

Process Manual for 100 TPD BioDiesel Plant

Production of biodiesel from Acid Oil by two-step catalyzed processes

The production of biodiesel from Acid Oil is carried out by two-step catalyzed processes i.e. esterification and transesterification reactions followed by the separation and purification processes. First the Acid Oil is preheated, because it usually a semisolid material at room temperature ($30\pm 2^\circ\text{C}$). The Acid Oil is melted at 80°C and the preheated Acid Oil is then transferred into the reactor for pretreatment of Acid Oil using PTSA (esterification), followed by an alkaline catalyzed transesterification process. The final step is separation and purification of biodiesel obtained from the two reactions.

Pretreatment of Acid Oil by esterification reaction using PTSA: The acid catalyst PTSA is added into the preheated Acid Oil in the presence of methanol to reduce the free fatty acid (FFA) of Acid Oil by converting it into fatty acid methyl ester (FAME). In the first step, acid catalyzed esterification, reduces the high FFA content of Acid Oil to less than 2%. The optimum conditions for pretreatment process by esterification are 0.75% (w/w) dosage of PTSA to Acid Oil, 10:1M ratio, 60°C temperature, 60 minutes of reaction time and 400 rpm stirrer speed.

Alkaline catalyzed transesterification reaction: The treated Acid Oil by acid catalyzed esterification is considered as the pre-treated material for transesterification process. The process conditions for transesterification reaction are maintained to the molar ratio of methanol to Acid Oil 10:1, reaction temperature 60°C , reaction time of 60 min, stirrer speed 400 rpm and 1% wt/wt KOH.

Separation and purification of biodiesel obtained from two-step catalyzed processes: In order to remove excess methanol in the biodiesel, the product is allowed to cool, which results in separation into two layers. After 24 hour separation time, the upper phase consists of biodiesel, while the lower layer contains the glycerol. Finally, the biodiesel is then washed by Magnesium Silicate.

Step I: Raw Materials

Methanol: The stoichiometric quantity is usually 12.5% of methanol by volume of vegetable oil, that is, 125 milliliters of methanol per liter of oil. Excess Methanol is needed, to achieve 98% conversion. For waste oils, the excess is usually 100% of the stoichiometric amount. So for stoichiometric ratio of the oil you are using is 12.5%, that is 125 ml of methanol per liter of oil, the excess would be 125 ml, for a total amount of methanol of 250 ml per liter of oil.

Oils with higher molecular weights need higher excesses. So, for fresh oils, you can try 60%, though 67% or more would be better. For palm kernel or coconut, closer to 100% excess would be better. For tallow and lard, use higher excesses. For used oil, WVO, waste vegetable oil, often contains animal fats from the cooking, use 67% minimum excess. For heavily used oils with high titration levels, use higher excesses, up to 100%.

Since you do not know what kind of oil your WVO is, use 25% methanol, 250 ml methanol to 1 liter of oil. If you have taken care with the titration, used accurate measurements and followed the instructions carefully, you should get a good, clean split, with esters on top and the glycerine and free fatty acids cleanly separated at the bottom. If you have trouble separating the two layers, with a lot of frothing, that could be because the process did not go far enough and unconverted material is forming

emulsions, try using more methanol next time. If everything works well, try using less amount of methanol. You will soon figure out what is best for you.

Catalyst: The catalyst used is Potassium Hydroxide (KOH, Caustic Potash). It is hygroscopic. It absorbs water from the atmosphere. So make sure you get fresh material, and keep the container tightly sealed. It usually comes in three grades: flakes and 5mm pearls or half-pearls are 96-97%, small pearls (1-2 mm) are 99%+, but more expensive. Either will do.

To find out content of Free Fatty Acids in waste oil, you have to titrate.

Reagent: Just use a 0.1% KOH solution (dissolve 1 gram of KOH, in distilled water, to make 1 liter solution).

In a beaker take 1 ml of vegetable oil, and dissolve it in 5 ml of Acetone. Use phenolphthalein as indicator. Titrate till the colour of the solution in the beaker, changes from colorless to slight pink. Note the reading in Burette.

Quantity of KOH: For 1,000 liters of vegetable oil,

Quantity of catalyst KOH for reaction: 3.8 Kg.

Quantity of catalyst KOH for neutralization of free fatty acids: 1 Kg of KOH is required for every milliliter of 0.1% solution used in the titration.

