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A review on glycerol purification consequent to its formation as a byproduct in biodiesel manufacture by trans-esterification process of fats

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Abstract
Production of biodiesel is becoming popular for its obvious reasons. Tranesterification technology is till date the main method to get fatty acid methyl esters or biodiesel. Glycerol formed as a byproduct in transesterification could be utilized after freeing it from contaminants. This short review provides critical and essential process parameters firstly to have pure biodiesel product and more particularly to get pure glycerol byproduct, both being used in their purer forms for different purposes. The work of several workers suggests that glycerol washing as a focus comprise raw glycerol being treated with a few physicochemical processes and enhance its purity to as high as over 95% which since from commercial angle
is a good achievement. The steps suggest what among others are safe process steps, what physical processes are best suited and what practices yield highly pure glycerol. Not only the chemicals like solvents utilized in the process could be recovered but also value-added pure byproduct glycerol could be produced on a substantial scale from biodiesel industry.
Keywords: Glycerol washing, purity, biodiesel, recovery, solvents, physico-chemical processes

Glycerol is one of the chief byproduct obtained after the alcohol mediated transesterification process of conversion of fats into biodiesel. Generally about 10% of glycerol is obtained as a byproduct in biodiesel industry. The crude glycerol surplus is often the scenario in biodiesel companies. It is profitable to utilize glycerol in a more value added manner, to use it for manufacture of animal feed stock, cosmetic and drugs.

Good efforts have been made to optimize production of biodiesel as well as to recover methanol being used as a catalyst in trans-esterification reaction. There also have been reports to purify glycerol byproduct for the reasons of exploiting its commercial potential. The purification processes reported have been met with effectively since the cost and purity in high measures are among the goals of industry. The glycerol recovery also adds on the profitability of process and commercial viability of the process itself. Therefore, the recovery and purification of glycerol is a welcome step. Focused research to free glycerol from process contaminants is not only meaningful from profitability but also could become a necessity, since there is a high demand for glycerol in the markets of it being used as a starting material for production range of chemical products chiefly from pharma industry among others. Thus, washing to free contaminants from glycerol could serve the industry essential requirement to produce quality products as well as minimization of waste chemicals in chemical product manufacturing industry.

***Biodiesel process steps critical to consequent purification biodiesel and glycerol are the following*:** Free fatty acid (FFA) test is critical to the feedstock to be transesterified; a 5% FFA could entail to be processed for the production of biodiesel oil[1].

There are several algorithms available that suggest ratios and proportions of diesel to alcohol as well as alkali reactants used in transesterification process. The best option could be that right a mix of catalyst and alkali (that form sodium methoxide that reacts and converts fats to fatty acid methyl esters which is known as biodiesel).

A two-stage process is suggested that has potential of using lesser alcohol quantity:

First stage

(i) 80 percent of the alcohol and catalyst is added to the reactant oil in the first reactor.

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(ii) A glycerol removal step before entering subsequent reactor.

Second stage

(i) 20 percent of the alcohol and catalyst is added to the glycerol freed contents taken in subsequent reactor.

The two stage process happens to be superior to addition of alcohol in single stretch[2].

Glycerol wash process: The biodiesel formed in the reactor itself could be the vessel where washing could be done. The glycerol could be injected into the open space of the reactor, heating the stock to 65^0C followed by a minimum of 30 minute of longer shaking and allowing the contents of the reactor to settle. Glycerol being denser settles at bottom layer and biodiesel as the top layer.

The washing of waste glycerin byproduct from biodiesel plant has benefits; the washing process will minimize the water content of the biodiesel, lowers the acid value of biodiesel, and is a way to recover biodiesel that is trapped into glycerol. The process can also free the methanol which is used as a catalyst in the manufacture of biodiesel.

The glycerol volume injected into vessel will be more in the event water is absorbed into the glycerol or it will be less if the biodiesel and methanol are released into the biodiesel.

Glycerol Separation: The fatty acid methyl esters are to be freed from glycerol and this is achieved by just a settling process since glycerol is less soluble than the esters. The process could be hastened by centrifugation. The excess of methanol, however results in slower separation since it acts as a solubilizer and this fact emphasizes titrated amount of usage of methanol. Removal of excess methanol is not recommended at this stage since the transesterification reaction is reversible and recombination of methyl esters can happen resulting in formation of monoglycerides.

The first step in refining the glycerol is usually to add phosphoric acid to split the soaps into free fatty acids and salts. The free fatty acids being insoluble in the glycerol will rise to the top, where they can be removed and recycled. The salts remain with the glycerol. One frequently touted option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization, so that the salt formed is potassium phosphate that has a value as fertilizer[3].

After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a vacuum flash process, or another type of evaporator. At this point, the glycerol should have a purity of approximately 85 percent and this is typically sold to a glycerol refiner. The glycerol refining process takes the purity up to 99.5 percent to 99.7 percent, using vacuum distillation or ion exchange processes[4].

