Biodiesel Processor System Manual

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CONTENTS

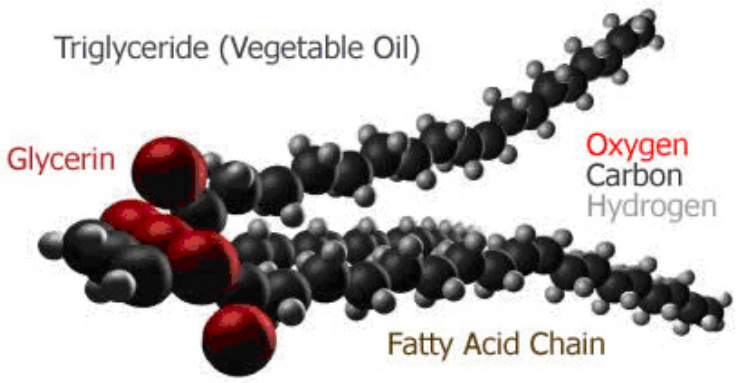
PART 1: INTRODUCTION

Biodiesel is a renewable fuel derived from a chemical reaction of alcohol and vegetable or animal oils, fats, or greases. These oils or fats are chemically altered in order to allow use in any diesel engine or home oil heating system, with little or no modification. A process called transesterification removes the glycerin component of the oil (which is a triglyceride molecule), resulting in a much thinner, or less viscous, product which stays liquid down to much lower temperatures. Biodiesel can be used in any diesel engine in pure form or blended with petroleum diesel in any percentage. Existing gas stations, pumps, and tanks can use biodiesel, providing a near seamless integration into our vast petroleum infrastructure. Even a commonly used blend of 20% biodiesel and 80% petroleum diesel (B20) will significantly reduce harmful pollutants, as well as carbon dioxide gas, reducing your vehicles contribution to climate change.

One of the most exciting aspects of biodiesel is the fact that it is readily produced from used restaurant fryer oils. Restaurants must properly dispose of significant quantities of waste veggie oil (often referred to as grease, or its trade name, yellow grease). The oil may therefore be easily be acquired for small scale biodiesel production operation. Using recycled waste fryer oil to produce biodiesel provides the benefits of a U.S. grown, renewable fuel, as well as offering a low cost option to recycle a waste product and put it to good use reducing carbon dioxide and other harmful emissions.

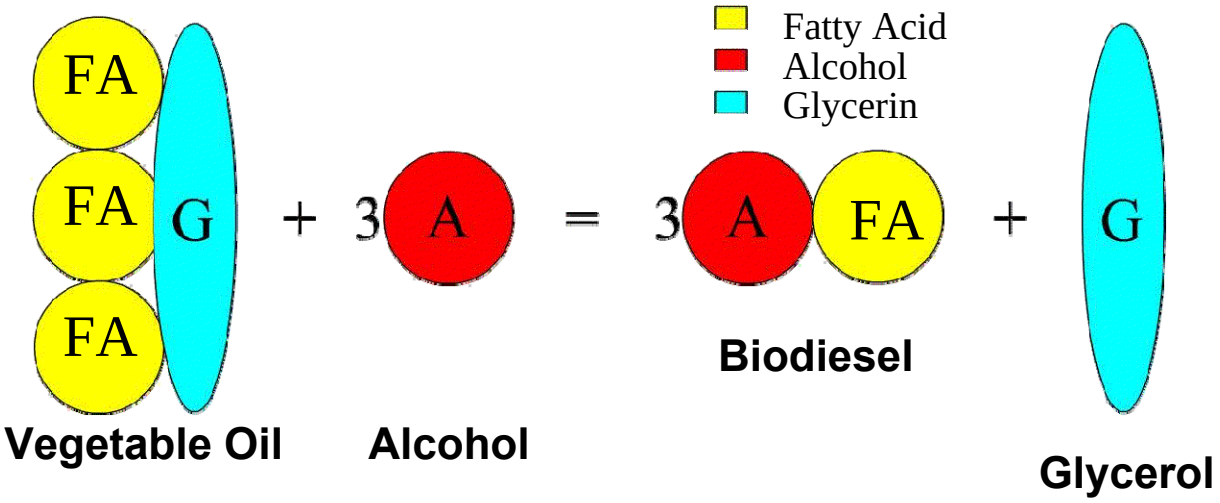
BIODIESEL CHEMISTRY

Biodiesel use should not be confused with the combustion of straight vegetable oil, or SVO. SVO may be used directly into a diesel engine. However, the fuel supply system must be modified by the addition of a second fuel tank, heating systems, and fuel switching to accommodate SVO (see Appendix B).

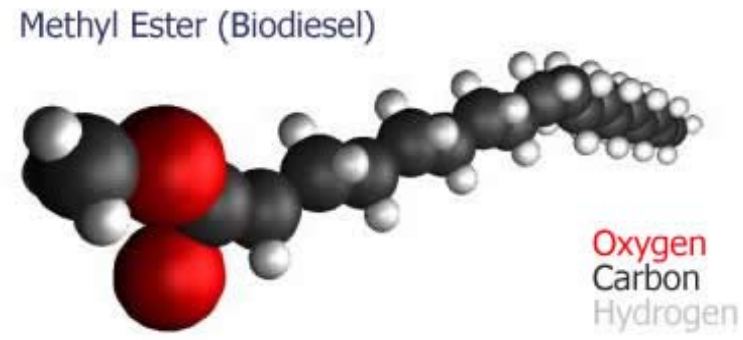


In the case of biodiesel, the engine and fuel systems are not modified, but we instead modify the fuel so that it can be used in any stock diesel engine. A typical vegetable oil consists of a triglyceride molecule as shown below.

