Technical Discussion of Community Scale Biodiesel Production

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Safety and Quality are Important!

Worker and Plant Safety:

- Top Management support
- Safety by Design (Engineering Controls)
- PPE
- Proper training
- Written SOPs, safety program, and training documents.
- Proper Training
- Hazard analysis and communication

Fuel Quality:

- Top Management support
- Written Quality Assurance Plan
- Test all fuel 30 days or less before shipping
- Create, send, and keep a Certificate of Analysis (COA) with every shipment
- Get periodic 3rd party full slate testing

Holding ourselves to high safety and quality standards strengthens our voice in the biodiesel industry

The Reactions

- Transesterification:

$$\text{Tri-Glyc} + 3\text{MeOH} \xrightleftharpoons{\text{KOH}} 3\text{FAME} + \text{Glyc}$$

$$\text{FFA} + \text{KOH}_{(aq)} \longrightarrow \text{Soap} + H_2O$$

$$\text{Tri-Glyc} + \text{KOH}_{(aq)} \longrightarrow \text{Soap} + \text{Di-Glyc}$$

- Acid Esterification:

$$\text{FFA} + \text{MeOH} \xrightleftharpoons{H_2SO_4} \text{FAME} + H_2O$$

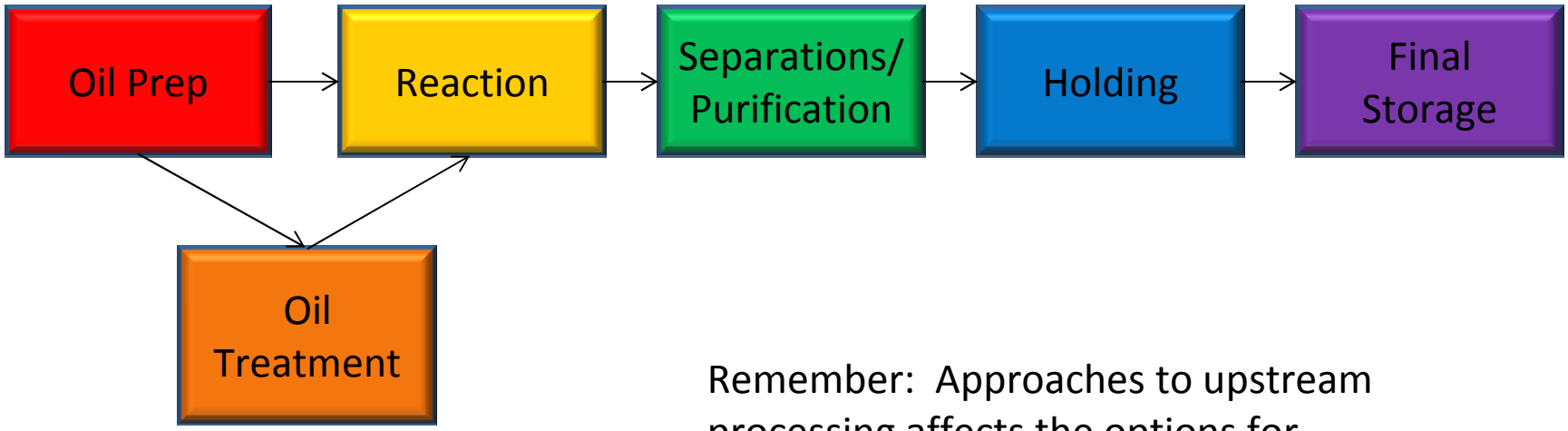
$$\text{Soap} + H_2SO_4 \longrightarrow \text{FFA} + KHSO_4$$

$$KHSO_4 + \text{Soap} \xrightleftharpoons{} \text{FFA} + K_2SO_4 \quad \text{(lesser reaction)}$$

$$\text{Tri-Glyc} + 3\ \text{MeOH} \longrightarrow \text{Glyc} + 3\text{FAME} \quad \text{(lesser reaction)}$$

Note: The forward and reverse arrows do not necessarily indicate whether the reaction is chemically reversible, rather they indicate the reversibility we may find in our process conditions.

