acid Pretreatment

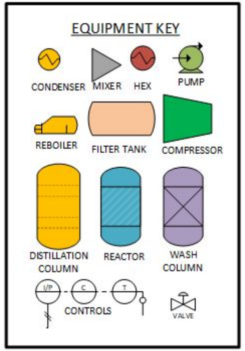
R1: SS Jacketed CSTR

6:1 molar ratio MEOH: oil

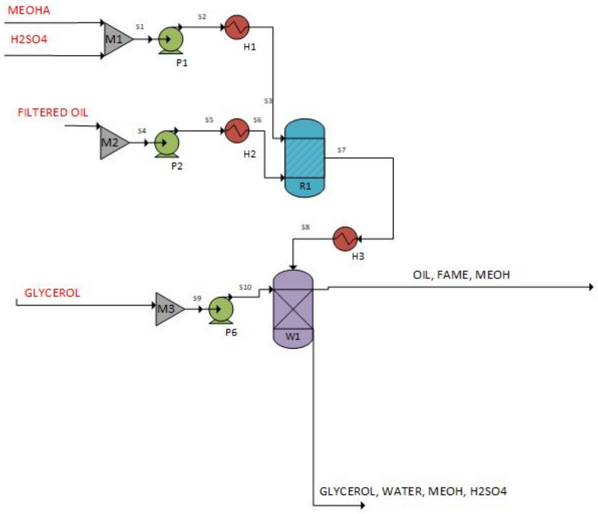
60°C , 4 bar

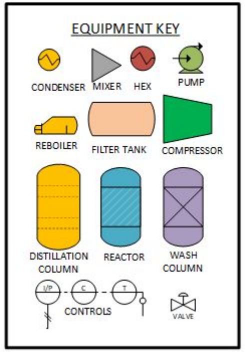
Eliminates 98% of FFAs [1]





[1] Y. Zhang, M. A. Dube, D. D. McLean, and M. Kates, “Biodiesel production from waste cooking oil: 1. Process design and technological assessment,” Bioresource Technology, vol. 89, no. 1, pp. 1–16, Jan. 2003.





Step 2:

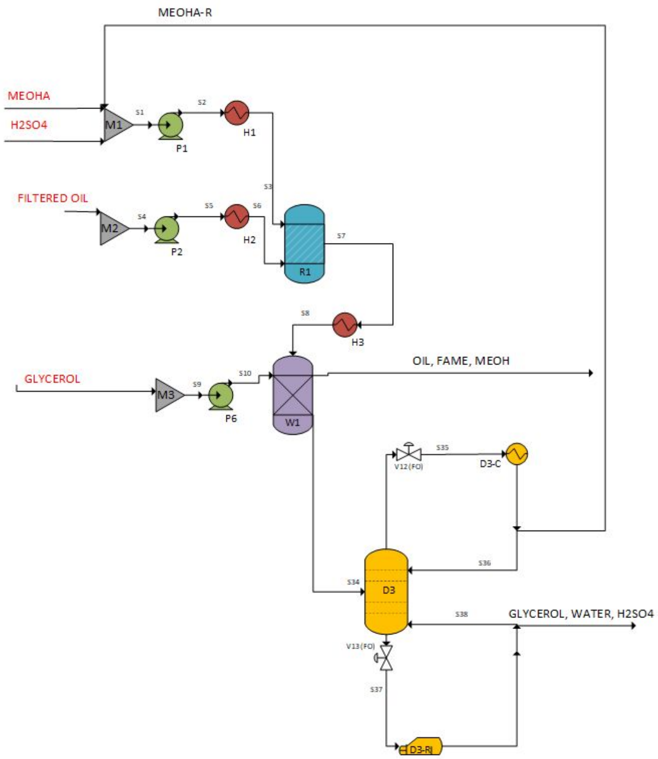
Glycerol Wash

W1: SS Trayed Column

6 stages

40°C , 1 bar

Separates H2SO4 from OIL/FAME prior to base catalysis



Step 3:

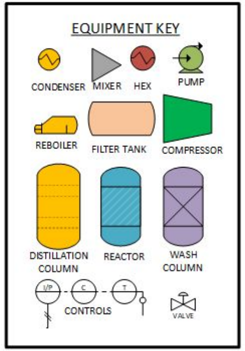
Methanol Recovery

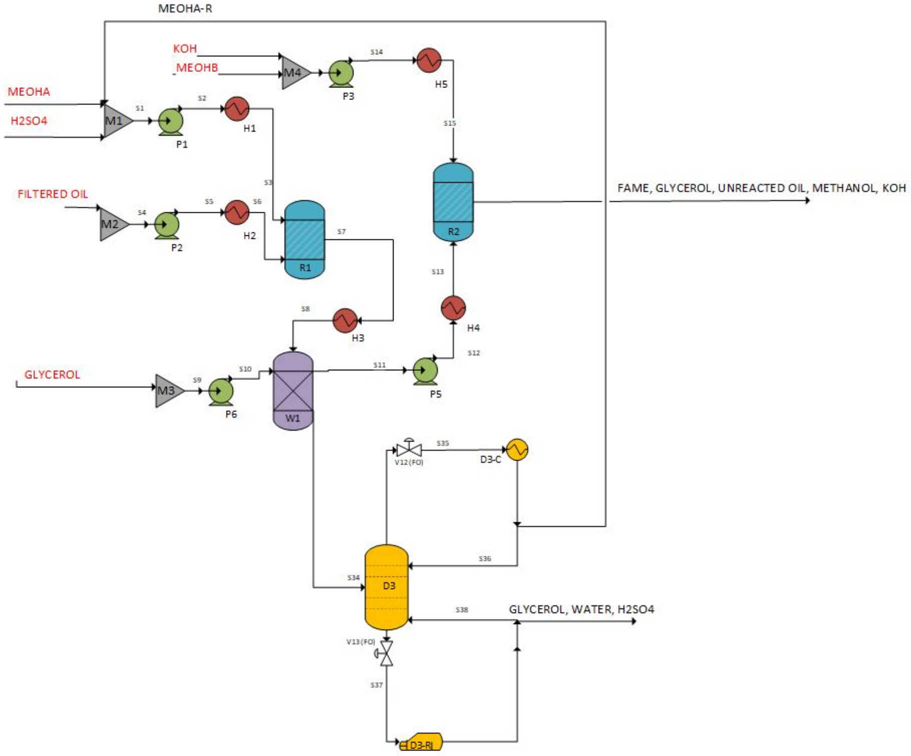
D3: SS Distillation Column

6 stages

<113°C , 1 bar

Recovers 94.5% of unreacted MEOH, for a 95 wt% recycle stream





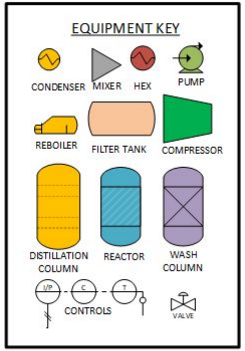
Step 4:

Base Transesterification

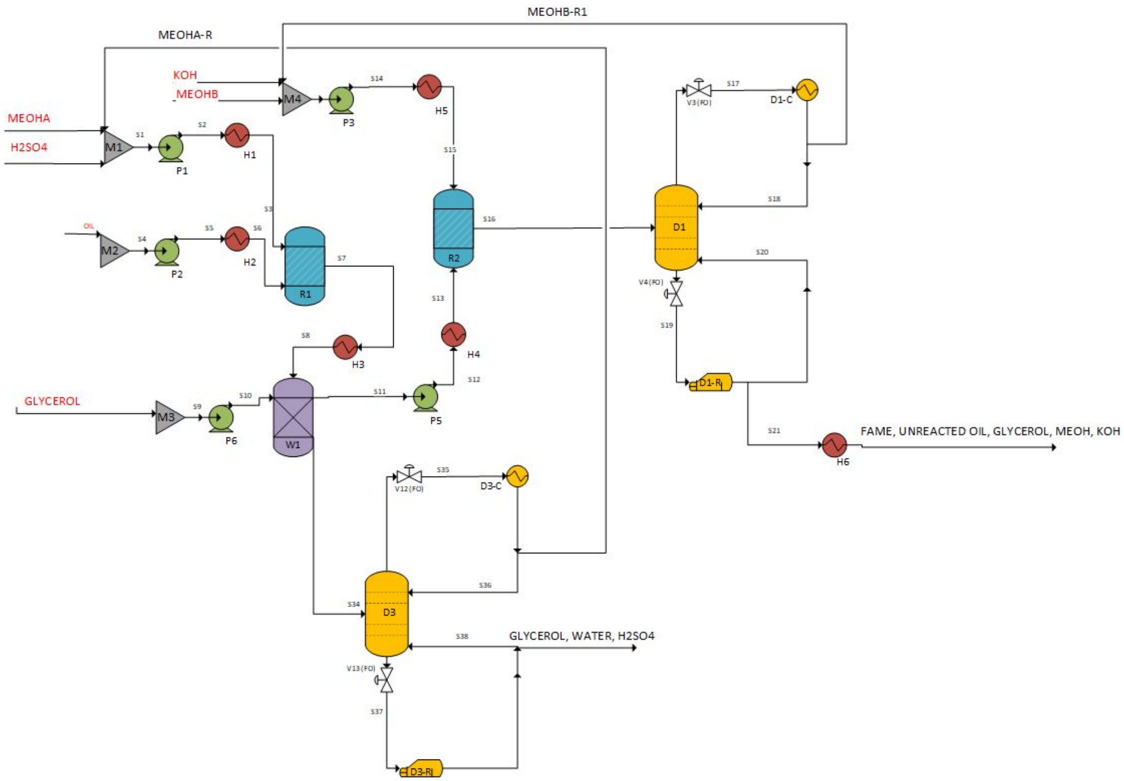
R2: Microreactor Assembly

600,000 microreactors in parallel

60°C , 1 bar



99.9% TG conversion
90.2% DG conversion
60.3% MG conversion
(from Python model)

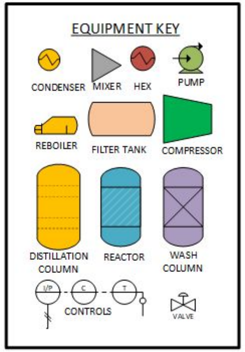


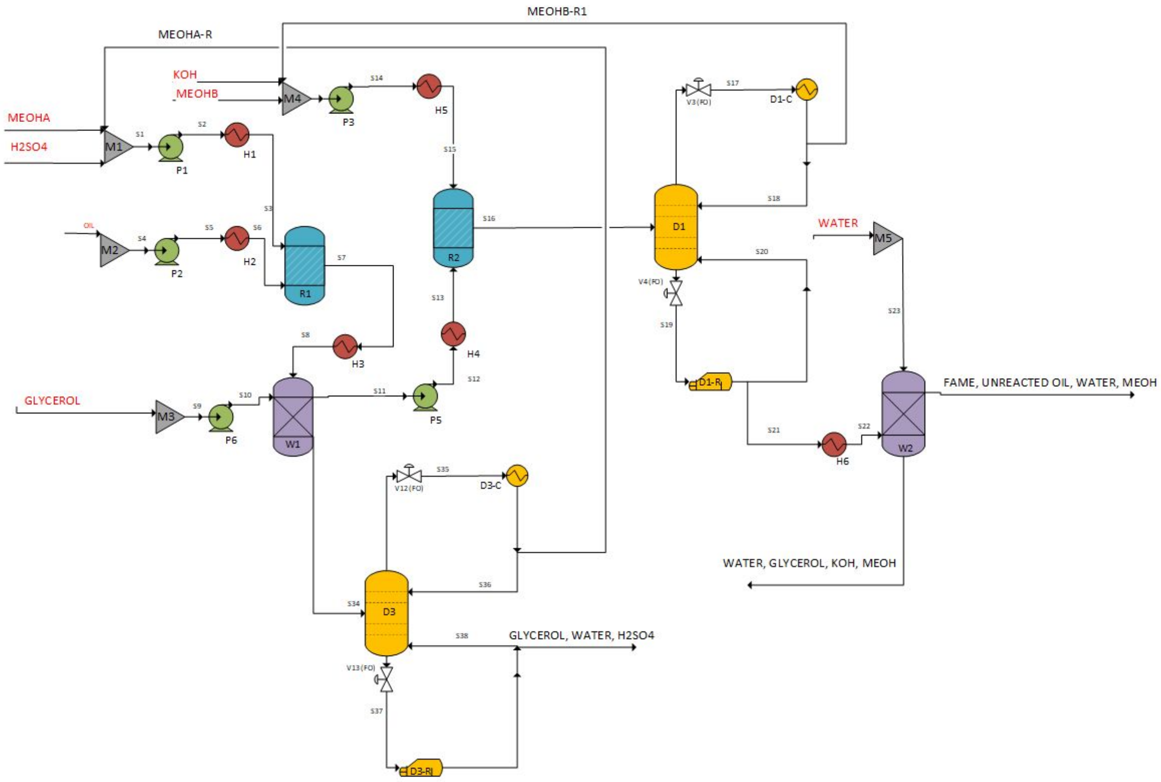
Step 5:

Methanol Recovery

D1: Distillation Column
6 stages
<113°C , 1 bar

Recovers 89% of unreacted MEOH, for a 97 wt% recycle stream



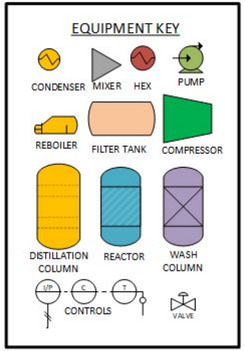


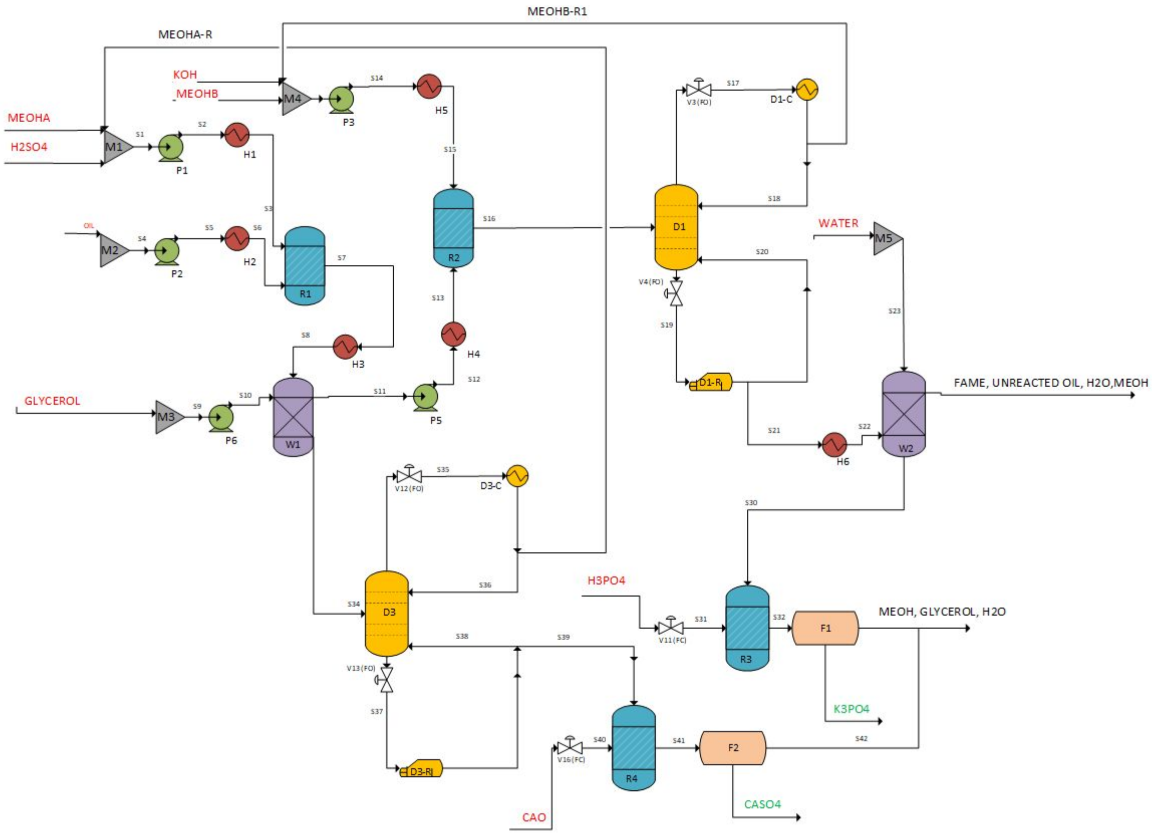
Step 6:

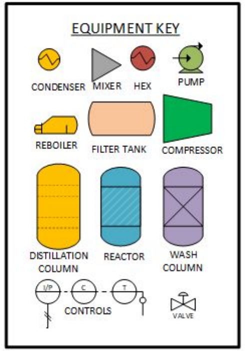
Water Wash

W2: Trayed column
6 stages
60°C , 1 bar

Separates KOH and GLYCEROL from OIL/FAME







Step 7:

Catalyst Neutralization

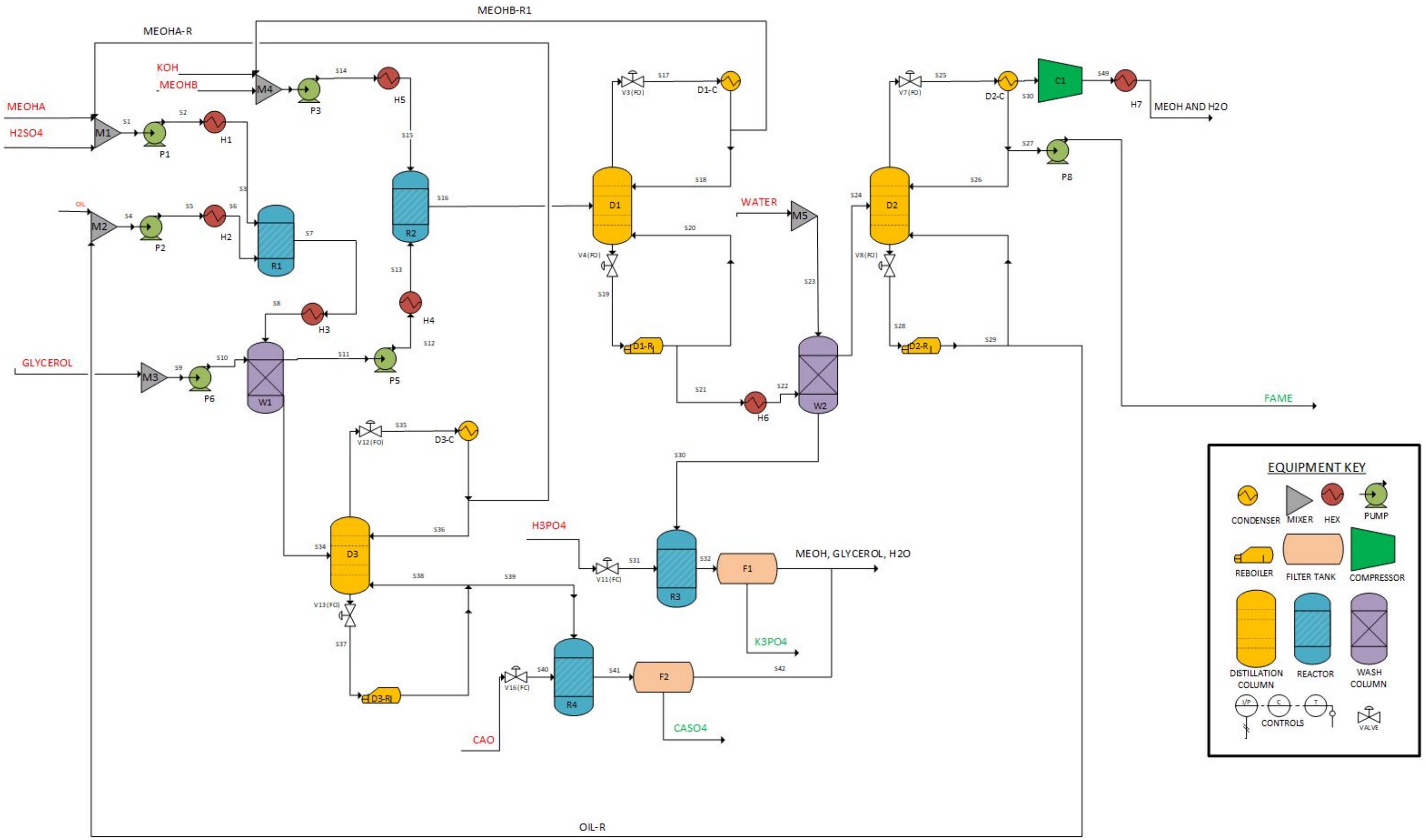
R3: Jacketed CSTR
60°C , 1 bar

Neutralize KOH with H_3PO_4 → K_3PO_4

R4: SS Jacketed CSTR
60°C , 1 bar

Neutralize H_2SO_4 with CAO → gypsum

F1 and **F2**: Filter Tanks separate precipitates



Step 8:

Oil Recovery and FAME Purification

D2: Distillation Column
6 stage
<245°C, 0.006 bar
Partial Condenser

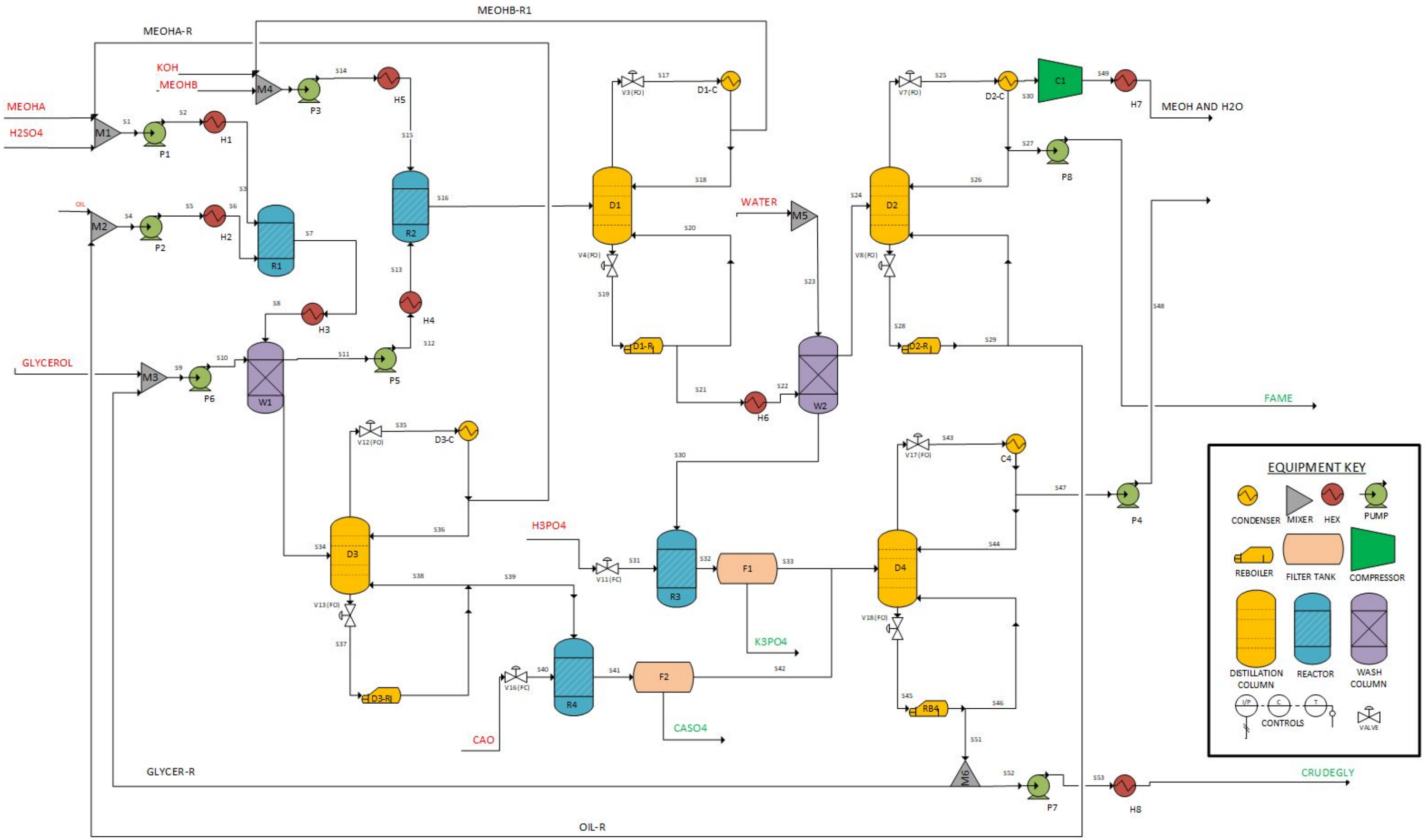
99.89 wt% FAME

Recycle unreacted TG, DG, MG

C1: Compressor
837°C

Returns WASTEH2O to 1 bar

H7: SS Hex
Cools to 60°C



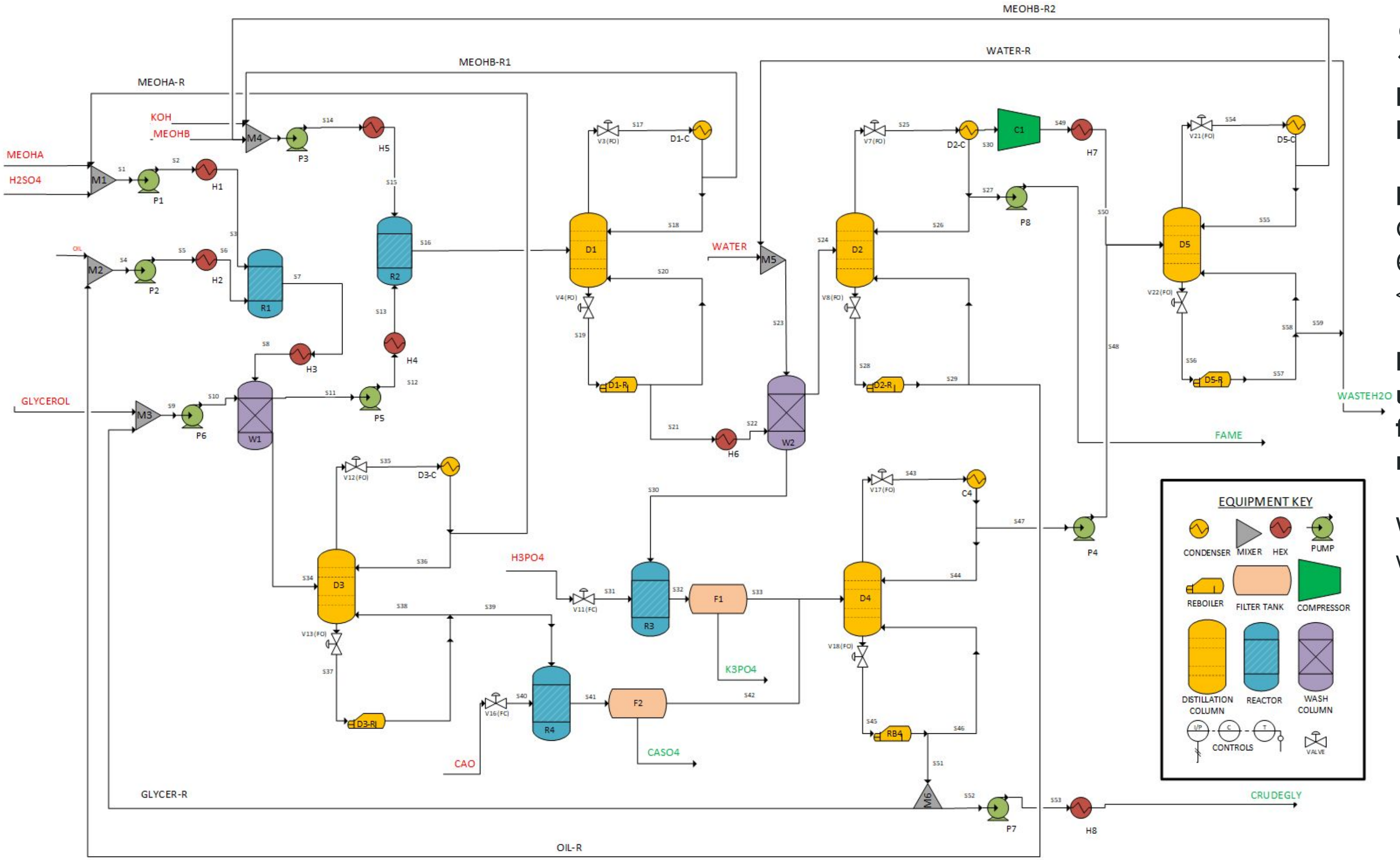
Step 9:

Glycerol Recovery

D4: Distillation Column
6 stage
<120°C , 0.45 bar

88 wt% GLYCEROL, 10 wt% MG
Bottoms recycled to W1 or sold

H2O and MEOH Distillate



Step 10:

Final Methanol Recovery

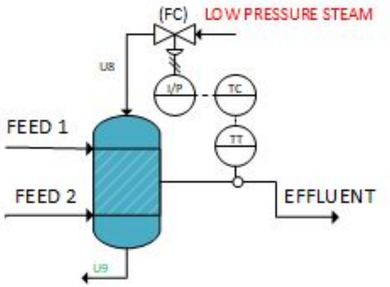
D5: Distillation Column
6 stage
<113°C , 1 bar

Recovers 95% of unreacted MEOH, for a 99 wt% recycle stream

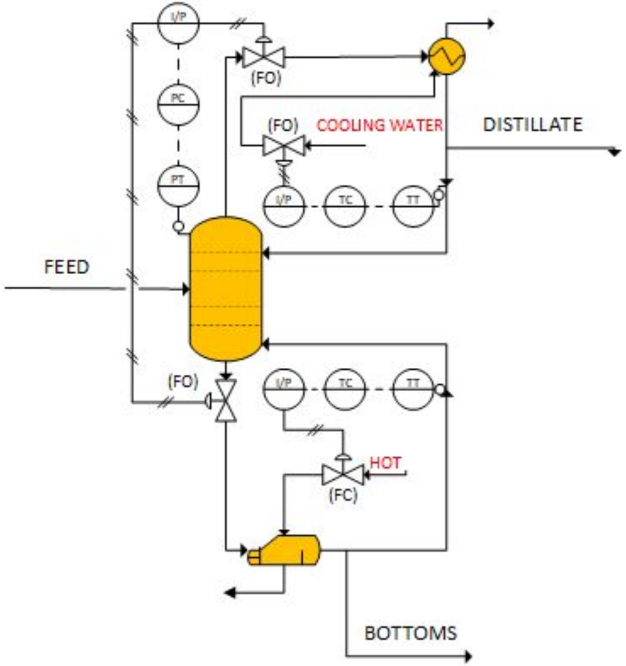
WASTEH2O is 1 wt% MEOH

Control Systems

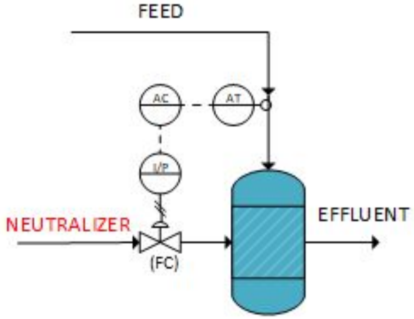
Reactors R1 and R2
Temperature Control



Distillation Columns D1-D5
Dual Temperature Control
Pressure Control

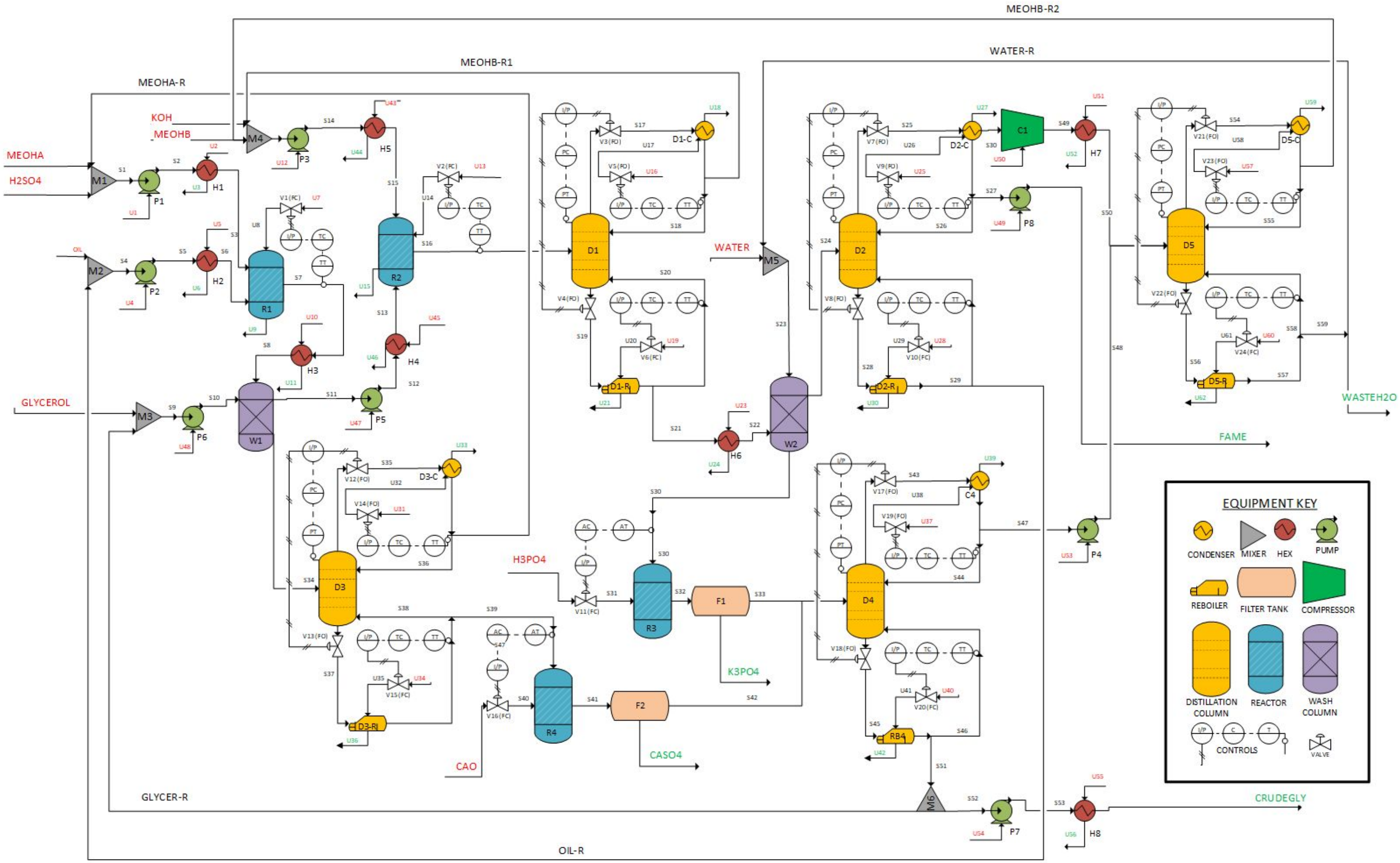


Reactors R3 and R4
Concentration Control