There are many types of fatty acid chains, and the makeup of these will determine both the properties of the vegetable oil AND the final biodiesel product. Being a "tri"-glyceride, there are three fatty acid chains bound to one alcohol molecule, a molecule of glycerin (or glycerol). To produce biodiesel, the glycerol is split away with the aid of a catalyst, and the remaining free-floating fatty acid chains are then capped off with a lower level alcohol molecule such as methanol or ethanol. Methanol is presently the lowest cost option, as well as a bit easier to use. However, methanol is currently produced from natural gas, while ethanol is typically produced from corn, or other renewable feedstocks making it a more attractive feedstock from a renewable or sustainable perspective..



In its most simple form, the transesterification process, shown above, is merely a heated mixing process, where warm veggie oil is mixed in the presence of a catalyst. The glycerol molecule is striped away, and replaced with three individual methanol molecules to make there biodiesel molecules. This is called transesterification since the



both the starting triglyceride and resulting biodiesel molecules fall into the organic chemistry category of an ester. Therefore, they are trans - ester - ified.

Next, we the startup of a number of different sized production and distribution operations including some a business model for a 1/8 million gallon per year cooperative. This will be followed by the discussion of the logistics and technologies required to bring biodiesel fuel to your local region. Although this report focuses on the State of Michigan, most of the information presented pertains equally to any location throughout the country.

PRODUCTION TECHNOLOGY

The major steps required to synthesize biodiesel are as described below.

Purification of Waste Oil Feedstock

If waste vegetable oil is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze to give salts of the fatty acids instead of undergoing transesterification to give biodiesel.

At home, this is often accomplished by heating the filtered oil to approximately 120°C. At this point, dissolved or suspended water will boil off. When the water boils, it spatters (chemists refer to it as "bumping"). To prevent injury, this operation should be done in a sufficiently large container (at most two thirds full) which is closed but not sealed.

In the laboratory, the crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration. However, the viscosity of the oil may not allow the drying agent to mix thoroughly.

Neutralization of free fatty acids

A sample of the cleaned oil is titrated against a standard solution of base in order to determine the concentration of free fatty acids present in the waste vegetable oil

100 lb Oil + 21.71 lb Methanol →

100.45 lb Biodiesel + 10.40 lb Glycerol + 10.86 lb Excess Methanol

sample. The quantity of additional base catalyst required to neutralize the acid is calculated.

Transesterification

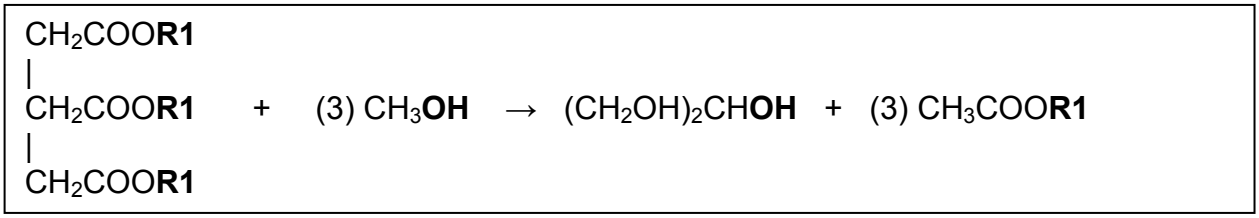
While adding the base, a slight excess is factored in to provide the catalyst for the transesterification.

The calculated quantity of base (sodium or potassium hydroxide) is added slowly to the alcohol and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess is added to drive the reaction to completion.

The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil, and the mixture is heated (typically 50 °C) while agitating with a mechanical paddle or mix pump for several hours (2 to 4 typically) to allow the transesterification to proceed.

Once the reaction is complete, the glycerol will precipitate out and fall to the bottom. The bottom glycerol may then be drained off from the bottom, leaving approximately 85% of the original reactants as a top layer of biodiesel and some remaining alcohol. The excess alcohol can be distilled off from the crude biodiesel and/or the crude glycerol. More excess alcohol remains in the glycerol than the biodiesel, and often the alcohol in the crude biodiesel is not reclaimed for small scale operations. This residual alcohol can be extracted with a water wash, or merely by evaporation (either passive, or via an air bubble wash). If water washed, the biodiesel must then be dried by distillation, evaporation, or with a drying agent.

The Reaction



Triglyceride + (3) Methanol → Glycerol + (3) Biodiesel Esters

Where the R1, R2, and R3 represent the long fatty acid chains different for the various oil feedstock. We typically see soy and sometimes canola in the restaurant used oil market.

During the transesterification process, the triglyceride is reacted with alcohol in the presence of the catalyst. The main reason for doing a titration to produce biodiesel, is to find out how much additional alkaline is needed to ensure a complete transesterification in the presence of additional free fatty acids found in used oils. Experimentally, 6.25 gm

per liter of NaOH produces a very usable fuel. From field experience, a recommendation (without titrating) might be to use about 6 g NaOH when the waste vegetable oil is light in color and about 7 g NaOH when it is dark in color.

The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the lipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

Base catalyzed mechanism

This reaction is base catalyzed using a chemical such as dry sodium hydroxide (also called NaOH, caustic soda, or lye), dry potassium hydroxide (KOH, or caustic potash), or a prepared solution of sodium or potassium methoxide. The dry catalyst (KOH or NaOH) is dissolved in the alcohol to make a convenient method of dispersing the otherwise solid catalyst into the oil. The catalyst needs to be very dry, and exposure to free air will allow it to absorb moisture. Therefore, minimize the amount of time that any containers are left open, and tightly seal lids for storage. Any water in the process promotes the production of unwanted soaps and inhibits the transesterification reaction.

Once the alcohol / catalyst mixture is made, it is added to the triglyceride. There are several competing reactions, so care must be taken to ensure the desired reaction pathway occurs. Most methods do this by using an excess of alcohol.

The acid / base catalyzed method is a slight variant and is not covered here.

The Process

- Preparation: care must be taken to monitor the amount of water and free fatty acids in the incoming biolipid (oil or fat). If the free fatty acid level or water level is too high it may cause problems with soap formation (saponification) and the separation of the glycerin by-product downstream.