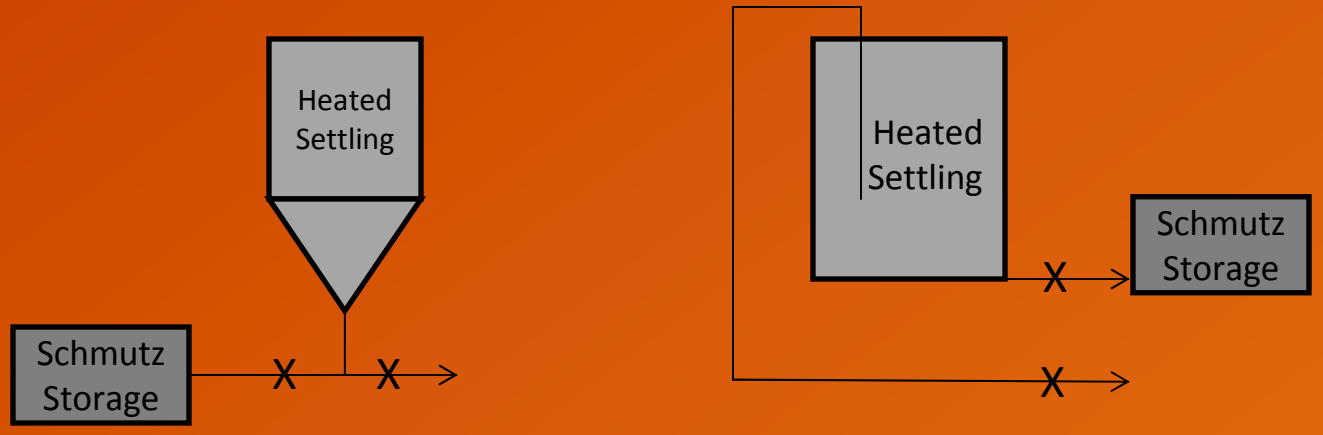
A General Biodiesel Production Process



Remember: Approaches to upstream processing affects the options for downstream processing

WVO Preparation (Schmutz removal)

- Typical assumption: WVO from a restaurant contains 15–20 vol% food/water (schmutz) and has 2–10 wt% FFA
- Schmutz is often removed using heated settle (165 – 185 °F) followed by filtration.
- Insulated tanks save $$$!
- Filtration is optional (100 micron recommended)
- This typically reduces moisture to ~0.7 mass% (7000 ppm)



WVO Preparation (moisture polishing)

- Good separation from Schmutz is important because food particles hold water.
- After Separation, heated recirculation overnight with an open lid is an effective and simple way to polish moisture from 7000 ppm to < 500 ppm.
- Ventilation is important if moisture polishing is done indoors; the fumes are irritating to the nose, throat, and lungs.

Oil Treatment

- If the oil is raw and unrefined, then degumming should be done.
- If the FFA > 7 % then the oil should be treated before transesterification.
  - Caustic stripping using glycerin
  - Acid Esterification
  - Glycerolysis

Oil Treatment (Caustic Stripping)

- Add ~half a batch worth of glycerin bottoms from a previous batch to a full batch worth of oil. Entire contents should be ~140 °F.
- Turn on recirculation pump and shine a light through a bottom site tube, when it stops looking like bottoms, stop the pump and allow to settle for ~ 30 minutes.
- Repeat 3 times and allow to settle for an hour after third mix.
- Drain glycerin, and react batch.

Notes: the color change between phases can be subtle and difficult to discern. Overmixing can exacerbate the situation.

Typical results:

Initial FFA = 4.2 % Final FFA = 3.0 %

Initial moist = 0.74 % Final moist =0.54 %

Oil Treatment (Acid Esterification)

- There are several ways to perform this FFA reducing technique. I recommend the below method because it does not result in an acidic methanol side stream.
  - Prep oil to < 300 ppm moisture.
  - Using the soap and acid values, calculate the acid and methanol required. Note: use 98 wt% sulfuric acid.
  - Mix acid with methanol thoroughly then add the solution to the oil at ~140 °F.
  - Mix for 2 to 8 hours testing the FFA periodically until it is reduced to ~2% or lower.
  - Subtract the amount of methanol used in the esterification from the typical batch recipe. Use the remaining amount of methanol to mix the methoxide solution and proceed with a two stage reaction.

