Methanol Purification for Low-Cost Biodiesel Production

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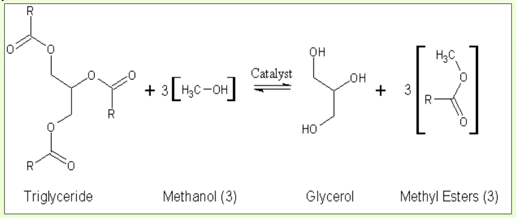
Sponsored by Beaver Biodiesel, LLC.

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.



• 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)

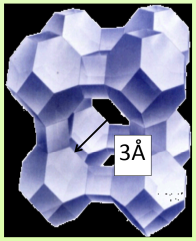


Image from: http://www.molecularsieve.org/Zeolite_Molecular_Sieve.htm Accessed 5/15/2011

•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 H_2O and reject 4.1 Å methanol.

•Adhesion of the water molecules with the zeolite surface is exothermic, releasing $\approx 4200 \frac{kJ}{kgH_2O}$.

•Water is held against interior pore surfaces through weak Van Der Waals forces.

Objective Statement

Design a cost effective process to dehydrate 200 GPD of 90% methanol by mass to 99% methanol by mass for use in biodiesel production.

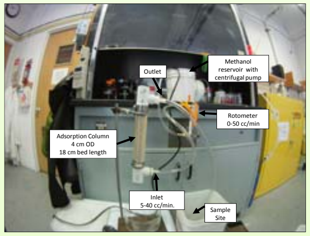
Methodology

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.

•Upflow design
•85-95 % MeOH by mass at inlet
•Superficial velocities of 1-4 cm/min
•Sample, test specific gravity and temperature, then translate data to MeOH purity (% by mass)



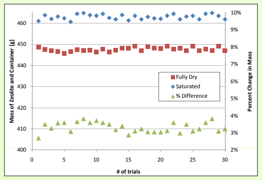


Figure: Cycling experiments indicate zeolite is fully capable of 30+ regeneration cycles without loss of adsorption capacity

Regeneration

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

Results

Adsorption

Adsorption experiments indicated a process with effluent recycle is needed to utilize zeolite adsorption capacity effectively.
Experiments with model adsorption column indicated a superficial velocity of 1 cm/min to be the optimal velocity for scale-up design.

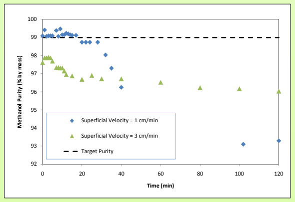


Figure: Methanol purity (% by mass) of effluent from model adsorption column for superficial velocities of 1 and 3 cm/min. Superficial velocity of 1 cm/min was selected for basis of scale-up design.

Regeneration

Experiments with a number of different drying methods indicate the need for an *in situ* regeneration method, as the zeolite is prone to fracture 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.

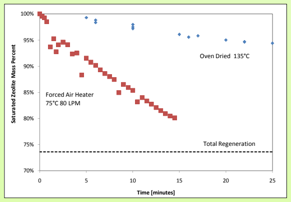


Figure: Saturation of zeolite over time during regeneration by two different drying methods. forced convection is necessary for economical drying.

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 200˚C.
We recommend 150˚C incoming air to minimize combustion risk and capital expenditures.
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.

$$m_{air} = (m_{air1} + m_{air2}) = \left[\frac{m_{H_2O}\left(\int_{T_i}^{T_{Sat}} C_{p,H_2O} + \Delta H_{rxn}\right)}{\int_{T_{i,Air}}^{T_{f,Air}} C_{p,Air}} \right] + \left[\frac{m_{H_2O} \times \Delta H_{vap}}{\int_{T_{i,Air}}^{T_{f,Air}} C_{p,Air}} \right]$$

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

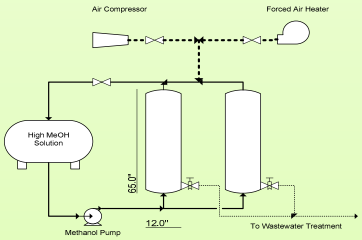


Figure: Proposed design of the methanol dehydration/zeolite regeneration system. Dual reactors are connected to the methanol reservoir in an up-flow configuration to allow for the low rate of flow. The exiting lines for the purified methanol become the feed lines for the compressed air and heated air during the regeneration phase of the process. Compressed air should be used to remove hold up of bulk solution. Recommended heated air flow rate is 10 m^3/min.

Figure: Gantt chart outlining 24 hour purification cycle for 200 GPD, 90 % methanol by mass for the recommended purification process.

Economic Analysis

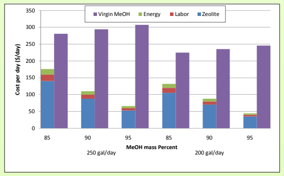


Figure: Estimated operational cost compared to virgin methanol cost for same volume of purified methanol for 200 or 250 GPD and 85, 90, or 95% methanol by mass. Operational costs are broken into energy, labor, and zeolite costs.

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

Part	Type	Quantity	Cost
Forced Air Heater	Taketsuna TSK-51B	1	$3000
Liquid Solution Pump	Dayton Centrifugal	1	$400
Piping	1 1/2" galvanized	≈30 ft.	$17.00/ft.
Valves and Fittings	Air/Water Tight	5-7 valves	$80.00/valve
	Valves and Sealing Fitting	Many misc. fittings	$200
		Total	$4670.00

Table: Estimated payback period in days to recover capital investment from methanol savings for proposed purification process

Methanol Volume (GPD)	Methanol Purity (% mass)	Payback period (days)
250	85	47
250	90	27
250	95	21
200	85	56
200	90	35
200	95	26

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