- Catalyst is dissolved in the alcohol using a standard agitator or mixer.

- The alcohol/catalyst mix is then charged into a closed reaction vessel and the biolipid (vegetable or animal oil or fat) is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol.

  The reaction mix is kept just below the boiling point of the methanol (which is 64.5°Celcius, or 148°Fahrenheit) to speed up the reaction. The reaction will take place at room temperature, but approximately 130 °F is recommended as a compromise of speed and safety. By no means do you want to exceed the boiling point of the alcohol, or you will build up pressure and emit toxic vapors. Recommended reaction time varies from 1 to 8 hours; under normal conditions the reaction rate will double with every 10 °C increase in reaction temperature.

Excess alcohol is normally used to ensure complete reaction. Typically 20% methanol is used.

- The glycerin phase is more dense than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

- Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

- The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin (water and alcohol are removed later, chiefly using evaporation, to produce 80-88% pure glycerin).

- Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage.

PART 2: TRAINING

1. Read this entire manual
2. Watch the operations video (located at www.oakland.edu/BIOMASS)
3. Perform the one liter biodiesel lab process, including wash & dry of product
4. Take the Biodiesel Production Quiz, below and turn in to lab admin.
5. Assist with a qualified operator on one full process from oil to dry product
6. Verify all of the above has been done and then you will be added to the trained operator list. After logging (5) five processes runs, you are eligible to become a qualified trainer for new users.

PART 3: SAFETY PROTOCOLS

- Training Requirements (see Part 2)
- Operating Procedure (see Part 4)

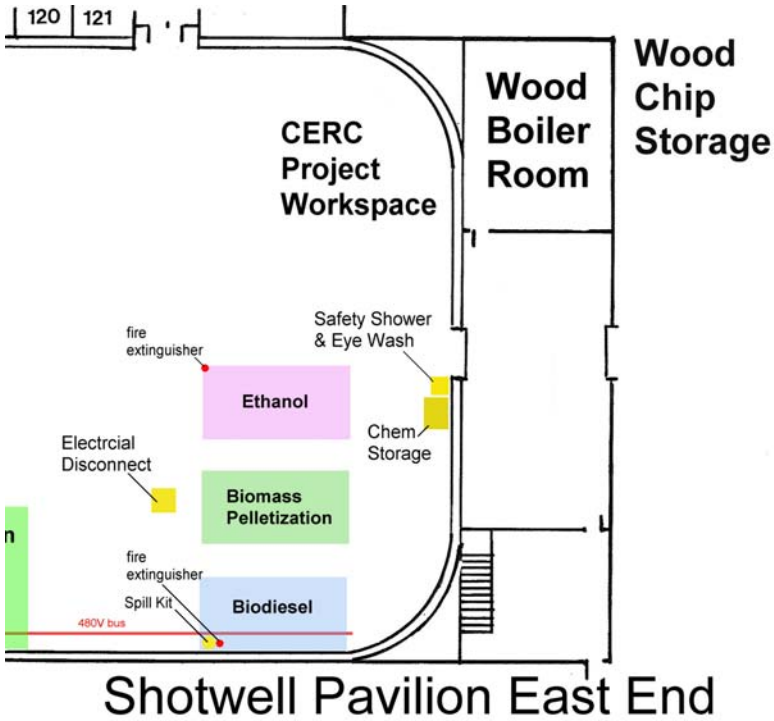
Emergency Contact Numbers
- Jim Leidel, Director, 248-765-2027 cell
- OU Police, 911
- Steve Kent, Operations, 248-765-4800

Safety Data Sheets (SDS) will be located at the biodiesel processor as well as with the OU INC operations management. SDS's for the following chemicals will be available for review: biodiesel, methanol, ethanol, glycerin, sodium hydroxide, & potassium hydroxide

Apparel: When operating any step of the biodiesel, or any other CERC equipment, please wear Closed Toe Shoes. The following additional Protective Clothing must be worn in individual steps when handling chemicals:

- Dust Mask (when handling NaOH or KOH)
- Goggles and Gloves (when handling methanol, ethanol, NaOH or KOH)

Emergency Safety Equipment
Be familiar with the locations of all of the following emergency gear:
- Safety Shower
- Eye Wash
- Spill Kit
- Fire Extinguishers: for biodiesel, use the FOAM type, or silver canister, not the red ones. There are two as shown here on the map)



Chemical Storage Cabinet
must be used to store excess methanol and all KOH & NaOH. One drum of methanol may be kept out by the processor, sealed.

Cleanup
- Leave the area cleaner then how you found it. Spend at least 15% of your time on cleanup duties and organization. Put tools & chemicals away and dispose of trash.
- Disposal of oily rags: Dispose of oily rags in a plastic trash bag and place in dumpster outside the pavilion. Do not place oil soaked rags in indoor trash bins.
- Sheets of fibrous Absorbent Pads are available and should be used strategicly around the biodiesel space. We have been obtaining absorbent pads from Eco Paper, Bill Icikson, 1150 W Hamlin Drive, Rochester Hills, (248) 652-3602

