

***Ins and Outs of Methanol
Recovery and Reuse in
Biodiesel Manufacturing***

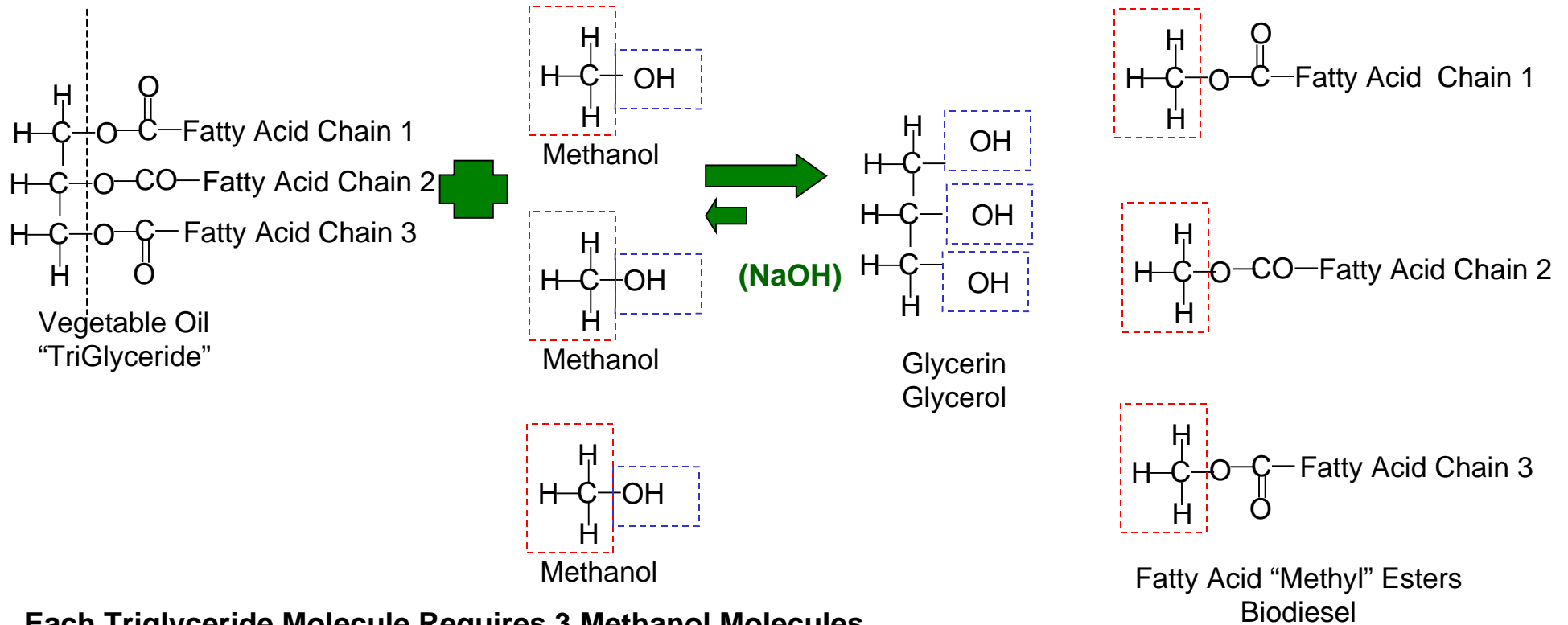
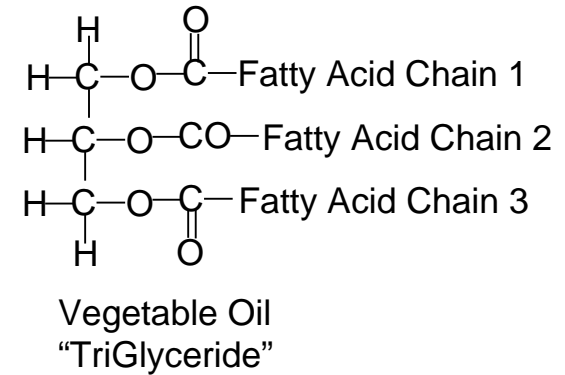
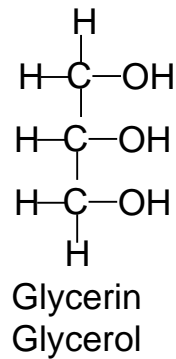
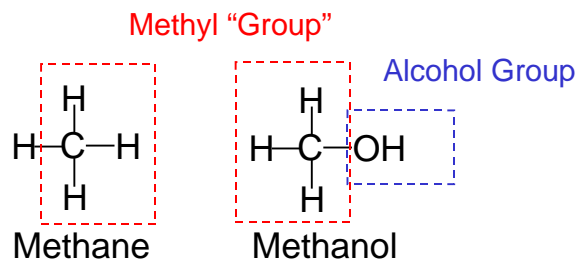
The Biodiesel Collective Conference

