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Glycerol production and its applications as a raw material: A review

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ABSTRACT

Glycerol is a valuable byproduct in biodiesel production by transesterification, soap manufacturing by saponification as well as hydrolysis reaction. The purity of glycerol obtained is low due to the presence of impurities such as remaining catalyst, water, soaps, salts and esters formed during the reaction. Purification of glycerol as well as the conversion of glycerol into valuable products has attained growing interest in recent years due to the dramatic growth of the biodiesel industry. This paper reviews different methods of producing crude glycerol as the major by-product. Purification of glycerol was reported as well as value-added products produced from glycerol.

Contents

1. Introduction

Glycerol, also known as glycerine or propane-1,2,3-triol, is a chemical which has a multitude of uses in pharmaceutical, cosmetic, and food industries. It can be produced as a by-product from saponification and hydrolysis reactions in oleochemical plants as well as transesterification reaction in biodiesel plants [1]. Glycerol produced from oleochemical or biodiesel plant is in crude form that contains

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various impurities such as oily, alkali, and soap components, a salt or diols, depending on the processes and the type of materials processed [1,2]. It is normally referred to as crude glycerol. Crude glycerol obtained from the biodiesel plant consists of glycerol, water, organic and inorganic salts, soap, alcohol, traces of glycerides and vegetable colour [3]. While crude glycerol produced from the hydrolysis reaction contains glycerol, water, free fatty acid, unreacted triglycerides, organic and inorganic salts and matter organic non-glycerol [1]. For the reaction of saponification of fats or oil, crude glycerol has been reported to contain glycerol, fatty acids and salts [4]. Further crude glycerol is a low value product as its low purity limits its application as feedstock in industries. The development of conversion processes for crude glycerol to other value-added products is being thoroughly investigated; however, the techniques are not widely commercially adopted in Malaysia at present. Purified glycerol can be sold as a commodity because it is still highly required as an important industrial feedstock especially in various chemical industries. Consequently, a development of purification methods is necessary to produce highly purified glycerol as feasible industrial feedstock [5].

Presently, numerous purification techniques of crude glycerol have been developed such as conventional filtration, microfiltration, and ultrafiltration using organic polymer membranes, simple distillation, vacuum distillation, chemical and physical treatments, ion-exchange technique and adsorption. By combining two or more of these techniques would lead to higher purify glycerol [6]. This paper reviews the methods employed to produce glycerol as well as the purification technologies.

2. Physical and chemical properties of glycerol

Glycerol is an organic compound and it has the chemical formula $C_3H_8O_3$. It is synonymous to glycerine, propane-1,2,3-triol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, and glycyl alcohol. Glycerol is a low toxicity alcohol that consists of three-carbon chain with a hydroxyl group attach to each carbon. It is derived from natural or petrochemical feedstocks [7]. Glycerol is virtually nontoxic to both human and environmental. Physically, glycerol is a clear, colourless, odourless, hygroscopic, vicious and sweet taste liquid. The boiling point, melting point and flash point of glycerol is 290 °C, 18 °C and 177 °C respectively [8]. Under normal atmospheric pressure, glycerol has a molecular weight of 92.09 g/mol, a density of 1.261 g/cm^3, and a viscosity of 1.5 Pa.s [9]. The extensive intermolecular hydrogen bonding is responsible for high viscosity and boiling point of glycerol. Glycerol is able to attract and hold the moisture from the air and it is not altered when contact with the air [10]. The three-hydroxyl groups in glycerol dominate its solubility. It is completely soluble in water and alcohols, slightly soluble in ether and dioxane, but insoluble in hydrocarbon [9]. It is also a good solvent for many substances such as iodine, bromine and phenol due to the presence of the hydroxyl group. Glycerol is chemically stable under normal storage and handling conditions, nevertheless, it may become explosive when it is in contact with strong oxidizing agents such as potassium chlorate [10]. Glycerol is a reactive molecule that posses larger number of reactions due to the presence of primary and secondary alcoholic groups that can be replaced with other chemical groups. Furthermore, it undergoes various reactions to form other derivatives such as ether, ester, amine and aldehyde.

