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POSSIBILITIES OF USING BIODIESEL BY-PRODUCT: GLYCEROL

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ABSTRACT
A rapid growth in biofuels production leads to a surplus of by-products generated. It is an effort to their economic and environmental friendly use.This paper reports the possibilities of production and purification of glycerol as by-product of biodiesel, soap and fatty acid industry. It is first step for his chemical, his biochemical and energetic applications.

KEY WORDS: *Biodiesel, glycerol, purification, refining*

INTRODUCTION

Glycerol (also known as glycerin) is a polyol (1,2,3-propanetriol), naturally occurring in the structure of triglycerides, which are fatty acid esters of this alcohol. It is a colourless, odorless, viscous liquid with a sweet taste very soluble in water.

Currently, there are o lot of of glycerol application suitable for this substance (more than 2,000) in different fields such as the cosmetic, pharmaceutical or food industry, where it is mainly employed as humectant, thickener, lubricant, sweetener or anti-freezer, among others uses.Glycerol is also appreciate raw material, which offers various types of chemical reactions – oxidation, hydrogenolysis, dehydration, esterification, etherification, oligomerisation, carboxylation or pyrolysis/gasification. Glycerol has been found to be an interesting reaction medium in organic synthesis, both with and without the help of a catalyst. One of the possible new uses of glycerol and its derivatives is usage as a solvent.Glycerol-derived solvents can be classify into two very different groups. In the first one, there are “classical” glycerol derivatives that have been traditionally used as solvents, such as esters (like acetins), carbonates (glycerol carbonate), acetals (glycerol formal) and ketals (solketal). In the second group,there are organic solvents that are usually prepared from other sources, but for which synthesis starting from glycerol have been described, and may become competitive as the price of glycerol decreases. It is the case of propylene glycol, 1,3-propanediol, ethyl lactate or butanol.[1]

Usage of crude glycerol is limited by its impurities.For example, impurities in crude glycerol has shown an inhibitory effect on high cell density production of phytase. [2]As well as, a high content of sodiumand potassium can inhibit the microbial activity, in crude glycerol. The concern of major health safety and environmental issue for residual methanol in biodiesel and glycerol is due to the toxicity of methanol, in which the emission of excess methanol can have serious effects to the environment and public health. Therefore, the excess amount of methanol needs to be removed from the glycerol phase and recycled back. [3]The goal of the purification process is to enhance usability of glycerol by removing unwanted impurities according to different sets of standard and purposes.

1. GLYCEROL PRODUCTION

Glycerol production is realized in two different routes, synthetically from propylene (a petroleum-derived product)and via natural processes.

SYNTHETIC ROUTES

Because of the high industrial demand of glycerol, chemical transformations from propylene were developed in the past to synthesize glycerol (Fig. 1). The most used is epichlorohydrin hydrolysis. This reaction is reversible and is also used for the preparation of epichlorohydrin (this substance is used in a wide variety of manufacturing applications, including epoxy and phenoxy resins and textiles, ion exchange resins, rubbers, paper saturated resins and agricultural products. The most familiar epoxy resin is used as a coating on the inside of food and beverage cans to prevent rusting). Chlorine-free processes from propylene include the synthesis of glycerol from acrolein and propylene oxide. [4]Since 2004, after the development of biofuels is the production of glycerol not applied anymore (not economical).

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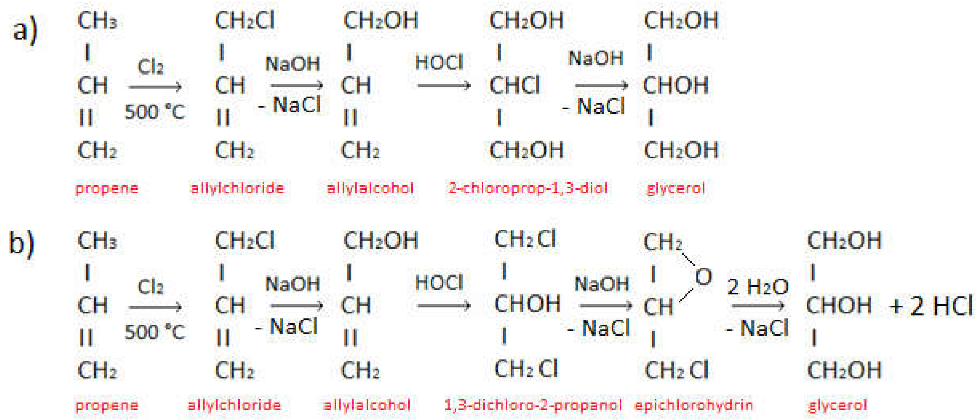

Fig. 1: Two synthetic routes of glycerol production from propylene

NATURAL ROUTES

Glycerol is currently produce from the transesterification process during biodiesel production and the saponification and hydrolysis processes in fatty acid manufacturing plants. Only smaller amounts of glycerol is produce by fermentation processes (mainly for the food and pharmaceutical industry).