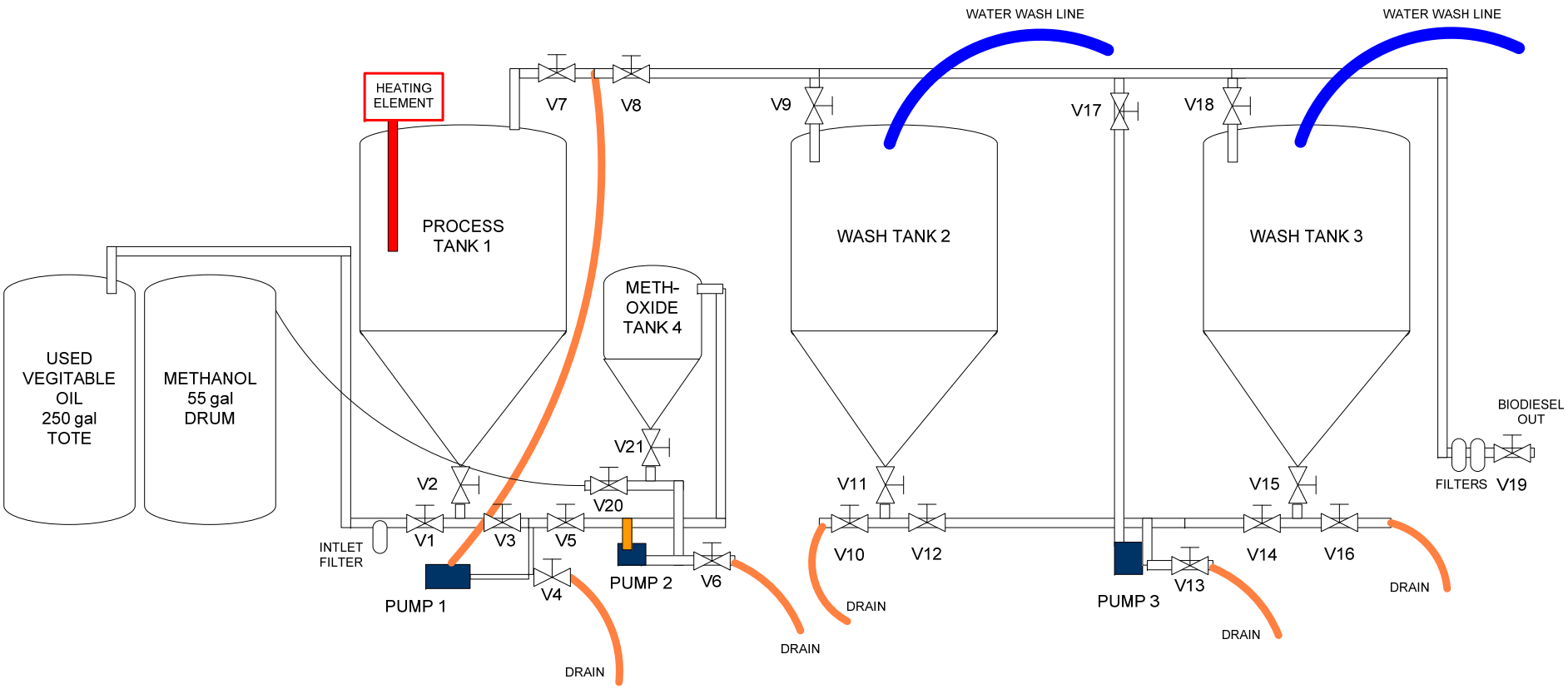
- Shutdown Procedure: Refer to "Operating Procedure" (see Part 4, below)
- Lock out / tag out process: (under review for next revision of this document)

PART 4: OPERATIONAL PROCEEDURE

Note: At least one authorized & trained individual must be present during operation of the biodiesel system. A list of trained personnel will be on file with the OU Clean Energy Research Center management.

To be certified to operate, you must complete all Training Items listed in Part 2.

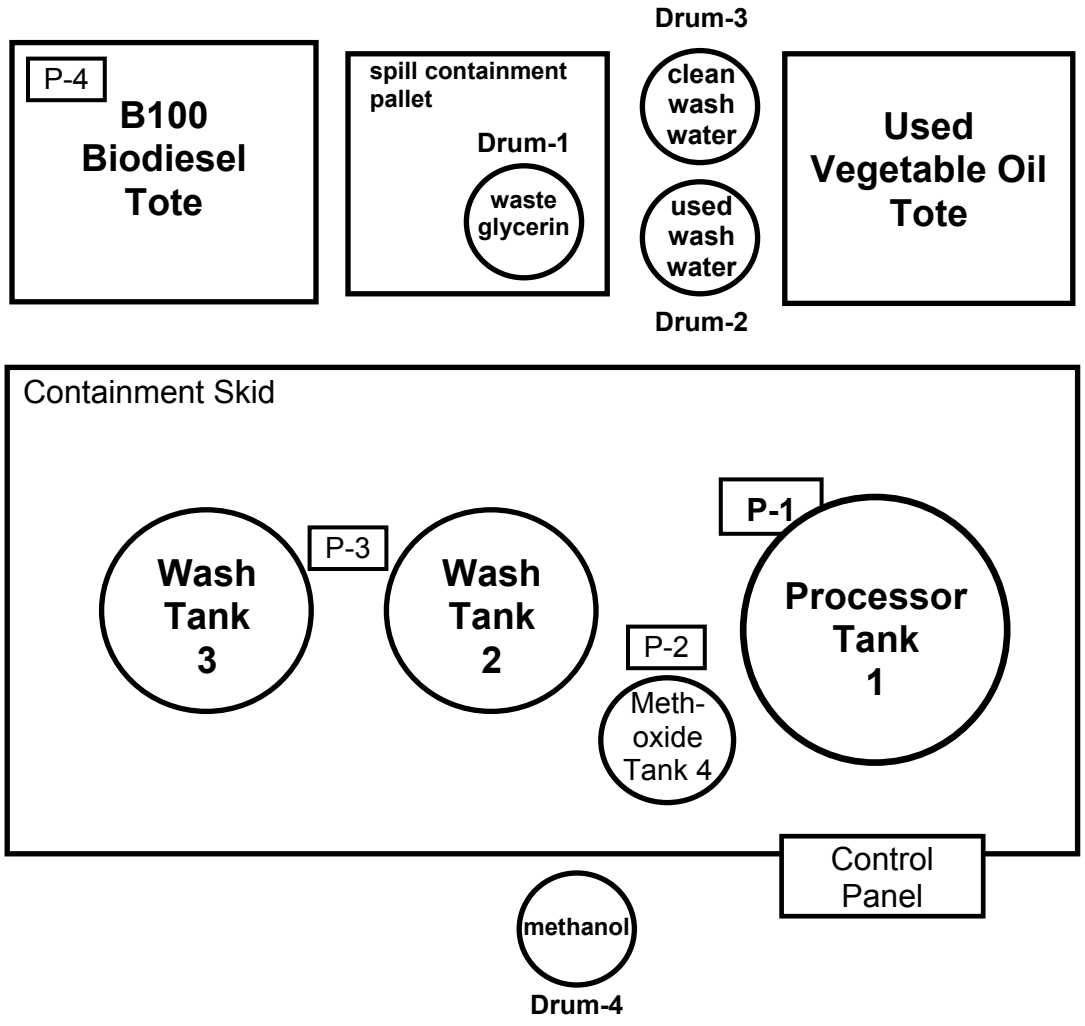
The following pages illustrate and detail the Oakland University processor and its operation.



