A Novel Membrane Reactor for the Continuous Production of Biodiesel

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Outline

- Background
- Challenges to biodiesel quality and profitability
- A solution to the challenges!
- Results, concluding remarks

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Background

- Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from lipid feedstock (e.g. vegetable oils and/or animal fats).

Lipid (TG) + alcohol → Fatty acid alkyl ester (FAAE or biodiesel) + glycerin

TG + alcohol → DG + FAAE
DG + alcohol → MG + FAAE
MG + alcohol → FAAE + Glycerin

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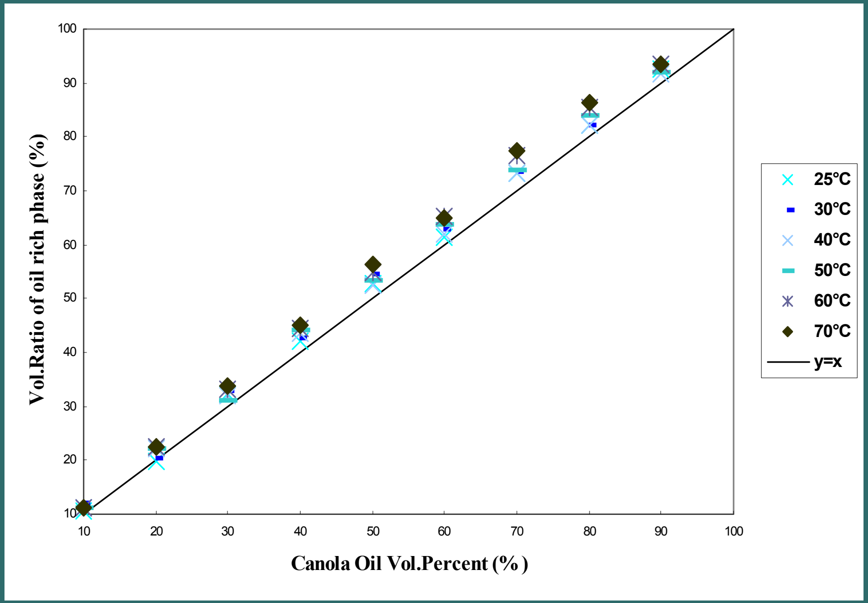
Current challenges in commercial production of biodiesel

1. Mass transfer limited reaction rate: lipids and methanol or ethanol are immiscible under normal reaction conditions.
   – Improve mixing (energy costs)
   – Mutual solvent (separation costs)
   – Other alcohol (cost)



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Current challenges in commercial production of biodiesel

2. Incomplete conversion due to reversibility of transesterification reaction: leads to low quality biodiesel (presence of TG, DG, MG) and loss of reactants.
   - Force equilibrium to products by adding excess alcohol (costs)
   - Use of extreme reaction conditions (energy costs)
   - Multiple water washes (cost, generation of waste)
   - Unreactables?

"Reaction completeness is the most critical fuel quality parameter." (Van Gerpen 2005, *Fuel Proc. Tech.*, 86:1097-1107)

Current challenges in commercial production of biodiesel

3. High cost of virgin feedstock leads to use of low cost feedstock which is high in water and/or FFA:
   - difficult downstream purification (soaps)
   - poor cold flow properties
   - 2-step acid/base or 1-step acid reaction (see Zhang et al. 2003 *Biores. Tech.* 89:1-16, 90:229-240)

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Current challenges in commercial production of biodiesel

4. Traditional downstream purification such as water washing to remove excess alcohol and catalyst may generate large amounts of toxic waste water and incur high energy costs.
   – Heterogeneous catalysts?

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Current challenges in commercial production of biodiesel

5. Most commercial processes are run in batch mode.
   - Continuous reaction can lead to reduced down-time, higher throughput, more stable operation.

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Objectives

- Develop a continuous reaction process for the production of biodiesel and overcome the challenges due to mass transfer limitations, incomplete conversion, use of high FFA feedstock and downstream purification.
- Investigate different factors affecting the production process and the biodiesel purity.

A promising solution: membrane reactor

- Definition: a device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure.
- Theory: due to the immiscibility of lipid feedstock and alcohol, lipids form droplets which are excluded from passing through the membrane pores. The micro-porous inorganic membrane selectively permeates FAAE, alcohol and glycerol while retaining the emulsified oil droplets.