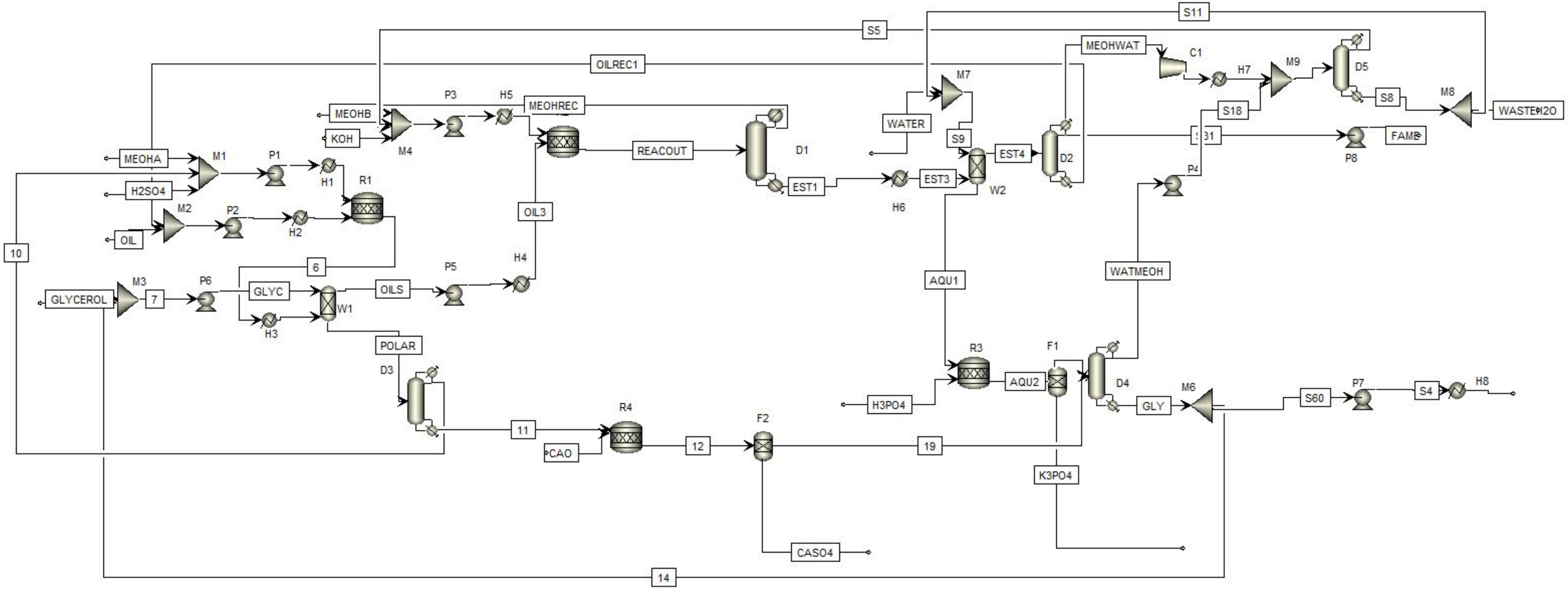


P&ID

With Utilities and Controls



Aspen Plus Simulation of the Process



Simulated Results: 16767 kg/hr of 99.89 wt%* FAME = 36.7 MMgal/oper-yr

*Exceeds ASTM standards of 99.76 wt% [1]

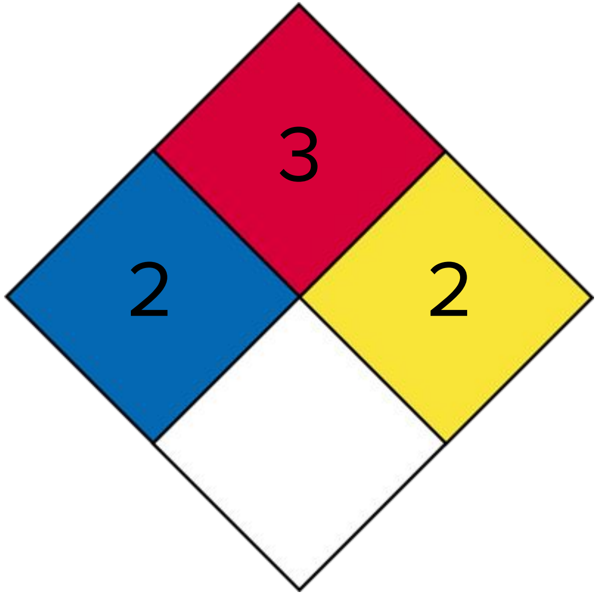
[1] "ASTM Biodiesel Specifications," Alternative Fuels Data Center: ASTM Biodiesel Specifications. [Online]. Available: https://afdc.energy.gov/fuels/biodiesel_specifications.html. [Accessed: 10-Jan-2020].