Example: If your titration was 5 ml, you need 5 Kg of KOH to neutralize Free Fatty Acids. Use $5 + 3.8 = 8.8$ Kg KOH per 1,000 liter of oil. One more complication, check the purity of your KOH, it's generally about 92%, sometimes less, check the label. Common one is half-pearls assayed at 85%. Adjust the basic quantity accordingly: the basic 3.8 Kgs would be 4.5 (4.470) Kgs for 85% KOH, or 4.15 (4.130) Kgs for 92% KOH. KOH dissolves in methanol much more easily, and doesn't clump together.

First titration: An electronic pH meter is best, but you can also use pH test strips (or litmus paper), or phenolphthalein solution. Dissolve 1 gram of KOH in 1 liter of distilled or de-ionized water (0.1% lye solution). In a smaller beaker, dissolve 1 ml of Vegetable Oil from which moisture is removed in 10 ml of pure isopropyl alcohol. Warm the beaker gently by standing it in some hot water, stir until all the oil dissolves in the alcohol and the mixture turns clear. Add 2 drops of phenolphthalein solution.

Using a graduated burette, add 0.1% lye solution drop by drop to the oil-alcohol-phenolphthalein solution, stirring all the time, until the solution stays pink (actually magenta) for 10 seconds. Take the number of milliliters of 0.1% lye solution you used and add 3.5. This is the number of grams of lye you'll need per liter of oil. With a pH meter or test strips, use the same procedure without adding the phenolphthalein. Add the 0.1% lye solution drop by drop as before until the pH reaches 8.5.

Second titration: Unless you have a very accurate scale, it's not easy to measure exactly 1 gram of sodium hydroxide. It's much easier to measure 5 gm than 1 gm, so mix 5 gm of sodium hydroxide with 500 milliliters of distilled or de-ionized water. Before titration measure out 5 ml of the stock solution, add 45 ml of distilled or de-ionized water. This makes a 0.1% solution. It's also not easy to measure exactly 1 milliliter of oil. Instead of the usual 1 ml of oil and 10 ml of isopropyl alcohol, mix 4 ml of oil in 40 ml of isopropyl alcohol in a glass beaker. Warm the mixture gently by standing the beaker in hot water, stir until all the oil disperses and it becomes a clear mixture. Then titrate as usual, measuring milliliters of stock solution used. When it reaches pH8.5 count up the number of milliliters used as normal and divide by 4. This will give a much more precise measurement. To save on isopropyl alcohol, use 2 ml of oil in 20 ml of isopropyl and divide the results by two, still twice as accurate.

Purity of Raw Materials: Impurities present in the oil also affect conversion levels. Under the same conditions, 67 to 84% conversion into esters can be obtained, using crude vegetable oils, compared with 94 to 97% when using refined oils. The free fatty acids in the original oils interfere with the catalyst. However, under conditions of high temperature this problem can be overcome. It was observed that crude oils were equally good compared to refined oils for production of biodiesel. However, the oils should be properly filtered. Oil quality is very important in this regard. The oil settled at the bottom during storage may give lesser biodiesel recovery because of accumulation of impurities like wax etc.

Raw material and its quality for the production of biodiesel

Vegetable Oil: Any sediment would collect at the bottom of the reaction vessel during settling of Glycerine and at the liquid interface during washing. This would interfere with the separation of the phases and may tend to promote emulsion formation. The oil must be free of moisture because every molecule of water destroys a molecule of the catalyst thus decreasing its concentration. The free fatty acid content should be less than 1%. It was observed that lesser the FFA in oil better is the biodiesel recovery. Higher FFA oil can also be used but the biodiesel recovery will depend upon type of oil and amount of sodium hydroxide used.

Alcohol: Methanol, as near to absolute as possible, can be used. As with the oil, the water affects the extent of conversion enough to prevent the separation of Glycerine from the reaction mixture.

Catalyst: Potassium Hydroxide. The corresponding alkoxides also can be used, but it is prohibitively expensive. Best results are obtained, if the catalyst is $\geq 85\%$ potassium hydroxide. Best grades of potassium hydroxide have 14-15% water, which can not be removed. It should be low in carbonate, because the carbonate is not an efficient catalyst and may cause cloudiness in the final ester. Sodium hydroxide pellets have given very good results. Because quantity of catalyst used is quite less, good quality catalyst (in spite of high cost) can be used.