July 18-20, 2008

Presented by Gary Schmidt



Basic Biodiesel Chemistry



Each Triglyceride Molecule Requires 3 Methanol Molecules

The Process

Add 100 lb. of TriGlyceride oil + 21.5 lb. methanol (6:1 molar ratio) 13 Gallons Oil + 3.3 Gallons MeOH

Plus 0.35 to 1.0 lb. of NaOH or KOH catalysts

To make 100.5 lb. Biodiesel + 10.5 lb. glycerin + 10.5 lb. of excess methanol + 0.35-1lb. Catalyst
13.6 Gal. Biodiesel + 1 Gal. Glycerin + 1.6 Gal. MeOH + Catalyst

Excess Methanol

Required to Force Reaction to Completion

6:1 Molar Ratio Typically Required (Double)

Results in 50% Methanol Excess

Ethanol Requires More Excess

Cheating Can Lead to Issues

The Products

Typical Post Separation-(Feedback from Customers)

Ester Phase

30% of Excess MeOH (~3%wt.)

<1%Glycerin

Trace Catalyst, Trace Water

Trace Other Stuff (Soaps and Un-reacted Stuff)

Glycerin Phase

70% of Excess MeOH (35-40%wt.)

Most Catalyst, Most Water

More Other Stuff

Why Recover MeOH?

Cost of MeOH

Virgin Material Costs

Pricing Volatility

Glycerin Disposal

Maybe Affected by MeOH Content

Required Removal from Ester Phase

How?

Ester (Biodiesel) Phase

Vacuum Flashing

Stripping with Air or N₂

Water Washing

Meeting ASTM 6751 and EN 14214 Specs

Glycerin Phase

Vacuum Distillation

End Point Dictates Process

Results in Crude Glycerin Product

Ester Phase (30%wt of Total Excess MeOH)

Vacuum Flashing

- Water* and MeOH both removed
- Can produce very low MeOH and water levels in Esters
- Can meet both ASTM and EN Specs
- Energy Recovery minimizes energy input
- Can control MeOH VOC emissions

