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Derleme/Review

Glycerol: A Major By-product in the Biodiesel Manufacturing Process

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ABSTRACT: The cost of biodiesel production can be reduced by a number of strategies such as utilization of waste cooking oils and non-edible plant oils as well as implementation of improved separation technologies. The predominant biodiesel production process involves a phase of transesterification that yields glycerol as a byproduct. The use of this glycerol is limited since it is considered an unrefined raw material that must be refined for its various types of use. In addition, processes dealing with the glycerol by-product can have economic benefits. Transesterification of oils in biodiesel manufacturing process produces glycerol as a main by-product. Increasing amount of crude glycerol has led to waste disposable issues. Recently, researchers have been studying the possibilities to convert the waste glycerol to useful products, wherein, microbial conversion of residual glycerol has been considered as an economically viable process. Microbe-assisted conversion of waste glycerol to valuable compounds such as methane, 1,3-propanediol, ethanol, succinic acid and H_2 have been reported. Microbial recycling of glycerol, byproduct of biodiesel production to biodiesel in engineered *Escherichia coli* strains was reported. The present review reveals that there are promising possibilities for the use of unrefined glycerol, which may help consolidate the sustainability of the biofuel market.

Keywords: Biodiesel, Crude glycerol, By-product, Utilization

Gliserol: Biyodizel Üretim Sürecinde Önemli Bir Yan Ürün

ÖZET: Biyodizel üretim maliyeti, geliştirilen ayırma tekniklerinin yanı sıra atık kızartma yağları ve yenilemeyen bitkisel yağların kullanımı gibi çok sayıda strateji ile azaltılabilir. Biyodizel üretim prosesi, başlıca gliserolün yan ürün olarak elde edildiği bir transesterifikasyon basamağından ileri gelmektedir. Ekonomik getirileri olan gliserol yan ürün prosesine ilave olarak bu gliserolün kullanımı rafine edilmemiş ham materyal olduğundan dolayı sınırlıdır. Ham gliserol miktarının her geçen gün artmasıyla atık bertaraf konuları da gündeme gelmektedir. Son zamanlarda araştırmacılar atık gliserolü faydalı bir takım ürünlere dönüştürme olasılıkları üzerine yoğunlaşmışlardır. Atık gliserolün mikrobiyal yolla metan, 1,3-propandiol, etanol, süksinik asit ve H_2 gazı gibi değerli ürünlere dönüşümünün mümkün olduğu kayıt edilmiştir. Bu derlemede ham gliserolün kullanım olanakları ve biyodizel piyasasında önemli bir yan ürün olan gliserolün değerlendirme yolları üzerinde durulmuştur.

