BIOdiesel Tech NOTES

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METHANOL RECOVERY FROM THE BIODIESEL PRODUCTION PROCESS

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Biodiesel is made by reacting a triglyceride (the component of oil or fat) or a fatty acid with an alcohol to produce a fatty acid alcohol ester, usually with the aid of a catalyst (such as sodium methoxide). It can be produced from many different alcohols but methanol is the simplest, most reactive and least expensive of all the alcohols, which makes it the product of choice for biodiesel producers. However, it is more dangerous to handle and store than some of the heavier alcohols, such as ethanol. The chemical formula for methanol is CH_3OH. It is a colorless liquid that is highly volatile (boiling point of 64.7°C) and flammable (flash point of 8°C), and burns with an invisible flame. It is very toxic and quickly absorbed into the body through the skin and lungs when workers are exposed to the liquid and/or the vapor. Appropriate safety precautions must be taken to avoid accidents. For more details on this subject, please see **TechNote #08 Safety Considerations for Biodiesel**.

Most of the biodiesel production methods require an excess of methanol over the stoichiometric ratio required for the reaction. Typically an excess of twice the required amount is used. Because of the nature of the equilibrium and reversible reaction for biodiesel production, the excess methanol is employed to favor a more complete reaction to achieve a higher quality product. In order to improve efficiencies and conserve resources, it behooves producers to recover and reuse the excess or residual methanol. This alcohol is distributed between the lighter biodiesel phase and the heavier (byproduct) glycerol phase.

When the phases are separated by gravity, centrifugation or some other method, the methanol recovery process begins. Sometimes a partial recovery is effectively made before separation.

This Technote describes some of the methods used to recover methanol as part of the biodiesel production process, as well as how to refine it for reuse.

Recovery methods vary greatly depending on the production processes and throughput. Considering a batch process, once the reaction is complete, approximately 90%vol of the contents of the reactor is the lighter biodiesel and 10%vol is heavier glycerol with the unreacted methanol distributed between the two phases at a ratio of 60:40 by weight. Since methanol is more soluble in glycerol, it tends to slow the separation of the two phases. If some methanol is removed from reaction mixture at this stage with heat and vacuum, it will hasten the separation process and may cause soap, an undesirable reaction product, to precipitate out as it is also soluble in methanol. Any alcohol remaining in the fuel layer will be washed out during the water wash step or flashed off if a dry wash method is utilized.

To recover methanol from the biodiesel, producers who plan to use ion exchange resin for the removal of soap and glycerol are advised to leave the methanol in until after the resin treatment. After methanol removal, the biodiesel is very dry and free of methanol. The methanol recovered, however, is wet and must be further refined by distillation or dried by molecular sieve in order to recycle it back into the biodiesel production process.

The process of removing methanol and water by flash evaporation requires several steps. The biodiesel or crude glycerol (depending on which stream is being processed) is heated to 140°C as it is passed through a

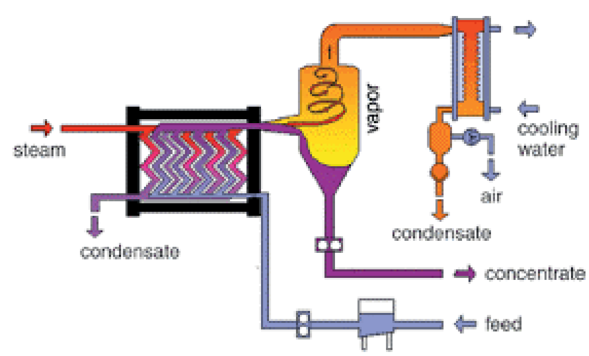

Figure 1. Flash Evaporator
Diagram Source:
spxflow.com/en/assets/pdf/Evaporator_Handbook_10003_01_08_2008_US.pdf

heat exchanger. It is then sprayed at an elevated pressure into a tank, sometimes under vacuum, where the methanol and water are instantly vaporized and drawn into a chilled condenser. After condensation, the vapor of methanol and water forms back into a liquid mixture for further purification. The residual fuel or glycerol that fall to the bottom of the flash drum are now dry and can be drained off into storage.