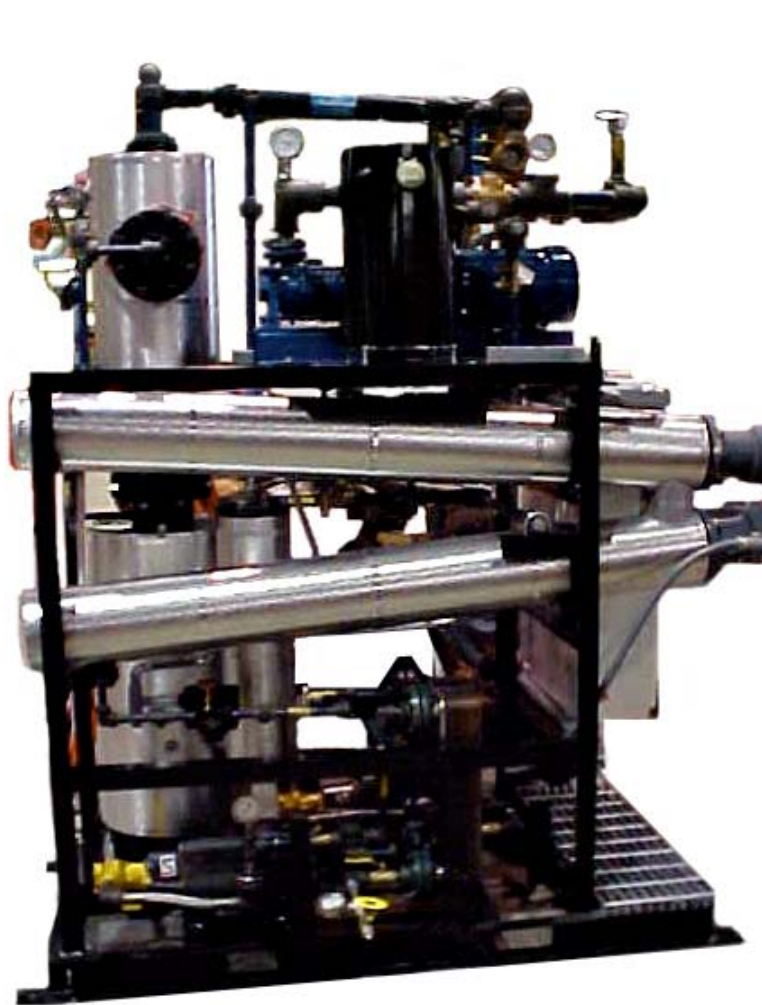
Stripping with Air or N2

- Water* and MeOH both removed
- High Air, N2 volumes required
- More difficult to meet specs
- More difficult to control VOCs

Water Washing

- Removes MeOH by extraction
- Meets ASTM and EN for MeOH ONLY not water
- Requires “Dryer” to reduce water levels

120 GPH Biodiesel Dryer



Glycerin Phase (70% of Total Excess MeOH)