Biodiesel System Schematic

Valve List:

V1: waste oil inlet valve
V2: process tank T1 bottom valve
V3: process tank T1 recirculation valve
V4: glycerin drain valve
V5: methoxide transfer valve
V6: pump 2 drain valve
V7: process tank T1 inlet valve
V8: transfer T1-T2 valve
V9: wash tank T2 inlet valve
V10: wash tank T2 drain valve
V11: wash tank T2 bottom valve
V12: wash tank T2 recirculation valve
V13: pump P3 drain valve
V14: wash tank T3 recirculation valve
V15: wash tank T3 bottom valve
V16: wash tank T3 drain valve
V17: tank T2-T3 recirculation valve
V18: wash tank T3 inlet valve
V19: biodiesel product outlet valve



Biodiesel System Layout

Biodiesel unit working Procedure

Processor Oil Fill

- POWER:
    - Turn ON the main Circuit Breaker, if it is off.
    - Turn ON the Biodiesel unit (Unit) circuit breaker, if it is off.
- Place the oil supply suction tube into the oil supply Tote
- Turn unit master panel control ON.
- Open valves V-1,3,7 to suction oil though P1 into the processor Tank 1.
- Close valves V-2,4,5,8
- Turn ON processor pump P1 at panel (If prime required, prime the pump).
- Fill the Processor tank to 60 gallon mark.
- Once achieve the required volume shut off the pump P1.
- Close valve V-1.
- Open process tank bottom valve V-2
- Start the processor pump again.
- Turn ON the heater Power from main Panel.
- Allow circulation until the temperature indicator on control panel indicates 120° F

Titration of Used Oil

- Refer to separate titration procedure & calculate total catalyst needed for batch

Preparation of Methoxide Tank

- Remove lid from Tank T4
- Go to chemical storage cabinet and retrieve methanol if a drum is not located at the processor. Only one drum of methanol is allowed to be out on the floor.
- Obtain Battery Operated Siphon pump off storage shelf
- Remove bung from stopper on Methanol drum
- Add 20% methanol to Tank T4 (12 gallons for a 60 gallon batch), and Replace T4 Lid and methanol drum bung
- If using any small containers, return methanol to Chemical Storage Cabinet. However, one 55 gallon drum may remain out near processor.
- Using the digital scale, weight the proper amount of NaOH or KOH wearing gloves and googles.
- Turn ON Methoxide pump P2.
- Slowly pour in the catalyst into methanol in T4. Put in only a cup or two at a time so as to not clog up the flow of methanol.
- Allow P2 to run for an additional 15 minutes after adding all catalyst, to ensue ALL catalyst is completely dissolved.
- ON to circulate materials for 10 minutes

Transfer Methoxide to Processor Tank

- With both processor pump, P1 and methoxide pump, P2 ON, Partially open methoxide transfer valve, V-5 (about ¼ open) to flow Methoxide into suction side of P1, and continue until all contents of Methoxide tank are drained out.

- Turn OFF Methoxide Pump, P2
- Close Methoxide Valve, P5 completely

Timed Process Mix

- Continue processing with Circulating Pump, P1 ON for 3 hours via the time delay relay installed in the control panel. P1 will continue to run until the timer automatically shuts off.
- Turn Off Electric Heat.
- The

Drain Glycerin from Processor Tank T1

- Place empty Glycerin holding tank next to hose connected to Gylcerin Drain Valve, V4
- Continue to drain Glycerin into tank until all Glycerin is removed from Processing Tank, T1
- Close Valve, V4

Transfer Methoxide mixture from Processor Tank T1 to Wash Tank T2

- Close Valve V7
- Open Connect Valve, V8
- Open Washer Intake Valve, V9
- Turn ON Processor Pump, P1
- Transfer Processor Contents
- Turn OFF, Processor Pump, P1
- Close Valve V2, V8 and Valve V9

Wash Methoxide Mixture

- Hook Garden Hose Reel to Sink Faucet
- Unroll Hose to Biodiesel Processor
- Attached Hose to Wash Tank Lid Misting Valve
- Turn Water Slowly On and control Misting via brass valve on end of hose
- Mist 10 gallons of water (see fluid level on side of tank)
- Turn off Water
- Place Wash Water Jug next to hose connected to Valve 10, Water Drain Valve
- Open Valve V11
- Turn on Valve 10 - Empty all water slowly to ensure no spillage
- Repeat Above steps at TOTAL of 3 Times (30 Gallon Wash)
- Test Mixure (SEE PROCEDURE)
- Close Valve V10

Transfer Mixture from Wash Tank T2 to Bubbling/Settling Tank T3

- Open Biodeisel Transfer Valve, V12
- Open Biodiesel Transfer Valve, V13
- Turn ON Transfer Pump, P3
- Fully Transfer all Biodiesel from Wash Tank, T2 to Bubbling/Settling Tank T3
- Turn OFF Transfer Pump P3
- Close Transfer Valves V11, V12

Bubble Wash of Biodiesel

- Open Lid To Tank T3
- Place Bubbling hose and rock in Tank T3 and submerge 1 foot
- Turn ON Bubbling Compressor
- Bubble for 4 or more hours