  Notes:

  Danger! 98% Sulfuric Acid is extremely corrosive. It damages many materials (including stainless steal). It is a very toxic health hazard.

  Be aware, this technique is sensitive to moisture, without tight moisture control, the batch can emulsify.
- Good for oil up to ~10% FFA

Oil Treatment (Glycerolysis)

- Uses glycerin to convert FFA's to glycerides
- Results in a low FFA oil from up to 100% FFA stream
- Requires high temps (in the 450 °F range)
- Established Technology
- See Kirk Cobb, "Energy Consumption: Acid Esterificatioin vs. Glyceroysis." *Biodiesel Magazine.* July 18th, 2012 for further discussion.

Reaction (Batch)

- Batch reactors (sodium/potassium hydroxide catalyzed):
  - Oil Quality: < 4% FFA and < 2500 ppm moist

    Note:FFA and moisture limits are related: if FFA is lower then higher moisture can be tolerated and vice versa.
  - Hold temperature as close to the boiling point temp of methanol (148.5 °F) as your process control will allow. Err on the side of lower.
  - Head space exchange with the methoxide mixing tank allows for vapor containment as well as some flexibility with temperatures at or slightly above the boiling point of methanol. Be care not to apply negative pressure to the reactor if it is not rated for vacuum.
  - 2 stage reaction helps bring reaction to completion.
  - Feeding the methoxide solution slowly at a point slightly upstream of the mixing pump inlet promotes good reaction.

Reaction (Continuous)

- Continuous reactors:
  - –Continuous cavitational reaction
    - Oil quality and catalysis is similar to that of batch discussion.
    - Streams mixed in a way that completes the reaction in-line and no further reactor tank recirculation is required.
  - –Heterogeneous type mineral catalysis
    - Plug flow reactor (packed column)
    - Similar reaction dynamic as traditional hydroxide that allows for continuous reaction
    - Maybe one plant in operation in the US based on this technology?
  - –Enzymatic catalysis
    - CSTR? (perhaps other continuous and batch options)
    - Can handle higher FFA and moisture in oil
    - Cleaner glycerin co-product
    - Pricey and fragile catalyst
    - Offers great potential; not sure at what scale
- Continuous reactors tend to operate best in 24/7 (or at long runs). Are continuous reacting schemes a wise direction for the community scale biodiesel sector?

Separations/Purification

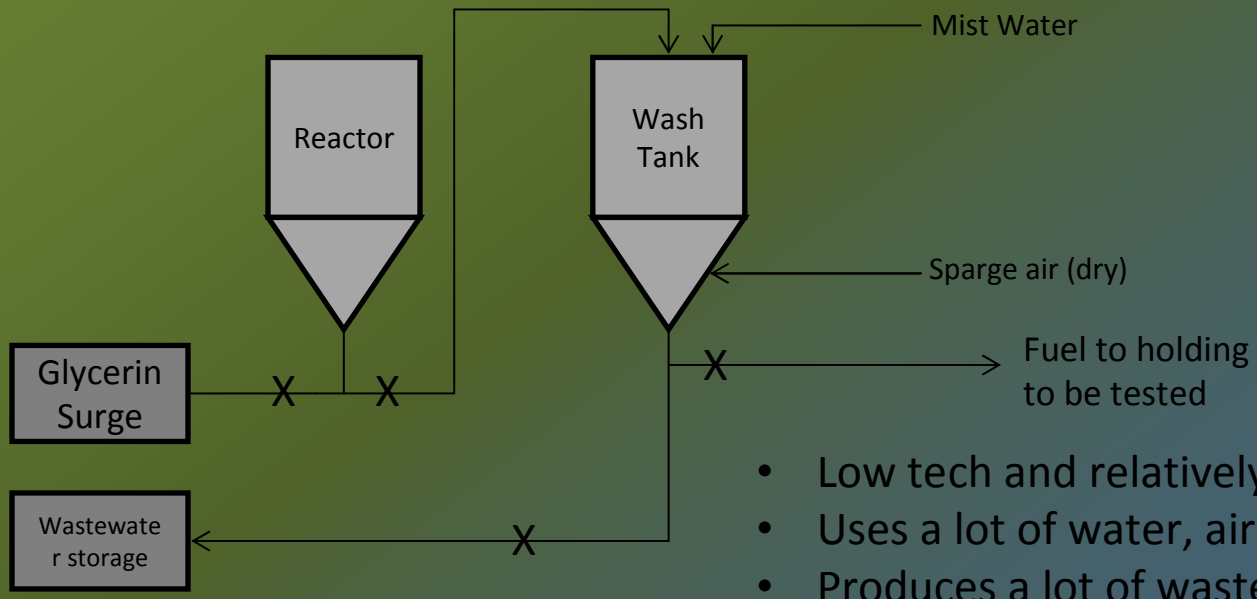
After the reaction is complete the reactor contains:

- Biodiesel
- Glycerin
- Methanol/methoxide
- Soap
- Moisture
- Residual mono-, di-, triglycerides
- Metal glycerides

The order and method each of these components are separated from the biodiesel are intertwined. Therefore it is more useful to look at overall separation/purification schemes rather than individual components.

Separations/Purification - Scheme 1

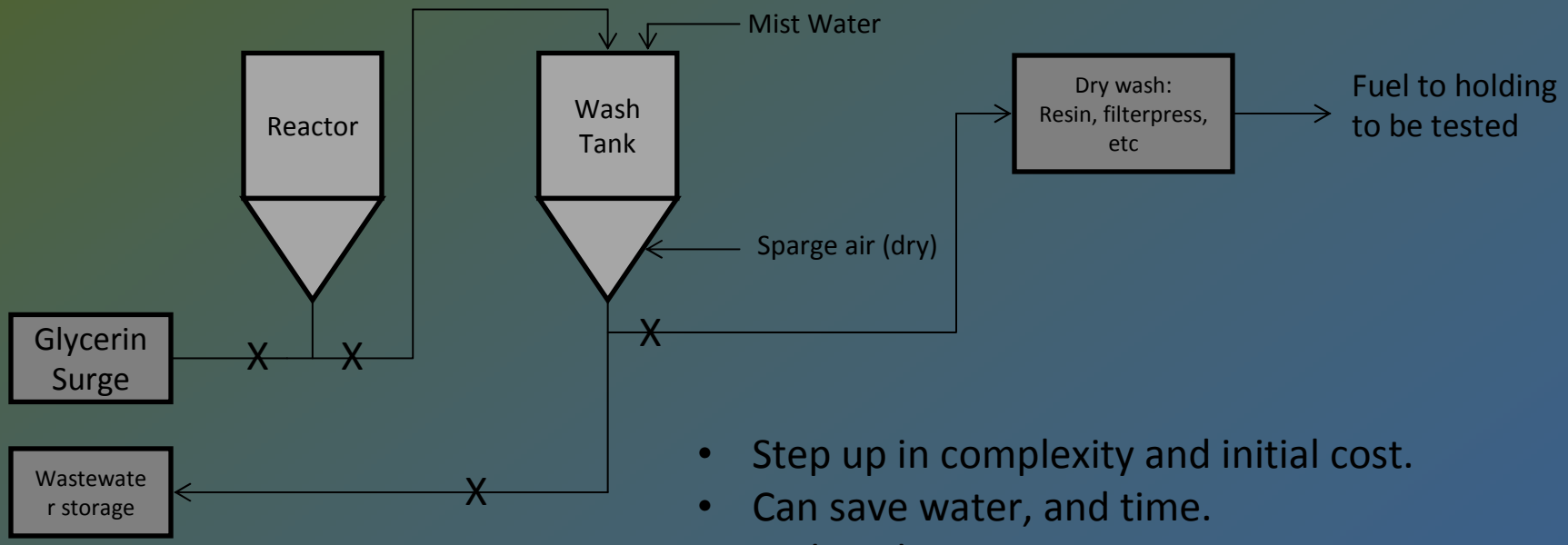
Gravity settle glycerin in a cone bottom tank, move to wash tank, water wash until soap is < ~30 ppm, then bubble or spray dry to <1000 ppm moisture.