Animal fats: The most prominent animal fat to be studied for potential biodiesel use is tallow. Tallow contains a high amount of saturated fatty acids, and it has therefore a melting point above ambient temperature.

Waste vegetable oils: Every year many millions of tons of waste cooking oils are collected and used in a variety of ways throughout the world. This is a virtually inexhaustible source of energy, which might also prove an additional line of production for “green” companies. These oils contain some degradation products of vegetable oils and foreign material. However, analyses of used vegetable oils indicate that the differences between used and unused fats are not very great and in most cases simple heating and removal by filtration of solid particles suffices for subsequent trans-esterification. The cetane number of a used frying oil methyl ester was given as 49, thus comparing well with other materials,

Removing fatty acids from Waste Vegetable Oils: In commercial oil refining, this is done with NaOH. Use the titration amount of NaOH, 1 gram for 1 ml WVO, and mix it with 40 ml of water per liter of oil. It gets hot. Using a stainless steel container, it is mixed by stirring. Add the dissolved NaOH to the oil (room temperature), stir gently by hand until thoroughly mixed. Settle overnight. This leaves soap stock at the bottom. The water is apparently in the soap stock. Filter to remove the soap stock, no need for fine filtering, fine steel mesh will do (like a fine tea strainer). Now process as usual for virgin oil, 3.8 grams NaOH per liter of oil, but use 25% methanol, 55° C, good and prolonged agitation as usual.

Reclaiming excess methanol: Depending on the kind of oil you use, it takes from 110-160 milliliters of methanol per liter of oil to form the methyl esters molecule. But you also need to use an excess of methanol to push the conversion process towards completion, the total used is usually 20% and more of the volume of oil used, 200 ml per liter or more. Much of the excess methanol can be recovered after the process for reuse, simply by boiling it off in a closed container with an outlet leading to a simple condenser. Methanol boils at 64.7° C, though of course it starts vaporizing well before it reaches boiling point. Unlike ethanol, methanol does not form an azeotrope with water and relatively pure methanol can be recovered, pure enough to reuse in the next batch.

Methanol can be recovered at the end of the process, or just from the glycerine by-product layer, since most of the excess methanol collects in the by-product and it's that much less material to heat. Start at 65 to 70° C, as the proportion of methanol left in the by-product mixture decreases, the boiling point will increase, so you'll have to raise the temperature to keep the methanol vaporizing, perhaps to as high as 100° C or more, though the bulk of it should have been recovered by then. If you're planning to separate the glycerine from the soaps (FFAs) and catalyst it's best to leave methanol recovery to later as the glycerine probably won't separate without the methanol. The excess methanol can then be recovered from the separated glycerine layer. To keep costs down, biodiesel producers try to salvage the unreacted methanol. There are two major methods to do this: heat extraction and vacuum/heat extraction.

Heat Extraction: Heat the second-stage product to 70° C in a sealed boiler or vessel and lead the fumes into a condenser. Intercept the condensed methanol in a liquid trap. Take great care because methanol is highly flammable and the fumes are explosive.

Glycerine: There is no set amount of by-product, such as 200 ml per liter, and there is no rule that the by-product must be solid at room temperature. What is much more important is that in each of the cases above, the test batch produced a good split, the glycerine separated and settled to the bottom, and, if the directions are followed carefully, the rest would have been good biodiesel, needing no more than settling and washing. The rule of thumb is 79 milliliters of glycerine for every liter of oil used (7.9%). And crude glycerine is not solid at room temperature. But the so-called glycerine layer is not just glycerine, it's a variable mixture of glycerine, soaps, excess methanol, and the catalyst KOH. The quantity varies according to the oil used (more with heavily-used oil), the process used (less with the acid-base two-stage method), the amount of excess methanol used (most of the excess methanol ends up in the by-product layer).

It's mainly the soaps combined with the glycerine that can cause it to solidify. Soaps made from saturated fats such as stearin are harder than those made from unsaturated fats such as olein, so the type of oil used makes a difference. More important is how much soap there is, the more soap, the more likely the by-product layer will solidify, no matter what oil you used.

Other factors are Excess methanol which makes the by-product layer thinner, Too much NaOH creates excess soap, Potassium hydroxide (KOH) makes the by-product slightly thinner than sodium hydroxide (NaOH).

Manufacturing Process for BioDiesel

The process recommended is Trans Esterification using Ultra Sonic equipment. Ultra Sonic Mixer makes intimate contact of raw materials. This leads to higher conversion in 1 hour time.