Transfer Biodiesel to Biodiesel Holding Tank

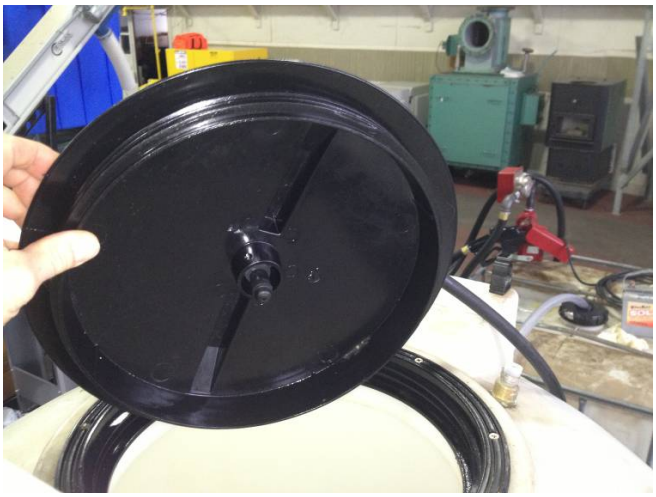
- Place Diesel Transfer Hose connected to Drain Valve V15 into Diesel Holding Container
- Open Diesel Drain Valve V15
- Turn Transfer Pump P3, ON and Transfer contents of Tank T3 to Diesel Holding Tank
- Turn Transfer Pump T3 OFF
- Close Valves V13, V16 and Valve V16

Shutdown Procedure

- ENSURE ALL VALVES CLOSED
- TURN OFF MAIN POWER
- SPEND SOME TIME CLEANING UP. Yes, that means YOU.