- *Fermentation from sugar*–alcoholic fermentation of sugar (Fig. 2) gives about 3 % glycerol. However, if the fermentation is done in presence of sodium sulphite, the yield can be increased to 25 %.

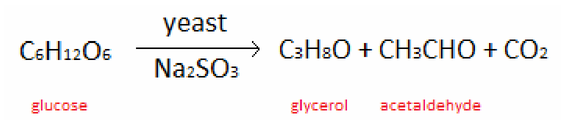

Fig.2: Glycerol production via fermentation process

- *Fat splitting*–is one of basic oleochemical process to produce fatty acid and glycerol (Fig. 3). For example, fat splitting of crude palm oil and palm kernel oil in medium pressure can produce around 50 –60 % of fatty acid and 9,8% glycerol. [5]

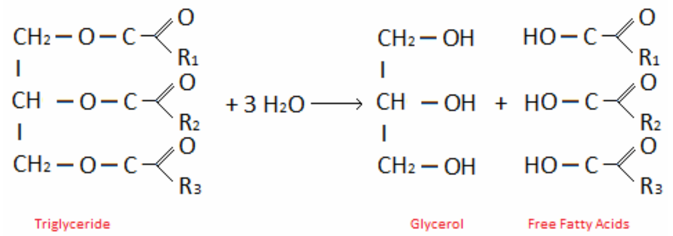

Fig.3: Glycerol production via fat splitting process

- *Saponification*–it is a base hydrolysis of fats and oils, which are chemically called as triglycerides. The reaction produces carboxylic acid salts (soap) and glycerol (Fig. 4).

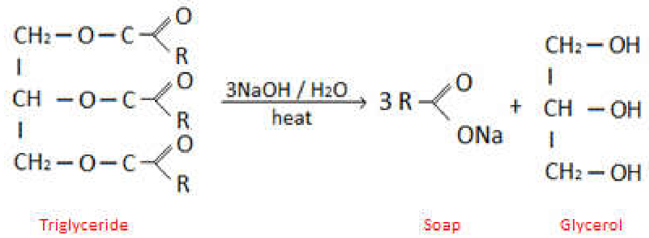

Fig.4: Glycerol production via saponification

- *Biodiesel production*–transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The reaction is shown in Fig. 5. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Glycerol is commonly separated by gravitational settling or centrifuging. [6]

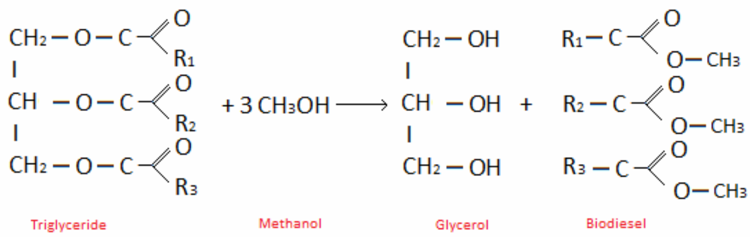

Fig.5: Glycerol production via transesterification of triglycerides with alcohol

2. CRUDE GLYCEROL PURIFICATION AND REFINING

The crude glycerol generated from biodiesel plants include many impurities and other chemicals, for instance, methanol, organic and inorganic salts, water, vegetable colours, mono and diglyceride traces and soap. The percentage of glycerol present in the crude glycerol can vary from as low as 45 % to upwards of 90 % depending on various reaction conditions, as well as the extent to which the crude glycerol is produced by the biodiesel plant. The chemical composition mainly depends on the type of catalyst used to produce biodiesel, the transesterification efficiency, and recovery efficiency of the biodiesel, other impurities in the feedstock, and whether the methanol and catalysts were recovered.[7][8]

The first step involves the removal of non-glycerol substances which can be achieved through precipitations during neutralization, whereby free fatty acids and some salts are removed. The next step is to concentrate the solution by evaporation in which alcohol is removed from the glycerol stream. The final step is the purification and refining stepwhich can be achieved to the desired degree with a combination of these methods which are vacuum distillation, ion exchange, membrane separation and adsorption.[9] The purification of crude glycerol is an expensive process, requiring expensive processing equipment. [7]

NEUTRALIZATION

Neutralization is the most common method as pre-treatment of crude glycerol purification processes involving a chemical reaction using a strong acid to remove catalyst and soaps. The reaction of acid with soap would produce free fatty acids and its reaction with base catalyst would give salt and water. The insoluble free fatty acids and some salts will rise to the top and can be easily skimmed off. The first step through the acidification process usually separates the crude glycerol into three layers of free fatty acids at the top, glycerol rich layer in the middle and inorganic salts at the bottom. The disadvantages of this procedure are: the repeated acidification would result in low glycerol yield and this technology requires further purification to produce high quality glycerol.