The acid catalyst process is not recommended as it requires higher energy. The material of construction of equipment is very expensive. Also this process is very slow and that reduces the capacity of the plant.

FEED STOCK PREPARATION TANK OT-01 / 06:

Waste oil is collected in these tanks. The waste oil from Tank Cars is unloaded in OT-01 using PT-3 pump. It is also unloaded in OT-06 using PT-8 pump. For a successful reaction the oil must be free of water. Methods of removing the water content is by Settling the water out. This method saves energy. Heat the oil in O-01 to 60° C, maintain the temperature for 15 minutes and then pump the top oil layer to OT-02 tank. Also heat the oil in O-06 to 60° C, maintain the temperature for 15 minutes and then pump the top oil layer to OT-07 tank. Drain out water from bottom from both the tanks from time to time.

FEED STOCK STORAGE TANK OT-02 / 07:

Let the oil settle for at least 24 hours in OT-02 and OT-07. Make sure you never pump oil to OT-02 or OT-07 to exceed its 90% level. Filter the used cooking oil first as usual through a Oil Filter Press.

Using pump PT-5 for OT-02 and PT-10 for OT-07 pump oil to VE-07.

FEED STOCK PREPARATION TANK VE-07:

Preparation of Oil:

1. Check that the valve on nozzle N1 of the catalyst reactor, VE-07, is closed.
2. Start pumping waste oil, at a rate of 4,000 liters per hour, in the VE-07 through line 50-OIL-01-CS, through nozzle N6 and fill up to 75% of tank level.
3. Make sure that the valves in cooling water lines 25-WAT-40-GI and 25-WAT-41-GI are closed and start steam through 25-ST-38-CS and maintain the contents to 80 deg C.
4. Once oil is heated up to 80 deg C, open valve on nozzle N1 on VE-07 and start pumping oil by P-08, through 50-WO-02-CS and 50-WO-03-CS to static mixer SM-11 and then to Ultra Sonic Unit UU-12, at a rate of 4,250 liters per hour. (along with methoxide stream when it is ready).

CATALYST REACTOR VE-09:

Preparation of Potassium Methoxide:

1. Check that the valve on nozzle N1 of the catalyst reactor, VE-09, is open.
2. Start pumping 99% pure Methanol, at a rate of 1,000 liters per hour, in the VE-09 through line 50-MET-04-CS, through nozzle N6.
3. After the vessel is half full, start agitator.
4. Open valve in line 50-MET-06-SS on nozzle N10. Start the Pump P-10. Check the quantity of KOH required as per free fatty acids in the oil. It should be added continuously. (It is described below under Catalyst) Through nozzle N11, slowly add required quantity of KOH.
5. Circulate all contents in VE-09 by pump P-10, for further 15 minutes. The temperature of mixture rises by 5 to 6 degrees C, which is normal.

6. Leaving the valve on nozzle N-10 open valves on Control Valve CV-6, start pumping the solution and adjust flow rate to 1,000 liters per hour. The Sodium Methoxide solution will pass through 50-MET-07-SS in Static Mixer SM-11 and then to Ultra Sonic Unit UU-12. (along with waste oil stream when it is ready).

BIODIESEL REACTOR VE-13:

1. Check that the valve on nozzle N3 and N4 on Condenser C-14 are open and check that cooling water pump is on, and cooling water is running in condenser.
2. Check that the valve on nozzle N1 of the biodiesel reactor, VE-13, is closed.
3. Fill the VE-13 up to 50% level and start agitator.
4. Open valve on nozzle N-1 and N-10 and start pump P-15.
5. When VE-13 is full to 80% level open valves on control valve CV-9 and through line 50-BIO-14-SS pump it to CE-16 at a rate of 4,000 liters per hour.

CENTRIFUGE CE-16:

1. Open valve in line 50-GLY-16-SS is open and continuously pump filtered glycerine to GT-14 by pump P-17.

WASHING TANK VE-16:

1. Open valve on N-6 on Washing Tank VE-16, and allow biodiesel to collect in VE-16.
2. Once VE-16 is full to 50% level, start agitator and add continuously 400 kgs of Magnesol. Maintain temperature of VE-16 at 80 deg C.
3. When vessel VE-16 is full to 80% level, open the bottom valve on nozzle N1 open, and pump the washed biodiesel using pump P-19 to PF-20, and then through 50-BIO-21-SS to BT-11 or BT-12, so as to maintain level in VE-16.