Front view of processor

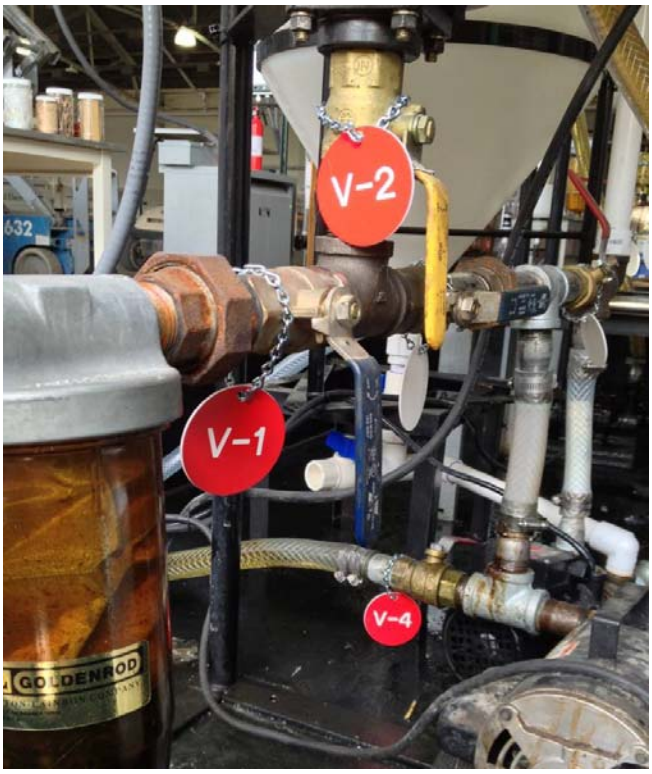
Control Panel



Underside of wash / settle Tanks 2 & 3 have a fine mist spray nozzle

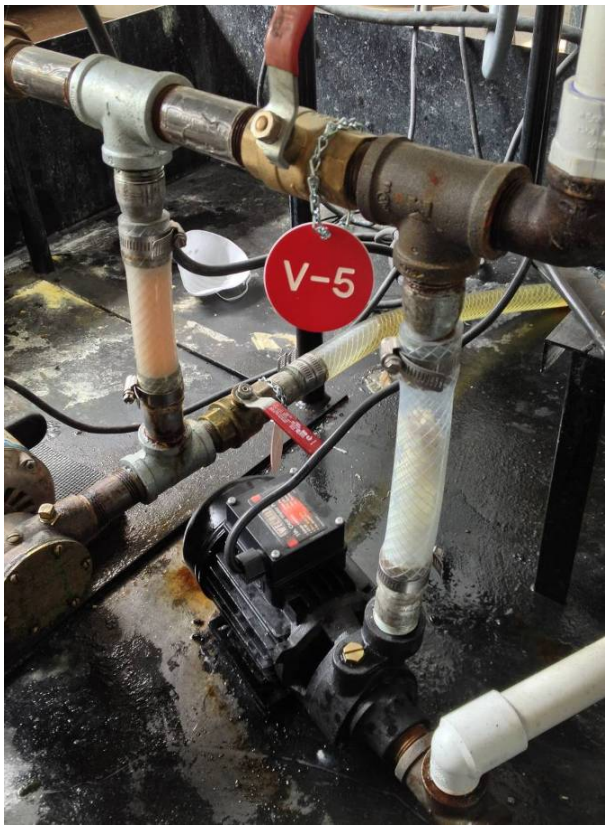
Main processor Tank 1

The red electrical box is the electric heating element



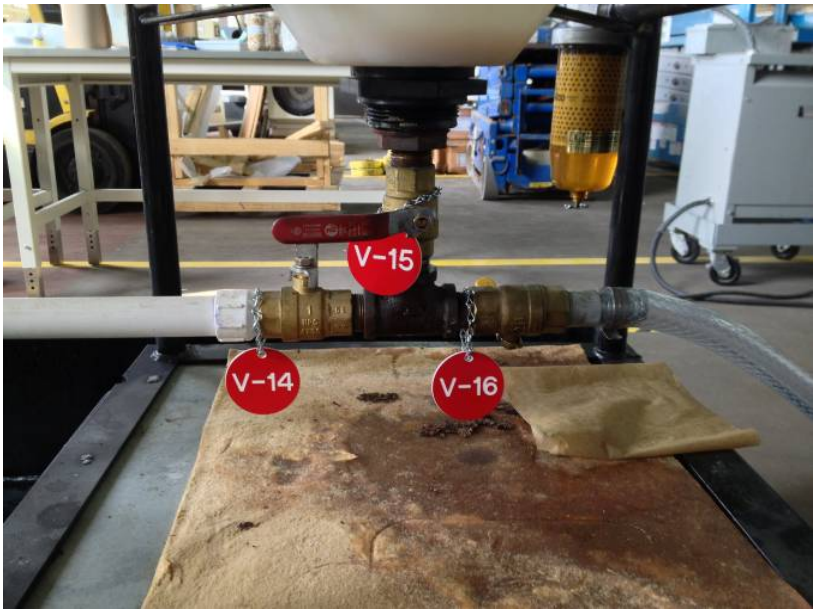
Valve assembly on the bottom of Processor Tank 1.

Main Processor Pump 1 is located on the bottom right of the photo.



Valve assembly on the bottom of wash Tank 2.

Valve 10 can be used as a drain.



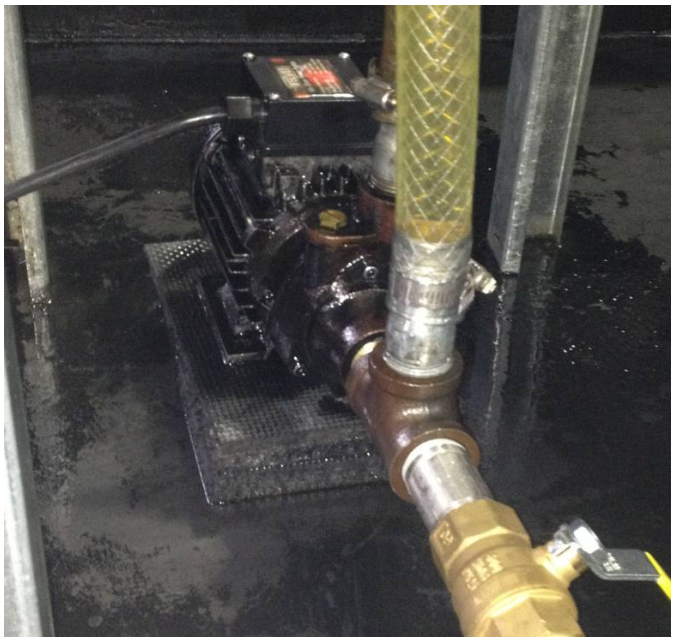
Valve assembly on the bottom of wash Tank 3.

Valve 16 can be used as a drain.

V-9 is the intake valve for Wash Tank 2

Used vegetable oil tote with the suction drop tube, suctioned by main Pump 1.

Main processor Pump 1



Transfer Pump 3

Leave the waste glycerine and other drums on the spill containment pallet.

Methoxide mix pump 2

Final product export to tote, via two inline filters

The biodiesel product Pump 4 is 12VDC powered by a battery.

The battery needs to be checked for voltage and charged occasionally.

If voltage is below 11.5VDC, please charge for a few hours.

PART 5: BIODIESEL LAB and QUIZ

Estimated time to complete: *½ hour Pre-lab reading*
1 hour Day One lab time
½ hourDay Two lab time
¼ hour Post lab Q & A

General Description

For more information, you can visit www.kitchen-biodiesel.com and www.biomich.com

In this lab, you will practice the biodiesel process by making a one liter batch of vegetable oil derived biodiesel in a 2 liter soda bottle. The lab uses NaOH (sodium hydroxide), but you may substitute KOH (potassium hydroxide) if you properly adjust the amounts used. The glycerol layer will settle out as a bottom layer due to its higher specific gravity. The biodiesel, or methyl ester, will float above since it is lighter. The glycerol can then be carefully drained off leaving a crude biodiesel product.

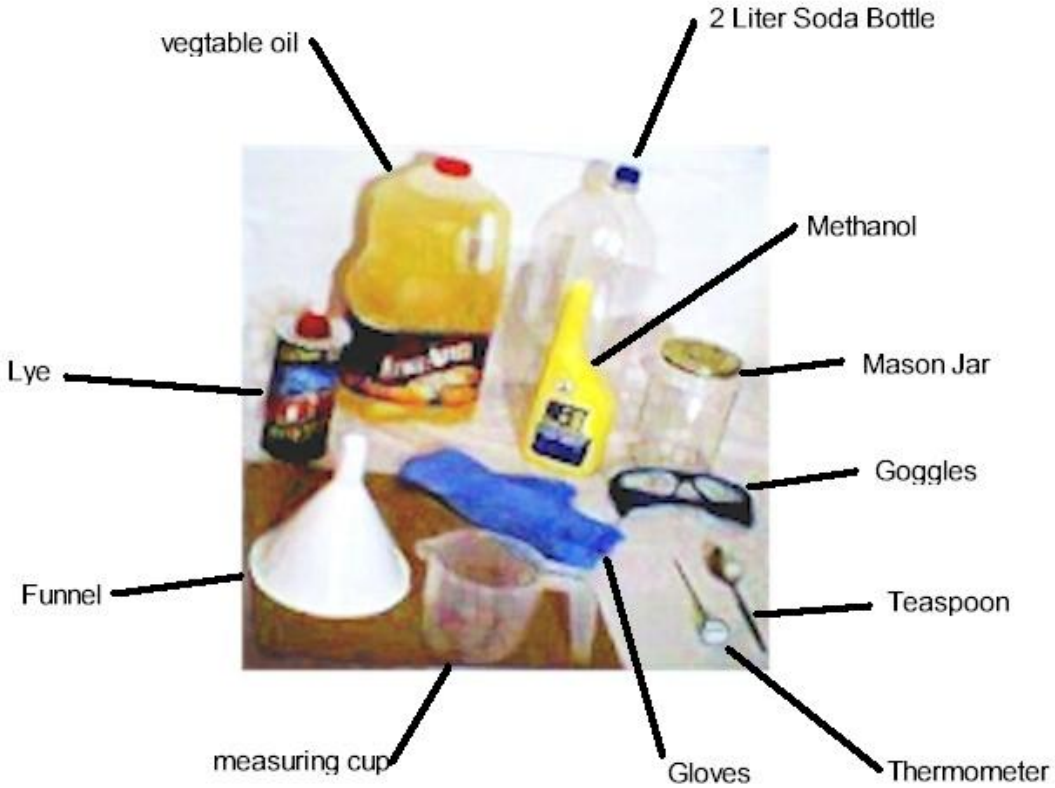
The fun part is that all of the materials and ingredients may be obtained from your local department store, or online (if you cannot find Red Devil lye, the NaOH may be found on soap making or animal hide tanning web sites).