Vacuum Distillation

Only Available Method

Water and MeOH Both Removed

Glycerin Disposal Dictates MeOH Level Required

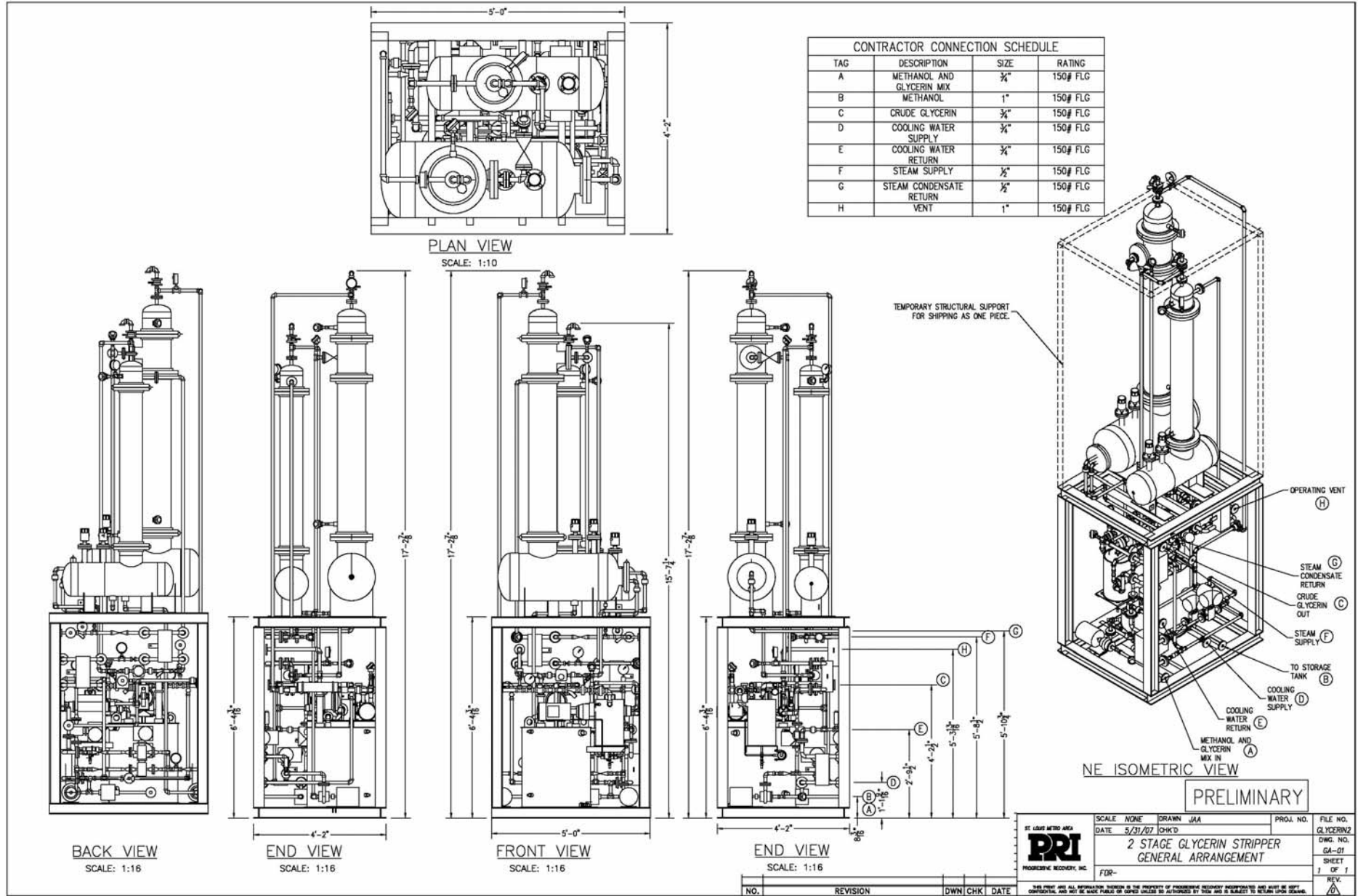
End MeOH Level Dictates Process

Costs vary significantly

Results in Crude Glycerin Product

Once Water and MeOH are Removed Glycerin Solidifies

350 GPH Glycerin Stripper



Issues

Water and What To Do About It

Sources

Feedstocks

Catalyst Blending

Esterification of FFA

Will Follow MeOH Almost 100%

Removed MeOH Will Contain ALL Water in Process

Water Can be Removed From MeOH

Distillation Column

Very Expensive

Molecular Sieves

Expensive and Limited to Small water %

Dry Feedstocks and MeOH Before Use

“Wet” MeOH Can be Blended for Use

Issues

VOCs are Everywhere

EPA Compliance Issue

Sources

Any Vented Tank, Drum or Process Vent
Created Anytime MeOH is Transferred
Volume Can be Significant From Process Vents

Safety Issue

Vapors Heavier Than Air will Linger in Low Areas
Vapor Air Mixtures Very Flammable
MeOH Inherently Toxic

Control

Condense Vapors with COLD
Use of N₂ Blankets and Conservation Vents
“Protecto Seal” Vents



Issues

Glycerin Solidification

Once Water and MeOH are Removed Below Certain Levels Glycerin Will Solidify When Cool

Care Must be Taken in Process Design to Keep from Causing Issues on Shut Down

Design of Storage and Handling Systems

Disposal?

Do not Remove Water and MeOH Below Thresholds

Adding Water (no MeOH) Solves Issue

Safety

Electrical Area Requirements

NEC Section 501

Class I Grp D, Div I and Div II Mandatory (X-Proof)

Indoor Ventilation

Proximity to Other Equipment

Storage and Handling

NFPA

Grounding and Bonding

Can I? Should I?

It's All (or mostly) About Money

Significant Capital Requirement

Removal of MeOH from Different Streams

Removal from Biodiesel Required

Removal from Glycerin Optional

Separation of Water from MeOH

Significant Capital Required

Purity of Waste Water an Issue

Water Wash Process May Dictate MeOH Removal

But I Want To

It's Still All (or mostly) About Money

Material Energy Consumption

Energy Use Can be Significant

Ongoing Expense

Variable Expense

Multiple Utility Requirements

Steam or Hot Oil Systems

Chiller Systems (in addition to Cooling Water)

But.....

It Really Is All (or mostly) About Money

Probably Not Justifiable Below 5-7MMGPY Production

Assume 11%vol of Production is Excess MeOH

1MMGPY Production=110,000GPY Excess MeOH

Capital Cost of all Equipment 400-500K Minimum
For Complete MeOH Recovery and Reuse

10MMGPY+ Plants Easily Justify

Co-Op or Third Party Processor Viable for Small Producers

Can Sell By-Product to Third Party for Processing or Resale

Co-Op can "Buy and Sell Back"

Watch Out for Recycling Regulations