METHANOL REMOVAL

In the transesterification process, excess methanol is used in most biodiesel production to get high yield of biodiesel. The excess methanol is distributed between the methyl ester and crude glycerol phase. Methanol and water can be easily removed by vacuum evaporation. Due to glycerol temperature susceptibility, inappropriate evaporation can result the glycerol decomposition. The purity of crude glycerol after methanol removal will be approximately around 85 %.

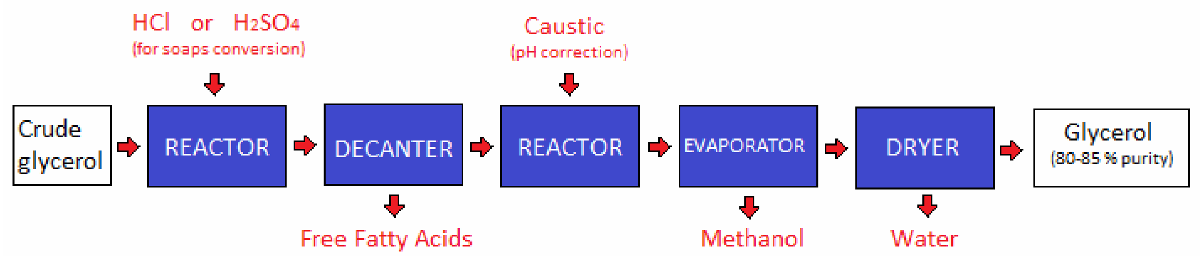

Fig. 6: Principal scheme of glycerol purification

VACUUM DISTILATION

Distillation is generally not applicable to substanceswhich are sensitive to thermal degradation or polymerize at elevated temperatures. In order to prevent degeneration of glycerol, purification has to be done in vacuum where the pH, temperature and pressure must be controlled. High-energy input requirement for vaporization and creates thermal decomposition due to high specific heat capacity of glycerol which makes the process costly. These are the reasons why vacuum distillation is the most common method for glycerol purification. [10] The advantages of these methods are: quality of producing glycerol and it is well established method. The disadvantages include, in particular high energy requirement, its unfeasible for small and medium enterprise, need high maintenance, and it is sensitive to feed stream variations.

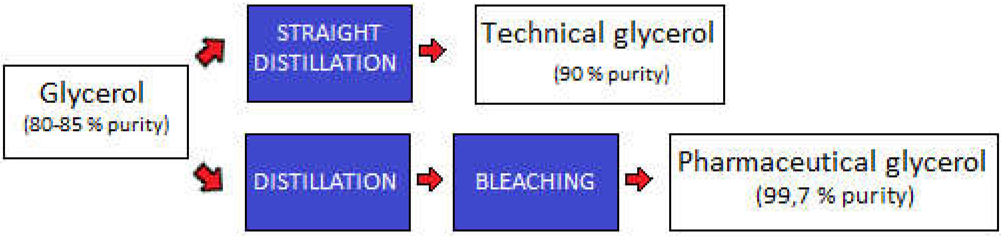

Fig. 7: Principal scheme of glycerol refining

ION EXCHANGE ADSORPTION

Several types of impurities such as fatty acid, inorganic salt and free ion impurities can be removed from crude glycerol by using ion exclusion purification techniques. However, for crude glycerol purification to be viable, issues concerning the ion exchange method such as fouling by fatty acids, oils and soaps, regeneration of the beds (chemical regeneration cost for resins is high for salt content)and large quantities of wastewater produced still remains a significant problem. This method is also nfeasible for high salt content glycerol.

ADSORPTION USING ACTIVATED CARBON

Adsorption with activated carbon is mainly used as the finishing step to further refine the purified glycerol; reduce the colour, as well as reducing some fatty acids and other components.This method is often inefficient for removal of other impurities.[11]

MEMBRANE SEPARATION TECHNOLOGY

The membrane separation process involved microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED). Different types of membrane are employed for different types of separation process, for example microfiltration involves in separation of particles, whereas separation of macromolecules uses ultrafiltration, and reverse osmosis is capable of separating ionic components. The advantages of these methods are: low energetic requirement, simplicity of operation, ease of unit scale-up and control, environment compatibility or large operation flexibility. Membrane technology is considered a good alternative with regards to current methods for glycerol purification process. However, the incorporation of membrane technology for industrial practice is still found to be lacking despite the obvious advantages of low energy and cost.[12]

CONCLUSIONS

Glycerol can be produced by many ways. After 2004, there were surplus of crude glycerol due to rapid development of biodiesel. The first step in rational utilization of glycerol is achieving a sufficient puritywith regard to the economic and environmental aspects of its use. Our contribution provides a brief summary of various opportunities for quality improvement for its next chemical, biochemical and energetic use.
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