Items required from student (one per lab group):

- One 2 liter (preferably clear) soda bottle, rinsed and completely dry.
- One liter of vegetable oil. Be creative if you choose, any veggie oil will do….

Items that will be provided for you:

- Gloves & goggles (please take care not to get NaOH on clothing, it will burn a hole)
- Pint mason jar & lid
- 200 mL of methanol
- 5 grams NaOH
- Funnel
- 2000 mL beaker
- Hot plate
- Digital scale



Vegetable oil

any oil will work, but Canola is one of the best for cold weather properties

Catalyst

NaOH - Sodium Hydroxide

Sold as Drain Cleaner in Hardware and Grocery Stores. Look by the Drano. Make sure the can reads "Contains Sodium Hydroxide"

Images courtesy of www.kitchen-biodiesel.com

Proper safety is important here. We are working with poisonous methanol and caustic lye.

DAY 1 **1 & 2.** Measure 200 mL of methanol directly into the mason jar. Our jars have gradations on the side.
3. Measure in 5 grams of NaOH, sodium hydroxide on the digital scale.
4. Screw on the lid very tightly and carefully. This is the most dangerous step. One partner can shake to dissolve the NaOH. It will generate some heat, but not too much pressure.
5 & 6. Measure 1 liter of your oil into the beaker and heat on the hot plate to 120 deg F.
7 & 8. Use funnel to pour carefully into the 2 liter plastic bottle. Then carefully pour in the methanol and NaOH mixture.
9. Close cap tightly. Shake vigorously off and on for about 20-30 minutes.
10. Crack the cap a bit to let air in as the mixture cools. Set aside. The glycerin should begin to separate and settle out in 20-30 minutes. The top portion is crude biodiesel.
DAY 2 **11.** A day or two later, return to inspect the glycerin separation.
12. Drain off the glycerin by inverting with your thumb over the top and slowly draining out. **13.** Slowly add a ½ liter to liter of water. It will get milky as it absorbs the soaps and remaining NaOH. Repeat 3-5 times until the water remains somewhat clear. If you overly agitate the mixture (especially on the 1st & 2nd washes, you could create a permanent emulsion, so go slowly.
14. Pour biodiesel into an open container and set out to dry for a few days. It could be microwave'd, but take care to remove any residual water droplets from the bottom that will still boil and make a steam explosion & mess.
15. Once crystal clear, the biodiesel is ready to use.

Quiz and Signature Page

In the space below, briefly describe your transesterification results, successful or not. (Just a few sentences) Describe any problems or special observations.

Questions:

1. What type of oil did you use? _____

2. Was the glycerin separation clearly visible? And what color is the glycerin?

3. What is the most common blend of biodiesel found in retail fuel stations? _____

4. What is the most common oil feedstock for U.S. biodiesel production? _____

5. What is the most common oil feedstock for European biodiesel? _____

6. In the OU processor, how many gallons of used oil is processed per batch? _____

7. In the OU processor, what step are you required to wear a face filter mask?

8. What is the most suitable type of fire extinguisher for a liquid or oil fire? _____

   and how many of these type are near the OU processor? _____

9. What's the minimum time that you spend on cleanup after every use? _____

Please print and sign your name below:

_____ _____

Printed name *Signature*

_____ _____

Email *Phone Number*

PART 6: FEEDSTOCK SUPPLY (more info to come…..)

The primary cost of biodiesel is the oil feedstock. For a soy oil base operation, the oil feedstock is typically 70-80% of the total cost of production. It takes about 7.3 pounds of fresh or used vegetable oil to produce one gallon of biodiesel.

The price of soybean oil varies widely but over the last few years has tended to stay in the range of $0.25 to $0.35/lb. This means the virgin feedstock cost will be between $1.75 and $2.56/gallon. The cost of yellow grease, or used & purified waste restaurant oil has tended to stay in the range of $0.15 to $0.20/lb. This means the virgin feedstock cost will be between $1.10 and $1.46/gallon.

The business model described here incorporates restaurant oil collections as part of the operations. A zero cost for oil is carried for the first years of operation, but labor and equipment costs are required to incorporate oil collections in the coop model. Presently, most restaurants pay a fee for a waste oil company to dispose of their used oil. The oil then makes its way to a rendering company who purifies it, and resells it as a commodity called “yellow grease” for the prices mentioned above.

The option to purchase a stable supply of yellow grease should be fully investigated during the coop planning phases. This would vastly simplify operations and startup logistics, but would also increase the cost of the final product.

Studies are available which have reviewed waste oil availability per person and per restaurant. One such study is available at www.biodieselmichigan.com. By studying 30 metropolitan areas across the United States, it was found that yellow grease production averaged 1.2 gallons / year / person and 847 gallons / year / restaurant.

Therefore, to support a 1/8 million gallon per year operation, 147 average restaurants will be needed for waste oil collections.