- Low tech and relatively simple to install
- Uses a lot of water, air (electricity) and time.
- Produces a lot of wastewater.
- Can be tough on yield.

Separations/Purification – Scheme 2

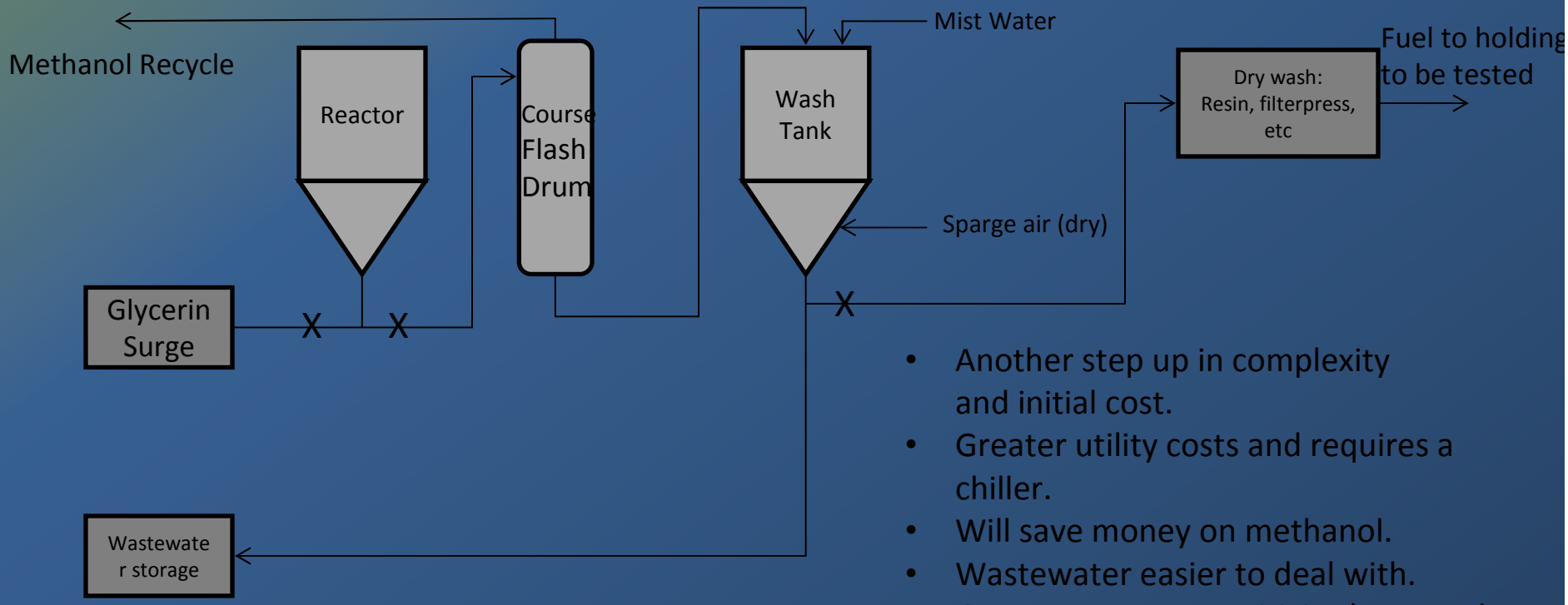
Add a dry wash step to scheme 1



- Step up in complexity and initial cost.
- Can save water, and time.
- Reduced wastewater stream.
- Similar or better on yield.
- Can save money if the process is well operated