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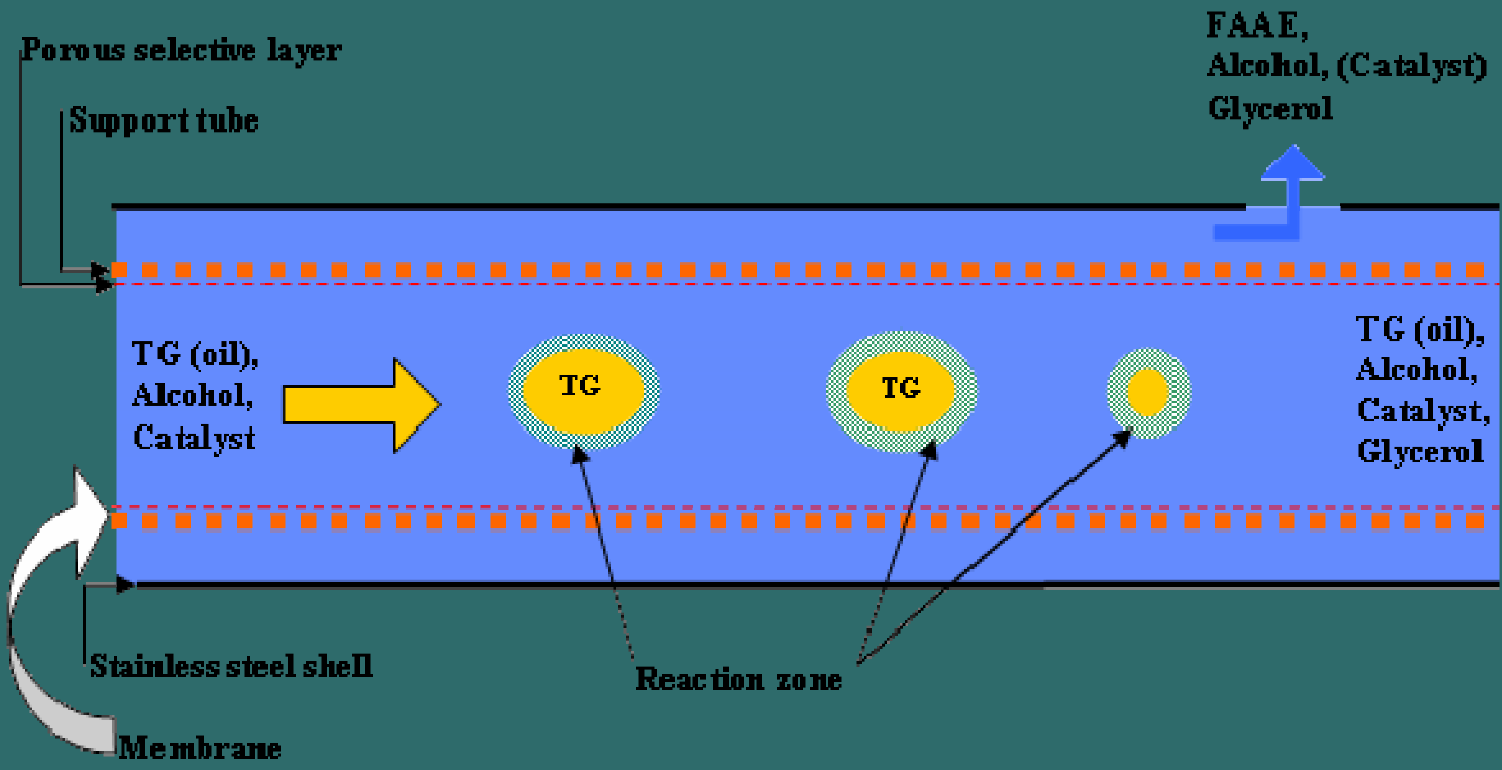
Principle