Safety: FMEA

- Several alarms will be added to the process
  - Upstream and downstream flow meters will alarm if there is a large leak anywhere
  - High pressure alarms will add a second layer of safety to reactor and distillation columns
  - Temperature alarms on distillation columns, reactors, compressors, before pumps
- Inherently Safer Design
  - Rupture Disks
  - Microreactor
  - Sloped floor leading to containment in case of release
  - Settling tanks will have safety margin in case of clogs
- Equipment made of corrosion resistant materials
  - Including all major unit ops., valves, and pipes
- Regular inspections to look for wear and other issues
  - Special attention paid to mixers and separators with solids

Safety: SDS Summary

- Methanol (vapor and liquid) [1]
  - Flammable
  - Toxic
  - Ventilation and gas sensors
- Sulfuric [2] and phosphoric [3] acid
  - Strong acids in concentrated forms
  - Corrosion resistant equipment
  - Regular inspections and preventative maintenance
- Potassium hydroxide [4] and calcium oxide [5]
  - Strong bases
  - Similar safety precautions to acids
  - Stored physically distant from acids



[1] Fisher Scientific, "Methanol, Lab Grade, 4L" Safety Data Sheet, January 8, 2015
[2] Fisher Scientific, "Sulfuric Acid 90-90%" Safety Data Sheet, April 22, 1999, [Revised February 2, 2008]
[3] Fisher Scientific, "Phosphoric acid, 85+% solution in water" Safety Data Sheet, July 6, 1999, [Revised January 28, 2008]
[4] Fisher Scientific, "Potassium Hydroxide" Safety Data Sheet, Junel 21, 1999, [Revised February 15, 2008]
[5] Fisher Scientific, "Calcium Oxide" Safety Data Sheet, October 24,2018

Economics

What it takes to break into biodiesel

Competitors

- Regional players
  - Collect oil from commercial settings
  - Process the oil
  - Sell to distributors with some margin added
- Some regional participants are offered by a parent company, bundled with other offerings
  - DarPro Solutions is a wing of Darling Ingredients, which converts edible and inedible fats into a wide range of specialty products
  - Biodiesel producers in the Midwest are often part of major agriculture companies, using their own soybeans and corn as fuel
- 1.8 billion gallons of biodiesel is produced annually
  - The biodiesel market is growing at a 6% CAGR

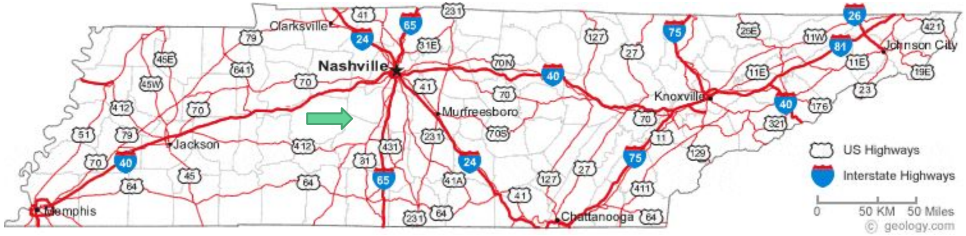
Our Differentiating Factors

- New feedstock (waste oil)
  - Allows us to purchase feedstock from sources not normally attached to the industry
- Customizable size
- Sales of glycerol byproduct makes us more environmentally friendly
- Microreactor is made of polycarbonate
  - Polycarbonate is recyclable

Biodiesel Market Pricing/Trends

- Sold at $3.73/gallon at the pump
- Sold wholesale at $3.01/gallon to distributors
  - Distributor takes 19% margin
- Argentinian and Indonesian imports are dramatically down
- Major oil refiners act as distributors and are our customers

Supply/Sales Strategy



Suppliers

- Quick Service Restaurants (QSRs) are known for their high use of cooking oil, especially those with fried food
- Chief sustainability officers often make decisions regarding supply chain sustainability
- Scaling up with these established customers will give us a reliable source of cooking oil, something that wouldn't be the case if we tried to target individuals

Location

- Boston, TN (30 miles SW of Nashville)
- Of the top 15 states in fast food consumption per capita, 13 are in the South or the eastern Midwest, making cooking oil readily available in TN and surrounding states [1]
- Biodiesel production is lowest in the South out of the major regions in the US
- Biodiesel consumption is led by trucks and Nashville is at the intersection of 3 major interstates (I-65, I-24, I-40), which trucks mostly travel on [2]
- Tennessee has no state income tax starting in 2021
- Warm enough climate to run biodiesel facility year-round

[1] https://www.businessinsider.com/states-with-most-fast-food-restaurants-per-capita-2018-6 [2] https://www.eia.gov/energyexplained/biofuels/use-of-biodiesel.php

Annual Revenue

Produce nearly 40 MMgy of biodiesel, priced at $2.41/gal to the distributor, which is 20% below market value, gives revenue stream of $93.5M annually [1]

Byproduct of 16 MM kg/year of glycerol, valued at $0.10/lb, gives revenue stream of $1.5M annually [2]

Total Annual Revenue = $95M at peak production

[1] https://www.card.iastate.edu/research/biorenewables/tools/hist_bio_gm.aspx [2] https://www.icis.com/explore/resources/news/2018/02/14/10193613/us-crude-glycerine-prices-could-dip-as-spring-nears/

Annual Costs

Raw Material - $65.5M, $52M spent on used cooking oil [1]

Production - $3.6M, split evenly between utilities and labor costs

Distribution and Collection - $3.5M, spent on renting tanker trucks per mile [2]

Reactor - 600K chips, totaling $500K per year

Total Annual Costs = $73M

[2] https://www.ams.usda.gov/mnreports/lswagenergy.pdf [2] https://www.ttnews.com/articles/cost-operating-truck-6-169-mile-atri-report-says

Initial Income Statement

Profit = $22M

Margin = 23%

Taxes = $0 due to federal incentives for biodiesel producers and no state income tax in TN, paired with the business setup as a strategic partnership [1]

EBITDA = $22M

EV/EBITDA = 17.15 for green energy sector [2]

EV = $374M

[1] https://www.tn.gov/revenue/taxes/hall-income-tax/due-date-and-tax-rates.html [2] http://pages.stern.nyu.edu/~adamodar/New_Home_Page/datafile/vebitda.html

Investment

Total Equipment and Installation Costs = $20.5M

Total Start-Up Costs = $93.5M

Initial Outside Investment = $93.5M (25% of enterprise value)

This investment will come from an individual or group and represents 25% ownership in the company, leaving the 5 other partners each with a 15% stake

Acknowledgements

Thanks to everyone who guided us throughout the project, especially:

- Mr. Rich MacLean
- Professor Abby Koppes
- Professor Webster
- Professor Pfluger
- Mr. Rob Eagan

Questions?