Purification of crude glycerol from biodiesel

Crude glycerol is the by product produced throughout the biodiesel production process. However glycerol produced at this stage is crude glycerol which is about 80% pure and contains other contaminants like methanol, water, salt and soap. Crude glycerol has approximately about 45% glycerol, 10-15% water and methanol, 10-15% salt, and 30% soaps by weight2. This crude glycerol is not a highly valued chemical so a purification process must be done to make the crude glycerol into useful glycerol used for industrial application. Due to large supply of crude glycerol, purifying glycerol will maximise the biodiesel production profits. During the refinement process into technical grade glycerol, the methanol is evaporated from glycerol fraction. The salt, methanol, odors, and water are removed. Crude glycerol refine into technical grade glycerol gives <97% purity. The technical grade glycerol is much more useful for industrial application as it removes the high cost of toxic waste disposal which increases the value of the end product.

The purity of glycerol determines the value of glycerol, the higher the purity of glycerol the higher the market value for glycerol. Glycerol refinement will help biodiesel plants turn into a stronger profit with its refined glycerol's since it cost less than fully refined grade. The refined grade greens the business as its takes less energy to produce and it is renewable. For this reason the demand for refining glycerol into technical grade glycerol and further has increased. The refining process is however currently expensive. USP (The United States Pharmacopeia) is highly purified glycerol, purity of glycerol > 99. 7%. This is a pharmaceuticals grade which is useful in cosmetics, personal care, food and other specialty application.

Typical Processes:

- Adsorption
- Vacuum Distillation
- Further purification
- Methanol Removal Step (Flash Evaporators or falling film evaporator)
- Neutralization Step (Soap Splitting)
- Crude glycerol
- Ion exchange

General process

There are many way to refine glycerol. Soap splitting is involved in all of the refining process as a glycerol pre-treatment step. The soap splitting involves to major separation step which removes methanol and salt. In all purification step process that are soap and other organic impurities need to be removed by centrifugation /filtration. Purification process can be done mainly in three steps.

Neutralisation involves in the 1st step which uses an acid to remove soaps and catalyst. FFA and salt will produce with the reaction of an acid with soap, and salt and water produces with the reaction with the base catalyst. Insoluble salt and FFA in the glycerol will precipitate out and some will be skimmed off. FFA and salt can also be eliminated by filtration. The colour of filtrate coming from neutralisation step is light brown or yellow colour. Removal of methanol is the purpose in 2nd step which is the preliminary stage of refining. Using a falling film evaporator or flash evaporators can be used to remove methanol from the glycerol. The advantage using a falling film evaporator is the short contact time and is better suited to this process because it decomposes due to temperature inclination of glycerol. The purity of glycerol is around 80% after the removal of methanol. In the 3rd step, a further purification of glycerol can be done by mixture of ion-exchange, vacuum distillation, adsorption, extraction and crystallisation, dialysis, precipitation. The glycerol is purified around > 99. 7% in the 3rd step of the purification.

Further purification

Ion exchange and concentration purification process

The ion exchange system uses cation, anion, and mixed bed exchangers to remove catalyst and other impurities3. The removal of ionic substances by ion exclusion chromatography is the concentration step. Due to their charge, the ionic substances are repelled from the resin surface which stays in the liquid volume. The non-ionic substances are accommodated in the resins and pores. Anionic and cationic ion exchangers are exchanged for wash water, which first removes the ionic substances in the liquid and later the non-ionic substances. Negative anionic ion exchangers are exchanged for hydroxide ions where as positive cationic ion exchanged for hydrogen ions. The purification step is the next step which uses ion exchangers. The removal of odour and colour, inorganic salts, soap and fat components are done by the purification process.

For smaller capacity plants, ion exchange purification of glycerol is a good alternative to vacuum distillation. However for this process ion-exchange is not economical since high salt content of glycerol issued from biodiesel production. When the salt content is around 5-7 percent range the chemical regeneration costs becomes extremely high. The disadvantage of the ion-exchange is that it obstructs the process obtaining high purity glycerol and also the system is fouling by soaps and fatty acids. The other shortcoming is the necessity for water evaporation after purification, which results in additional losses of glycerin, carried over by water steam4.