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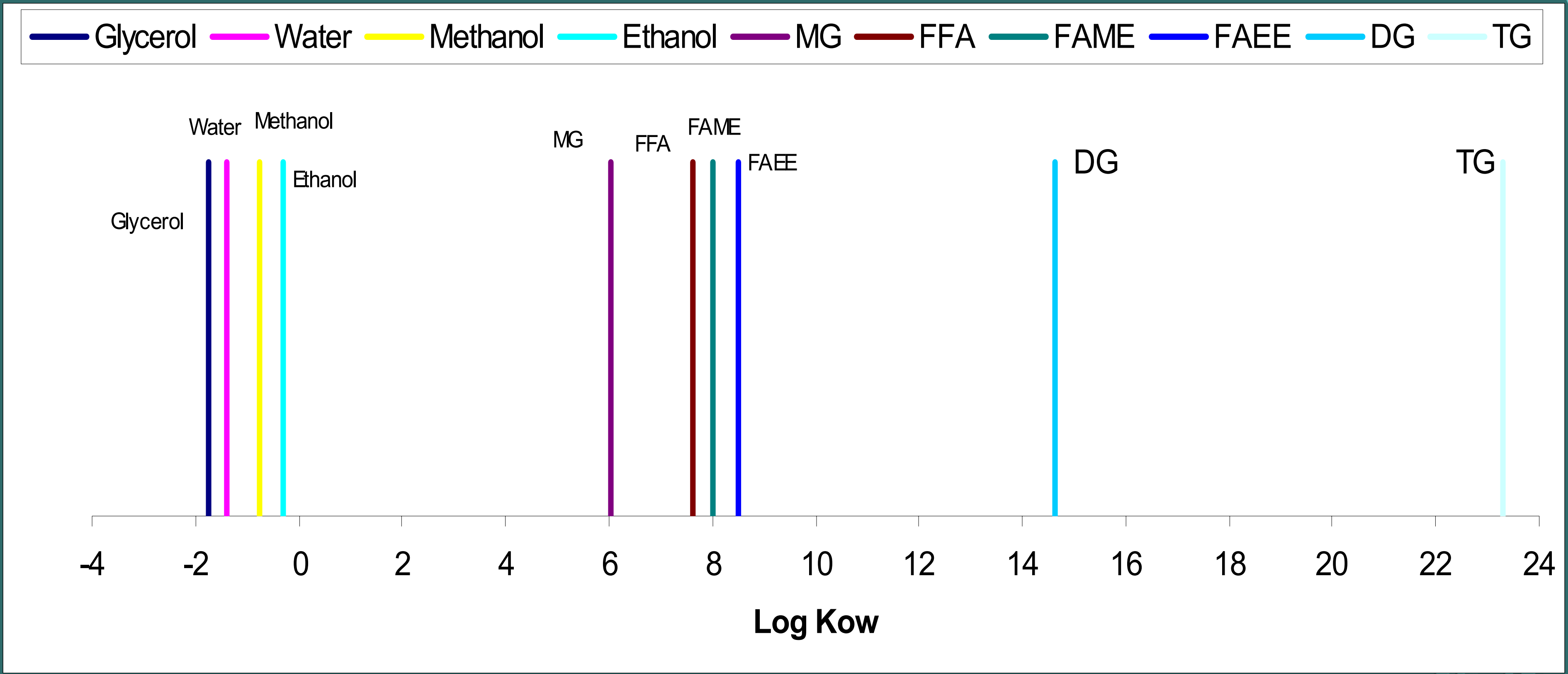
Principle