Separations/Purification – Scheme 3

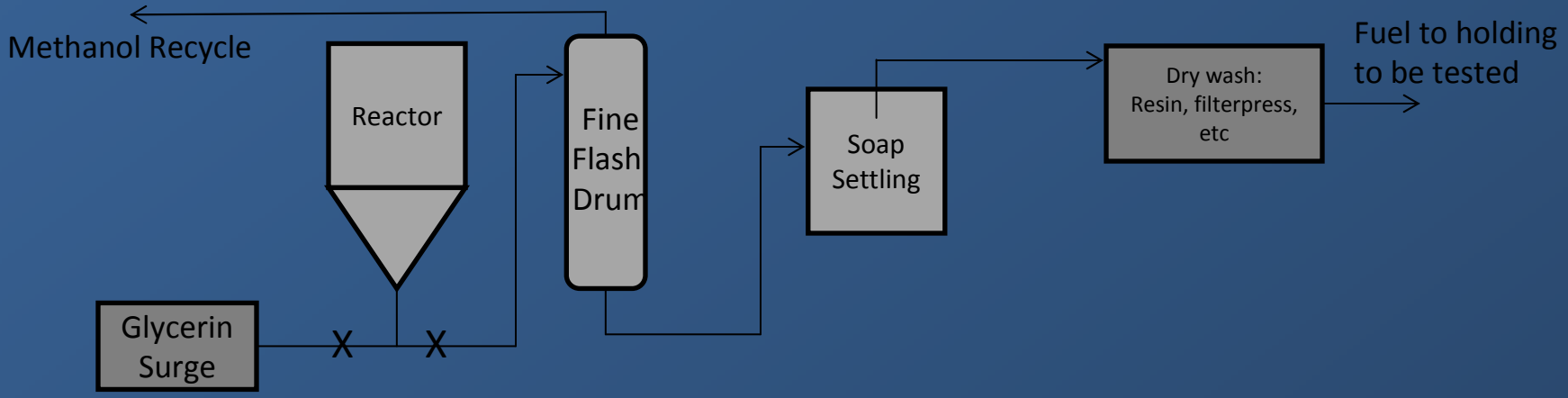
Add coarse methanol recovery to scheme 2



- Another step up in complexity and initial cost.
- Greater utility costs and requires a chiller.
- Will save money on methanol.
- Wastewater easier to deal with.
- Greater process sensitivity (can result in difficult to handle soap settling)