3. Source of glycerol

3.1. Transesterification reaction

Glycerol can be generated from transesterification of fat and oils in biodiesel plant. Transesterification is a chemical reaction whereby fat and oils (triglycerides) react with alcohol such as methanol in the presence of a catalyst to produce fatty acid methyl esters with glycerol as a byproduct, as presented in Fig. 1 [11]. The transesterification reaction is carried out in batch or continuous equipment. As the transesterification reaction progresses, the reaction stream is separated into two phases, which are biodiesel-rich phase (top layer) and glycerol-rich phase (bottom layer), due to differences in their densities and their polarities [12,13]. The production of 100 kg of biodiesel yields approximately 10 kg of impure glycerol, with purity of 50–55% [4]. Glycerol from the transesterification process has a higher salt content and excess alcohol. Today, the production of glycerol by transesterification of fats and oils in biodiesel industry has become a major source of glycerol production. However, the dramatic growth of the biodiesel industry has created a surplus glycerol that has resulted in decreasing glycerol prices and environmental concerns associated with contaminated glycerol disposal [14].

To produce biodiesel, a feedstock that contains fat or oils (triglycerides) can be used in the transesterification process. Ahmad et al. [15] stated that the cost of feedstock accounts for about 75% of the total cost of biodiesel production, thus, the selection of proper feedstock is important to ensure the low biodiesel production cost. In general, biodiesel feedstock can be categorized into three groups: first generation, second generation and third generation biodiesel feedstock as shown in Table 1. Enamul Hoque et al. [16] have produced biodiesel from used cooking oil and animal fat via transesterification process. At optimum conditions (methanol to oil ratio of 6:1, catalyst concentration of 1.25 wt% of oil, reaction temperature of 65 °C and stirring speed of 150 rpm), the maximum biodiesel yields achieved for beef fat, chicken fat and used cooking oil are 87.4%, 89% and 88.3%, respectively. The authors concluded that economically viable biodiesel could be produced from low cost feedstock through appropriate setting of process parameters in transesterification process. Miao and Wu [17] produced biodiesel from microalgae lipids using sulphuric acid as a catalyst via transesterification process. At optimum conditions (temperature of 30 °C and 56:1 M ratio of methanol), the best biodiesel yields were obtained in about 4 h of reaction time. Moazami et al. [18] estimated that 60,000 L of biodiesel could be produced from microalgae strain PTCC 6016 (Nanochloropsis sp.). However, despite of which feedstock is used to produce biodiesel, the by-product (glycerol) will be generated in the homogeneous or heterogeneous catalysed transesterification process. Asad-ur-Rehman et al. [35] investigated the crude glycerol produced from biodiesel production via transesterification of sunflower oil. The authors mixed the solution of methanol and sunflower oil (methanol: sunflower oil molar ratio of 10:1) at 400 rpm and 60 °C with 0.5% (w/w) of NaOH. The crude glycerol obtained have the following composition (w/w): 30% glycerol, 50% methanol, 13% soap, 2% moisture, approximately 2–3% salts (primarily sodium and potassium), and 2–3% other impurities (non-glycerol organic matter). Thompson and He [36] reported the characterization of crude glycerol obtained from different seed oil via a transesterification process. The transesterification process was conducted at 50 °C and at 240 rpm for 60 min using sodium methylate as catalyst. They reported that crude glycerol produced from the different types of feedstock is ranged between 60 wt% and 70 wt%. The results also showed that the crude glycerol yield for first-use oils ranged from 8.8 to 12.3 g per 100 g of input oil (~62 wt%). On the other hand, crude glycerol obtained from waste vegetable oil contain more soaps and impurities, average around

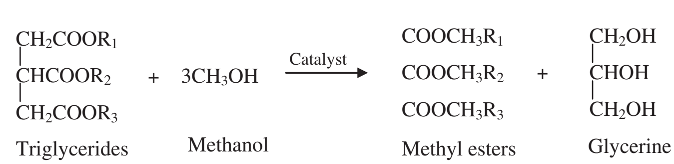

Fig. 1. Transesterification reaction.