Anahtar kelimeler: Biyodizel, Ham gliserol, Yan ürün, Değerlendirme

Introduction

Depletion of fossil fuels, increasing demand for fuels and environmental pollution have intensified the need for alternative fuels. Biodiesel is an alternative fuel obtained from fats and oils. Although biodiesel is considered a green fuel, it is expensive to produce due to the high cost of the feedstock. Alternatively, the feasibility of using low-cost feedstock such as waste cooking oil, nonedible oils and lipid rich microalgae have been investigated to lower the cost of biodiesel (Helwani et al., 2009; Siles et al., 2010; Carmee et al., 2015). This fuel has similar properties to that of diesel produced from crude oil and can be used directly to run existing diesel engines or as a mixture with crude oil diesel. It is used as a substitute for the conventional diesel fuel without requiring any major modifications in existing engines. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide (Helwani et al., 2009). Transesterification reaction is must adopted for the commercial production of biodiesel (Figure 1). The reaction can be catalyze either using homogeneous catalysts (acid or base) or heterogeneous catalysts (acid, base, or enzyme) (Helwani et al., 2009; Atadashi et al., 2010). During this reaction, a short-chain alcohol, such as methanol or ethanol, reacts with a triacylglycerol in the presence of a catalyst and forms glycerol and long-chain fatty acid esters. After reaction, the final mixture is formed by alkyl esters, residual alcohol, glycerol, and the catalyst, along with mono-, di-, and triacylglycerol, which are intermediate reaction products (Gomes et al., 2010). Biodiesel production from vegetable or animal feedstock inevitably results in the glycerine side-product. As much as 100 kg of glycerine is produced for every tonne of manufactured biodiesel (Singhabhandhu and Tezuka; 2010; McNeil et al.2012; Suzukil, et al., 2014). During biodiesel production, two phases are produced after transesterification and distillation of the excess alcohol. The upper ester phase (EP) contains the main product biodiesel. The lower glycerol phase (GP) consists of glycerol and many other chemical substances such as water, organic, and inorganic salts, a small amount of esters and alcohol, traces of glycerides, and vegetable colors. The exact composition of the raw GP depends on the method of transesterification and the separation conditions of biodiesel production, but the glycerol concentration is usually between 30 and 60 wt.% (Gomes et al. 2010; Hajek and Skopal; 2010). The ability of pharmaceutical and cosmetics industry to absorb the huge amount of glycerine produced is limited. It inspired the search for new and efficient methods of glycerine utilisation (Mcneil et al., 2012, Suzukil, et al., 2014).

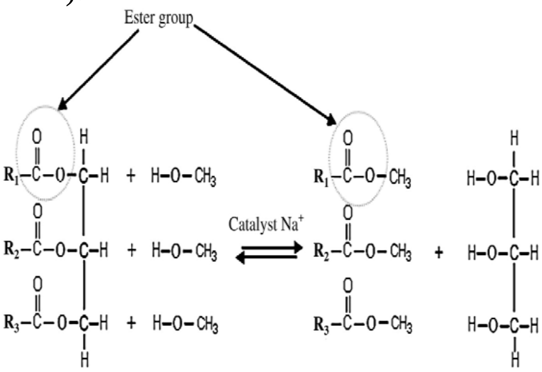

Figure 1. Transesterification reaction (Helwani et al., 2009).

An important parameter in the quality control of biodiesel is the amount of free glycerol, molecular glycerol dissolved in biodiesel. Its maximum limit is 0.02%. (Atadashi et al., 2010). High free glycerol content may result in decantation, storage, and engine fuel injection system problems. Free glycerol is also associated with fuel tank bottom deposits, which attract other contaminants, such as water, which in turn increases engine corrosion and reduces the engine’s useful life. Burning glycerol together with biodiesel may also result in hazardous emissions. At the end of the reaction, glycerol must be eliminated. Due to its low solubility in esters, separation is usually performed by either decantation or centrifugation. In the separation by decantation, the biodiesel and glycerol mixture is rested in tanks. The separation cost is low, but it is a slow process. In the centrifugation process, the mixture is fed into centrifuges for separation. Although the separationtime is greatly reduced, the investment required and the operating costs are high (Gomes et al., 2010). The aim of this study was to focus on ways of evaluate glycerol as a by-product in the production of biodiesel by transesterification .

Glycerin: a co-product of biodiesel production

Glycerin can be obtained from microbial fermentation, synthetics, petrochemical feedstock, the saponification reaction of soap production, and the transesterification reaction of biodiesel production. The inherent production of glycerol from the biodiesel process is substantial: about 0.1 m^3 of glycerol is produced per 1 m^3 of biodiesel (Singhabhandhu and Tezuka; 2010; Pott et al., 2013).

Glycerol is a trivalent alcohol widely used in the pharmaceutical, food, cosmetic, and chemical industries. It is produced from soaps which are obtained by saponification of triglycerides from vegetable oils or animal fats. During their saponification, triglycerides are converted by alkaline hydroxides into salts of fatty acids (soaps) and glycerol. Glycerol can also be produced from propene. Another possibility to gain glycerol is through transesterification of vegetable oils and animal fats. In the EU, the production of biodiesel was 7.56 million tons in 2008. Approximately one fifth of this amount is glycerol. This product is commonly called glycerol or 1,2,3-propanetriol, which is a colorless, odorless, viscous, and nontoxic liquid (Hajek and Skopal; 2010; Gomes et al., 2010).