METHANOL RECOVERY TANK VE-01:

1. Pump filtered glycerine from GT-14, using pump PT-16, through 50-GLY-22-CS so as to maintain 75% level in VE-01. Run the agitator. Start steam through 25-STM-35-CS, and maintain temperature at 65 deg C. Pump out crude glycerine using pump P-03, to crude glycerine tank GT-15. Recovered methanol flows by gravity to Recovered Methanol Storage Tank MT-20.

To shut down the plant, stop supply of oil, methanol and catalyst in respective vessels, and continue the process till all in process materials are totally processed.

Dry Washing: Purolite PD206 was developed and launched initially in early 2006. The product is used in columns to polish contaminants derived in biodiesel production to meet European / USA standards. It is primarily used to remove glycerine, soaps, cation salts (some derived from the esterification process catalyst), and water. It also has a very limited capacity for methanol and hence it is best to ensure you achieve good demethylation prior to the PD206 columns if you are to meet methanol limits / flash point defined in international standards for biodiesel.

A technical data sheet covering Purolite PD206 and other technical information covering frequently asked questions about our product is available along with. Since its introduction Purolite PD206 has been installed in small, medium and also large scale refinery installations with considerable success and there are no product failures in service to date.

The product can be used in two potential locations within the plant. In the majority of cases it is used in final polishing treating good quality biodiesel at specific flow rates of 2-3 Bulk Volumes / hour to achieve B100 specifications. On large installations

where glycerine loadings are high it can also be used before the demethylation stage operating at 1.5 – 3.0 Bulk Volumes / hour depending on the quality. In this location methanol regeneration is possible to prolong the resin life in this duty. If ionic loadings are low then we have found the resin can be regenerated 5-10 times before ionic exhaustion warrants a resin change.

In final polishing some use after water wash stages, but increasingly clients have optimised their plants and are now using the resin in place of water wash as the only polishing stage after demethylation. This avoids using the other more complicated and labour intensive systems which have effluent and waste disposal and fine filtration problems.

Plant Sizing - Purolite PD206: The resin is normally operated in 2 columns in series with preferably a minimum bed depth of 600 mm of Purolite PD206. A sample point is located after each column to check performance. When the lead column is fully exhausted the polisher is moved to the lead position and new resin is placed in the exhausted column and it is then put in the lag position to act as the polisher. This method of operation maximises the media life. By installing three vessels with one in standby with fresh resin it is possible to maintain continuous production.

The units when used as polishers are rated at 2-3 Bulk Volumes / hour flow rate. For example, on a flow rate of 300 litres per hour the recommended bed size would typically be 100-150 litres (100 litres at 3 Bulk Volumes / hour and 150 litres at 2 Bulk Volumes / hour). The better the influent quality the higher the Bulk Volumes / hour flow rate you can operate at.

Typical bulk density figures are given for PD206 on the attached Product Data Sheet to enable you to convert the volume to a weight of product. (we use 815 grams / liter for our calculations tower sizing calculations to work back to the weight of PD206 required).

It is suggested to allow 100% freeboard in the columns as the resin swells dramatically on the take up of moisture etc. To ensure the PD206 is retained within the vessel bottom collection systems (nozzles / laterals or wedge wire strainers) should be sized at 150 microns as the smallest beads are quite small when supplied as a dry product. Due to the large amount of resin swelling in this duty it is important that the height to diameter ratio is not too high. As a guide, it should be a maximum of 3:1.

Washing Vessel: The washing vessel is used as tower. It is manufactured in steel. It is important in any design to ensure you have the flexibility to have either column as the lead or lag unit and that you have sample points after each washing vessel and a means of easily removing and emptying the vessels when the media is exhausted and a means of easy filling with the new product. Plastics are not suitable for vessels / pipework in biodiesel applications. Designs of washing vessel is considered how you will remove and refill the vessel with fresh Purolite PD206 when it has been exhausted.

Typical Performance: In final polishing mode our wash vessel, used for producing good quality biodiesel, the Purolite PD206 can treat up to 2000 Kgs of biodiesel from 1 Kg of product. To date most customers are achieving between 500 – 1500 Kgs production per Kg of PD206 depending on feed biodiesel quality and the efficiency of their tower design. Good distribution / collection system design is essential at such low Bulk Volumes / hour rates if plug flow and maximum utilisation of the resin is to be achieved.