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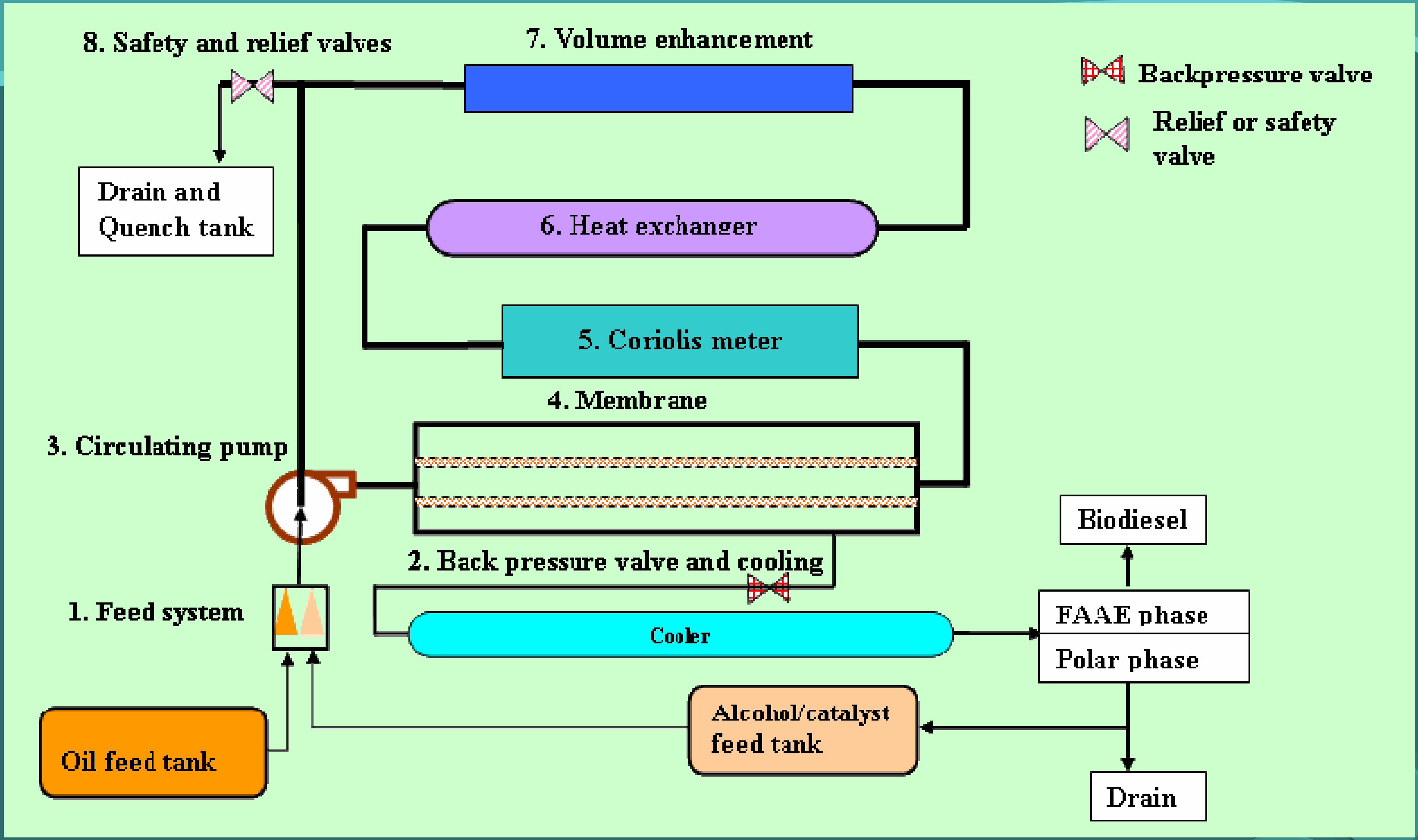
Inorganic membranes

- Inorganic to resist methanol, FAAE, catalyst
- Can be bundled to increase surface area

Prototype reactor



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Experimental

- **Reagents:**
  - Lipid feedstock: virgin canola oil, virgin palm oil, yellow grease, waste canola oil
  - Alcohols: methanol, ethanol, alcohol blends, denatured alcohol
  - Catalysts: sodium hydroxide, sulphuric acid
- **Reaction conditions:**
  - Alcohol:lipid molar ratios from 50:1 to ~6:1
  - Temperatures from 55 to 70^{o}C
  - Catalyst concentrations from 0.5 – 2 wt.% (base), from 1 – 5 wt.% (acid)
  - Circulating flow rates from 90 to 180 kg/min
  - Reactor residence times from 1 to 3 h
- **Characterization: HPLC, GC**