***Spectrum of glycerol recovery and purification – Reported processes*:** The foregoing gives an account from simple to more complex processes aimed to recover and purify the glycerol byproduct from biodiesel reactor plants.

A simple distillation process with water mix to obtain crude glycerol has been reported. The color removal along with the odor minimization of glycerol was achieved by usage of cellulose films according to a patent obtained by Gilbert in the year, 1938[5]. The purity of crude glycerol obtained was 95%. A Chinese study reports that effort to obtain highly purified glycerol from biodiesel a co-product was analyzed for composition of several ingredients and the results were glycerol (43.73%), Salt of fatty acid (21.73%), biodiesel (14.23%), and methanol (16.47%)[4].

A focused work informing about the refining technology of glycerol from byproducts of biodiesel indicated 99.6% purity at the end of processes like ion-exchange method where macroporous was used; After stopping stirring react mixture, the by-product was added 20% water followed by neutralization to ph of 4.5~5.5 by adding 50% H2SO4. Separation achieved by centrifugation with addition of 0.1% activated carbon, the reaction mix stirred 20 minutes at 80 ^{0}C and the negative ion and positive ions were removed through strong alkali and weak acid and resins[6].

A study conducted in 1941 reported that since the synthetic glycerol had lot of impurities, crystallization with a suitable solvent improved the purity[7]; however, the study was not related to biodiesel production. Yet another study, reported in the year 1956 tells about reduction of ion content to a low value by maintaining elevated temperatures and employing copolymer matrix yielded better results[8].

The quality of glycerol was improved by rising pH of glycerol byproduct to 9.67 using potassium phosphate followed by acidification to a pH of 4.67 to salt-out potassium phosphate. The quality of potassium phosphate improved with a spin-off benefit of improving purity of glycerol to 96.08% and the quality of free fatty acids reported was 99.58%[9].

Phosphates and usage of phosphoric acid in purifying glycerol: A study that related to purification of crude glycerol by using sludge derived activated carbon adsorbent prepared by chemical activation with H_3PO_4, K_2CO_3 and KOH was used for desulfurization of crude glycerol followed by a KOH-800AC treatment that remarkably improved the purity of glycerol. The adsorption process time including shaking rate had an influence on the purification of glycerol[3].

A Korean study attempting to purify crude glycerol from waste and used-oil as feedstock being transesterified reports chemical and physical treatments based upon repeated cycles of acidification using 1.19 M H_2SO_4; allowing phase separation and harvesting of the glycerol-rich middle phase followed by neutralization of the harvested glycerol phase with 12.5M NaOH; glycerol-enriched fraction was extracted by ethanol and finally a high purity glycerol (~93.34%) was obtained[10].

An interesting study is done to treat crude glycerol for purification using acids like concentrated sulfuric, hydrochloric or phosphoric acid and the results were compared. The study concludes that glycerol could be purified to an extent of 96%; effects of pH values on purification was studied and report that phosphoric acid was found to be the best purifying agent among the others[11].

It is reported that the sequence relating to the nature of solvents will effectively purify the glycerin. A glycerin purity of 99.2% was obtained when extracted by petroleum ether followed by toluene . Subsequently using activated carbon as an adsorbent and conducting absorption process twice is advised. This method had an advantage of attributing non-hazardous condition compared to the vacuum distillation process[12].

Summary and Conclusion**:** The gist of physico-chemical processes attempted for purification of glycerol as a byproduct obtained in trans-esterification process suggests: repeated and cyclic acidification using mineral acids to a desired pH level; leaving the reaction-wash-mix for certain time for settlement; washing of the glycerol phase by inorganic salt solution like sodium oxalate[13]; collection of purified glycerol phase by vacuum distillation or sequential washing in repeated cycles by usage of solvents, preferred solvents being petroleum ether and toluene. The de-colorization is achieved by usage of common color adsorbents like activated carbon. The physico-chemical processes employed by research workers are: vacuum distillation, micro-filtration, ion-exchange using resins; neutralization and centrifugation.

The crude glycerol will generally have soap, light solvents, water, methanol, fatty acid methyl esters (FAMEs), glycerides (mono, di and triglycerides) several types of free fatty acids (FFAs), and in varying proportions. Glycerol refining or purifying processes, therefore should aim to remove these contaminants with such physic-chemical interventions that augment to get pure glycerol and effectively get rid of interfering contaminants, with a consideration on the economics of the whole refining process. Usages of different strengths of phosphoric acid and process maneuvers have been adopted to get high purity glycerol as well as a few spinoff beneficial chemicals. Such processes yielded a level of glycerol purity to an extent of over 98%.

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Conflict of interest

The author's declares none.

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