Methanol Purification for Low-Cost Biodiesel Production

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Sponsored by Beaver Biodiesel, LLC.

Introduction

Biodiesel Production

Biodiesel is produced through a base catalyzed transesterification reaction using methanol and waste vegetable oils (Triglycerides) to produce fatty-acid methyl esters (biodiesel) and glycerol.

![Triglyceride to Biodiesel Reaction](image)

- Excess methanol is often used to ensure complete conversion of triglycerides.
- Unreacted methanol remains in the reactor as a by-product of the biodiesel reaction. Other minute by-products:
  - Water
  - Soaps
  - Mono- and di-glycerides

Methanol Recovery

- Unreacted methanol can be recovered, purified and recycled into the front end of biodiesel production by removing excess water (dehydration).
- Common dehydrating methods are distillation or adsorption using a molecular sieve.
- Distillation has been ruled out for this process due to low methanol production volumes.

Zeolite (Aluminosilicate Molecular Sieve)

- Methanol dehydration can be completed via adsorption of water into a porous molecular sieve.
- Aluminosilicate zeolites contain polar, 3 Å pores that attract 2.7 Å H₂O and reject 4.1 Å methanol.
- Adhesion of the water molecules with the zeolite surface is exothermic, releasing ~420 kJ/mole.

Methodology

Process design was split into a dual investigation of adsorption and regeneration experiments with 8-12 mesh, 3 Å zeolite beads.

**Adsorption**

Adsorption experiments conducted in model adsorption column to find superficial velocity suitable for scale-up.
- u<sub>flow</sub> design
- 85.95% MeOH by mass at inlet
- Superficial velocities of 1-4 cm/min
- Examples: test specific gravity and temperature, then translate data to MeOH purity (% by mass)

**Regeneration**

- Low shear methods to preserve zeolite life-span
- Methods involving heating to overcome enthalpy of adsorption
- Low capital and labor investment to maximize profitability
- Longevity experiments indicate high regenerability

Results

- Experiments with a number of different drying methods indicate the need for an in situ regeneration method, as the zeolite is prone to failure if moved.
- Two heat transfer regimes modeled: conductive and convective.
- Data indicate that heating without convection causes saturated conditions within the zeolite containing vessel and retards evaporative regeneration.

Proposal

The project team recommends a dual column design for water adsorption and zeolite regeneration for the methanol purification project.

Efficient Regeneration

Regeneration should be accomplished by heating the zeolite inside the reaction column with flowing dry air. Zeolite manufacturers recommend regeneration temperatures of between 135 and 300°C. We recommend 150°C incoming air to minimize combustion risk and capital expenditure. Mass flow rate of incoming dry air is determined through an energy balance on the system, divided into two phases: 1) heating water to the saturation point and 2) vaporizing the water.

![Regeneration Calculations](image)

Solving the equation and adjusting for 100% relative humidity conditions at the column exit, the total mass of dry air needed to regenerate the zeolite is approximately 2,300 kg.

Operating Description

Process Flow Diagram

Economic Analysis

![Economic Analysis Diagram](image)

**Table:** Capital cost estimation and equipment list for proposed methanol purification process.

<table>
<thead>
<tr>
<th>Item Description</th>
<th>Quantity</th>
<th>Cost (in $)</th>
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<tbody>
<tr>
<td>Flux Assembly</td>
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