Another method of recovering methanol from raw biodiesel or glycerol is by thin film or falling film evaporation. In an exemplary system, the methanol laden liquid is pumped into the top of a cylinder with multiple spinning plates in the center section. The liquid is thrown onto the heated walls by centrifugal force to create a thin film to facilitate evaporation of methanol and water. The vapors of methanol and water are removed from the system, condensed and passed on to the next stage of purification.

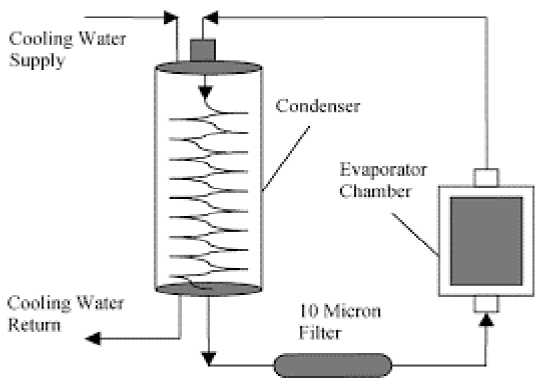

Figure 2. Thin Film Evaporator
Diagram Source: ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=1516180

A simpler type of evaporator (falling film) employs a series of static heated plates over which the liquid mixture flows by gravity. The thin layer of liquid spreads out over a large area which facilitates the evaporation of methanol/water (in this case). The vapor

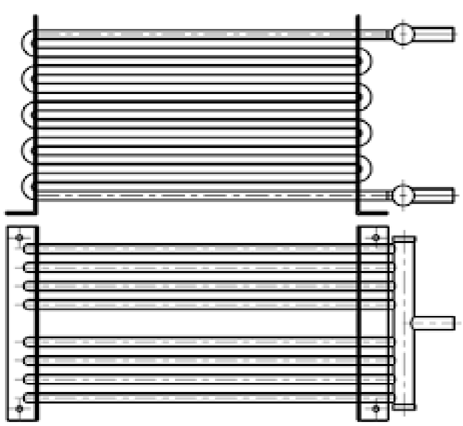

Figure 3. Falling Film Evaporator

is swept out and recovered as the less volatile phase is pumped off into storage.

The final step in the recovery process is to dry the methanol. Pure dry methanol is necessary to achieve a more complete reaction, free of complications, in producing biodiesel. The initial stripping of the methanol from the fuel and the glycerol with flash or thin film evaporation brings water with it, which is highly miscible with the alcohol. Separating the water from the methanol is typically done by distillation. While several types of distillation processes are in use, the one most commonly used in the biodiesel industry is vacuum distillation. The boiling point of methanol is 64.7°C and that of water is 100°C. Simple distillation where the vapors are fed directly into the condenser does not achieve a pure enough product for reuse. Therefore, a tall packed or stacked plate column of high separation capacity is needed. In this continuous flow situation, the liquid mixture is fed into a boiler which sends vapors up through the column. On the way up, the vapor mixture goes through a series of condensation and vaporization cycles until the more volatile methanol is taken off from the top and the less volatile water flows downward and drawn off at the bottom. Likewise, wash water containing methanol is processed in the same way.

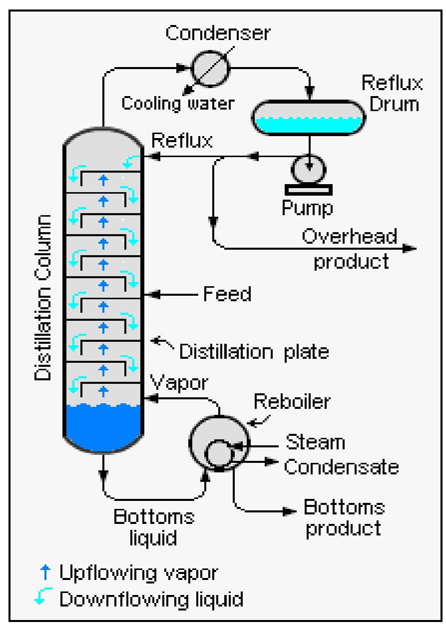

Figure 4. A Distillation Set-up
Diagram Source: deilataylor.com/eternal-round-and-distilling-souls/

Before using it in biodiesel production, the recovered methanol should be checked for its quality. The best quality measurement is dissolved water, which can be quickly made with a Karl Fisher titrator accurately down to 10 ppm.