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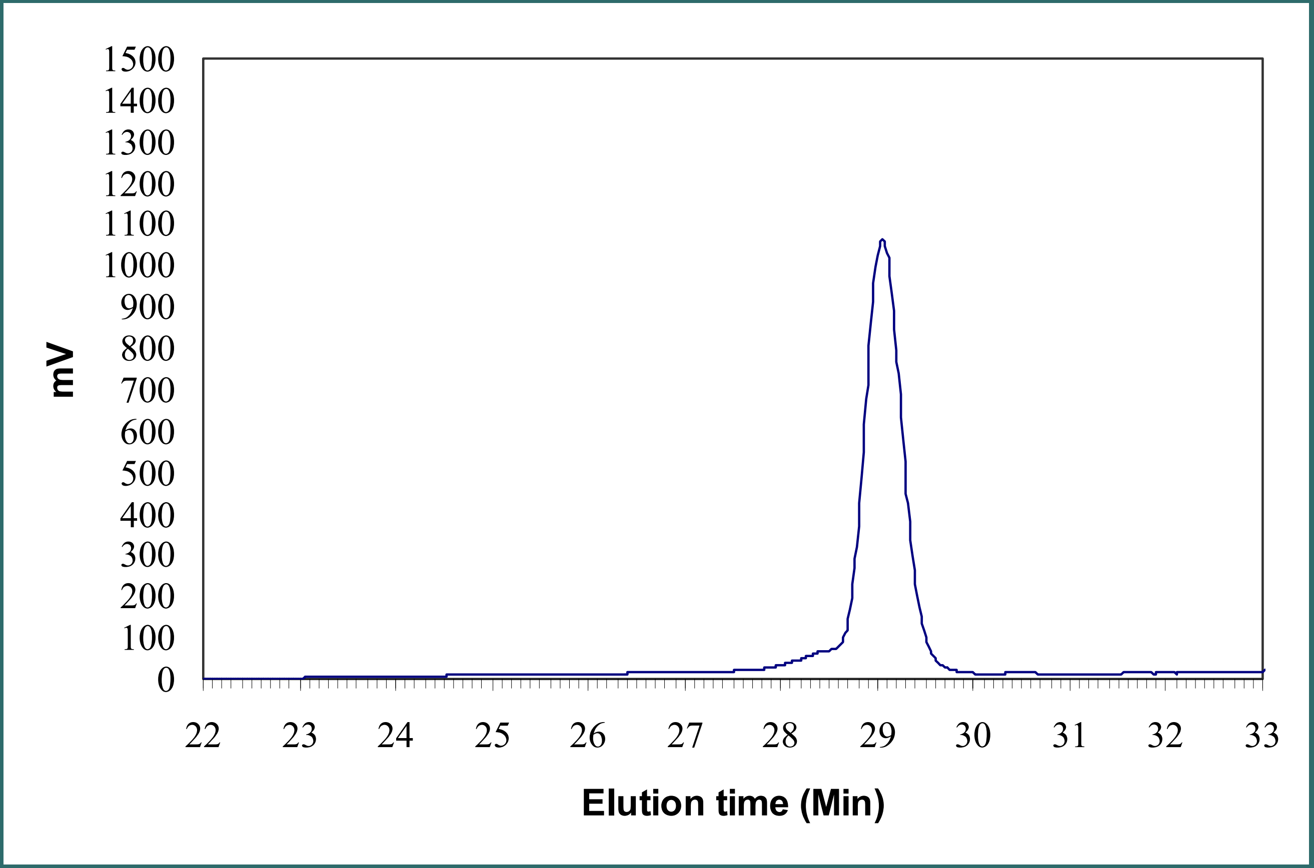
Experimental

- **Procedure:**
  - Alcohol/catalyst and lipid feedstock are charged to the reactor loop and heated to the reaction temperature.
  - Circulation pump is used to provide a cross-flow through the membrane reactor loop.
  - Semi-continuous or continuous feeding of alcohol/catalyst and/or lipid feedstock at a controlled molar ratio ensures a trans-membrane pressure causing the permeation of FAAE/alcohol/glycerol/catalyst while retaining the lipid feedstock inside the membrane reactor loop.

Results and observations

- Due to immiscibility of lipid feedstock and alcohol, emulsion formed in circulating loop of membrane reactor.
- Formation of large lipid droplets (diameters = 20 to 1800 microns) prevents permeation of lipid through membrane pores (pore diameter <1.4 microns).
- FAAE, alcohol and catalyst being miscible, pass through membrane pores. Some glycerol also passes through membrane pores.
- RESULT: NO lipids (TG, DG, MG) in the permeate stream! High conversions not required.
- Free and total glycerin contents of biodiesel easily meet international standards for purity.

Results and observations



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Results and observations

- Low quality feedstock (e.g. yellow grease, FFA content ~17wt%) reacted with base catalyst.
- Formed soaps appeared to be retained in membrane reactor resulting in straightforward purification of FAAE in the permeate.
- Membrane also retained particulate and unreactable matter, thus eliminating presence of stable emulsion phase on washing biodiesel.

Soaps

Washed permeate

Washed retentate

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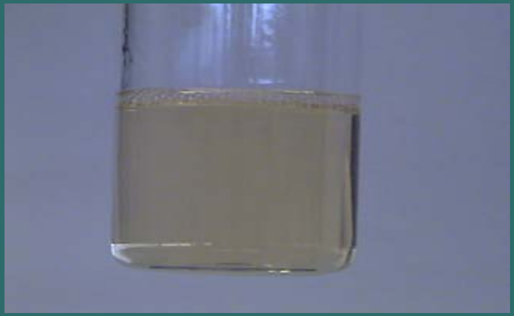
Results and observations

- **Permeate readily de-phased at room temperature:**
  - permitted recycling of polar phase from permeate stream
  - allowed for lowering of overall alcohol:lipid molar ratio to ~6:1.