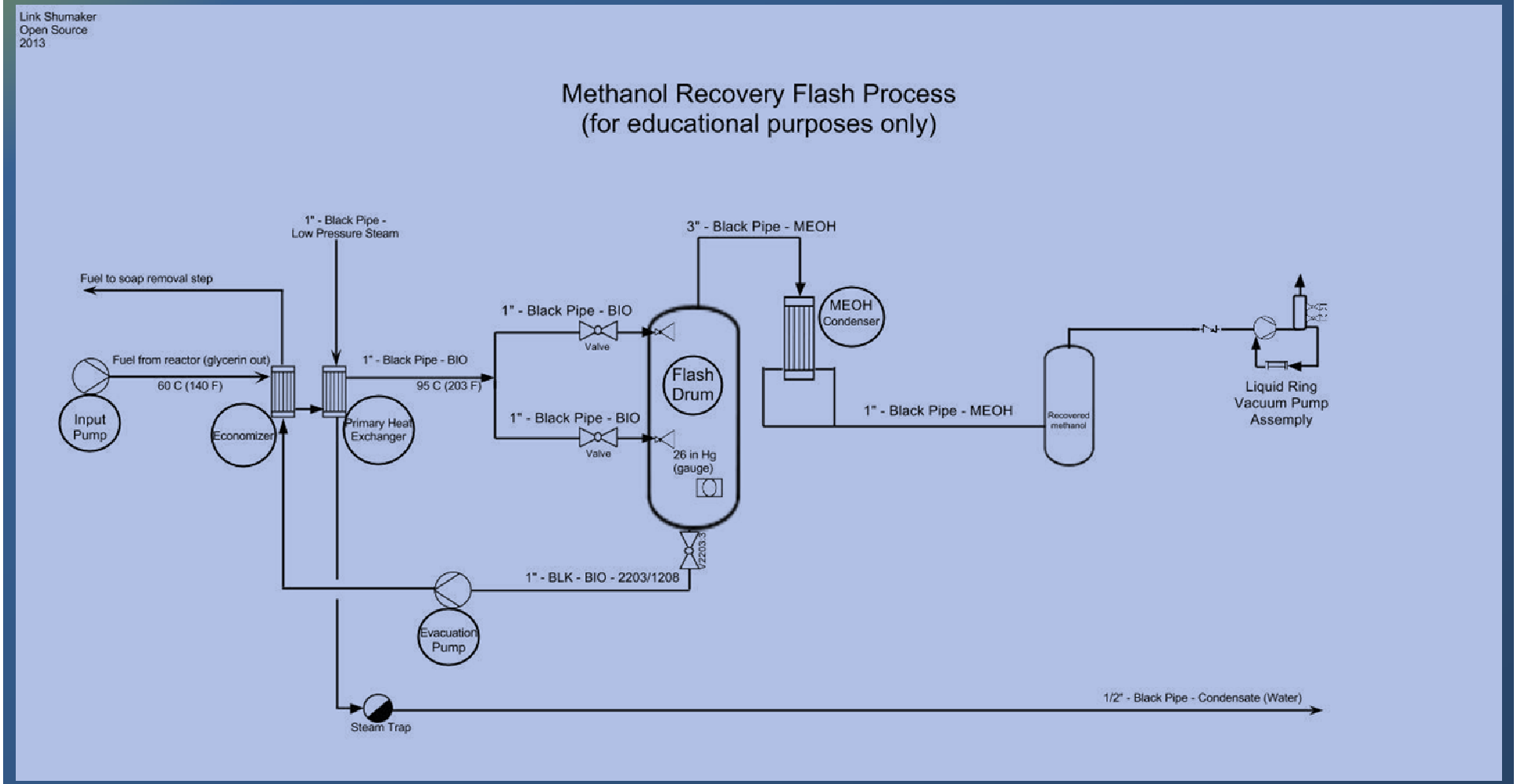
Separation/Purification – Scheme 4

Fine tune methanol recovery and eliminate water washing from Scheme 3



- Significantly more complex with associated initial cost
- More design required for flash to bring flash point into spec
- Wastewater is essentially eliminated
- Slightly greater process sensitivity
- Soap settling can present yield issues if not done effectively

Tangent on Methanol Recovery



Holding

- For ease of quality assurance it is worth having a holding tank before the final tank so certified in-spec fuel is not mixed with untested fuel.
- Fuel in the holding tank can be tested while in-spec fuel in the final storage tank is ready and being shipped.
- Stabilizer can be added in the holding tank.
- If fuel in the holding tank does not pass spec, it can be further polished in the same tank or sent back to process.

Final Storage Tank

- Only certified in spec fuel should enter this tank (can be internally and/or externally certified).
- Should be well sealed so moisture cannot enter. Desiccant on the vent is recommended and optional.
- Fuel held in the final storage tank for more than 30 days should be retested.

Final Thoughts

- Growing our institutional safety awareness, commitment to quality, and chemical processing insight will strengthen the Community Scale Biodiesel Sector.
- Collaboration is an enormous asset in our sector. Embracing the abundance of opportunity is easier for all of us when we share.

Handouts

Real Examples of printed Quality Assurance Manuals, Batch Sheets, SOP's, and a P&ID courtesy of

Midlands Biofuels

and

Kelley Green Biofuel

Thank You

- The Piedmont Biofuels crew
- BioJoe Renwick and Midlands Biofuels
- Kristopher Kelley and Kelley Green Biofuel
- Other open source and dedicated biodiesel enthusiasts.
- CBC organizers/contributors

Keep up the good work!

Questions and Contact

Questions?

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