Applications of glycerin

Pure glycerin is widely used in pharmaceutical formulations. Due to its properties, it is mainly used for improving smoothness, providing lubrication, and as a humectant found in many cosmetic products where moisturization is desired, such as in moisturizing hair conditioners. It is used in cough syrups, elixirs, expectorants, ointments, plasticizers for medicine capsules, ear infection medicines, anesthetics, lozenges, gargles, and as a carrier for antibiotics and antiseptics.

Glycerol is used as a component to produce polymers. For example, polyglycerol ester is used in biodegradable surfactants and lubricants; polyglycerol and polyglycerol methacrylates are used as wood treatments to improve its stability; and polyester polyols are used to produce polyurethanes, which are applied as coatings, foams, and sprays.

Glycerol also can be used as an emollient in toothpaste, skin creams and lotions, shaving preparations, deodorants, and makeup.

Glycerol can be used to preserve the freshness of tobacco products, and it has been used in alkyd resin production, which is an important element for surface coatings and printing inks. In paper production, glycerol is used as a plasticizer and lubricant, and in the textile industry, it is used for lubricating, sizing, and softening yarn and fabric (Singhabhandhu and Tezuka; 2010).

Products derived from biodiesel glycerol

With the increase in biodiesel production world-wide, the market saturation of glycerol, a by-product of biodiesel production, is inevitable. Besides the application to produce glyceryl ethers discussed previously, there are many other applications for use of crude glycerol as listed below:

(1) Catalytic conversion:
Propylene glycol, propionic acid, acrylic acid, propanol, acrolein, propanediol, etc.
(2) Biological conversion:
Citric acid, sophorolipids, 1,3-propanediol, etc.
(3) Fuel oxygenates:
Acetal (2,2-dimethyl-1,3-dioxolan-4-yl)
(4) Production of H_2 and syngas via steam gasification of glycerol
(5) As carbon source for bioreactors treating Acid Mine Drainage

(6) Agricultural usage:
Broiler feed, pig feed (Janaun and Ellis, 2010).

Biodiesel fuel (BDF) waste contains large amounts of crude glycerol as a by-product, and has a high alkaline pH. With regard to microbial conversion of ethanol from BDF-derived glycerol, bacteria that can produce ethanol at alkaline pH have not been reported to date. Isolation of bacteria that shows maximum productivity under alkaline conditions is essential to effective production of ethanol from BDF-derived glycerol. Suzukil, et al. (2014), studied that isolated the *Klebsiella variicola* TB-83 strain, which demonstrated maximum ethanol productivity at alkaline pH.

Yang et al. (2013), demonstrated that the feasibility of converting glycerol to FAEE. FAEE production with glycerol compared well with glucose as the carbon source by applying of a two-stage feeding strategy.

In a study, Mangayil et al., (2012) showed that bioconversion of residual glycerol from biodiesel production process to H_2 by an enriched microbial consortium is described. The enriched bacterial community comprised mainly of Clostridium species. The inoculum produced H_2 at wide pH and temperature ranges.

Nartker, (2014) demonstrated that waste glycerol has been used to increase the gas production and methane content of biogas within an anaerobic co-digestion process using primary sewage sludge.

One option is to produce hydrogen from the glycerol using a photosynthetic bacterium (Pott et al., 2013).

Conclusion

In biodiesel production through transesterification, glycerin is produced as a valuable co-product. Biodiesel production has increased in world-wide every day. Amount of waste glycerol as a by-product of biodiesel production has incresased, too. It must evaluate and introduce to market as a value product.

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