Homogeneous permeate

Cool to ~25°C

De-phased permeate:
FAAE
Glycerol

ASTM results

- Free glycerin: 0.002 mass% (max. = 0.020)
- Total glycerin: 0.037 mass % (max. = 0.240)
  - TG < 0.001 mass%

Permeate ~25^{o}C

Water wash

Biodiesel

Membrane reactor advantages

1. No bound glycerin
2. Enhanced reaction rate
3. Easy separation of products
4. High FFA feedstock handling
5. Continuous flow
6. Blocks most impurities
7. High purity biodiesel!

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Concluding remarks

- Membrane reactor for continuous production of biodiesel from various lipid and alcohol feedstock has been developed: results in high purity biodiesel which meets standards such as EN14214 and ASTM D6751.
- Ability of reactor to produce biodiesel from variety of lipid feedstock, some containing high amounts FFA, has been demonstrated.
- The membrane reactor was particularly useful in retaining TG, DG, MG, soaps and most of the glycerol. These findings indicate excellent potential for the commercial use of this reactor.

Concluding remarks

- Petrodiesel production: use of distillation to purify leaving behind tars
- Conventional biodiesel production: unreactables remain (distillation is not cost effective)
- Membrane reactor offers a radical change in quality: unreactables removed

Acknowledgements

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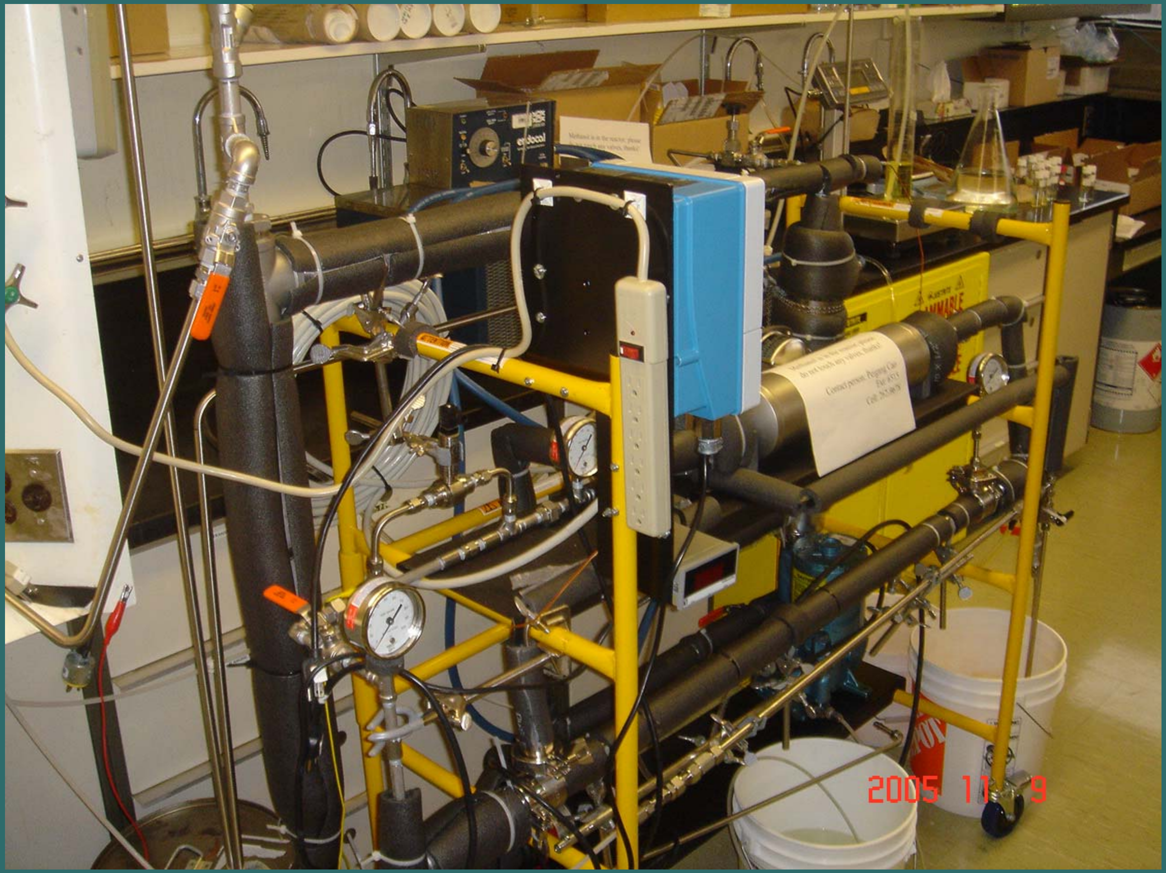

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