Vacuum distillation

Vacuum distillation with steam injection, followed by activated carbon bleaching is the commonly practised method for the final purification of glycerol. Evaporation of components can be accomplished in vacuum distillation. Vacuum distillation is also known as low temperature distillation. Vacuum distillation is used as separator in some separation techniques because glycerol is sensitive to heat and the compound splits into water and decomposes. Due to high boiling point of glycerol an extreme deep vacuum should be used to distil glycerol from inorganic salt.

The advantages of vacuum distillation are that it is a commonly well established technology as it produces high purity glycerol in high yield. Another advantage is it is the reduced temperature requirement at lower pressures. Vacuum distillation could be used without heating the solution. The number of equilibrium stages needed can be reduced by utilizing the vacuum distillation. The disadvantage of this process is that distillation of glycerol has high capital cost and it is energy intensive. This is because glycerol heat capacity is high which demands a high energy input for vaporisation. The vacuum distillation cannot proceed out continuously and is accompanied by considerable losses of glycerol. It been suggested that vacuum distillation of glycerol is best suited to operations > 25 tons per day3.

Column adsorption/crystallisation

An adsorption technique is an established technology for separating glycerol, ions, water and methanol. Odor and pigments can be eliminated by adsorption on activated carbon. Activated carbon in the adsorption process removes soluble substance from water. It is used to make the carbon extremely porous and therefore have a very large surface area available for adsorption. The large internal surface makes active carbon ideal for adsorption. The activated carbon functions longer when the pores are bigger. Using activated carbon is good in waste water cleaning. However activated carbon is expensive to regenerate the carbon.

Due to high pressure drop and high viscosity of crude glycerol, the operational cost of the column adsorption will be high. Chromatography separation is the new progress in adsorption techniques. Chromatography separation is used to separate small amounts of samples in laboratory. Some of the possible chromatography techniques are: ion exchanged chromatography, reversed phase, affinity chromatography and hydrophobic interaction, gel permeation or molecular sieves may be used as the solid stationary phase in column chromatography. Ion exchange chromatography as an adsorption provides an ionic environment which allows two or more solutes in the feed stream to be separated. Glycerol and water separation are based on particle size and affinity. Since water is difficult to separate from glycerol, a suitable type of adsorbent with respect to high separation efficiency at low pressure drops and at a high volume flow capacity is required.

New process route for glycerol purification

This process above can be either continuous or batch mode. The process consists of five separation steps: first reactor, second reactor, decanter, flash distillation column, and adsorption column. This new process developed by John E. Aiken claims to be able to produce glycerol higher than 99. 5% purity from typical crude glycerol6.

First reactor:

The crude glycerol is preheated first before heading for the first reactor. The purpose of the first reactor is by reacting glycerol and methyl esters to produce methanol and glycerides. The water and methanol removed when nitrogen is sparged. The gas runoff stream is passed through a condenser. The nitrogen is recycled back to the reactor when water and methanol are condensed (separated) through a condenser.

Second reactor:

The purpose of this reactor is that the unreacted methyl esters are reacted to produce triglycerides and methanol. Wash water has glycerol, is also added to the 2nd reactor. From the 1st reactor the liquid effulent stream is heated to preserve the 2nd reactor at 120-160oc just like the 1st reactor. Wash water is recycled when water and methanol is separated from nitrogen.

Decanter:

The purpose of decanter placed after the reactor is to get rid of the oil layer from glycerol stream by reducing the pH below 7 and also skimming it from the glycerol layer. In this tank glycerol stream is mixed with the recycled stream from the bottom of the flash column.

Flash distillation column:

In the flash distillation, the top column (vapour fraction) product is about 80-90% of glycerol from the feed stream is to be condensing in two condensers in series. Condensing glycerol is used in the first condenser whereas water condensing used in the 2nd condenser that will be sent to waster water stream. The heavy compounds and glycerol comes out of the bottom product (liquid fraction) is pumped back to the decanter. To prevent glycerol and salts build up in the decanter, some of is purged.

Adsorption columns

Removing the trace impurities and colour is the last step of glycerol refining. Ion exchange resins and activated carbon can be used as adsorbent material. Glycerol is then purified into a storage tank.