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Glycerol: Production, consumption, prices, characterization and new trends in combustion

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ABSTRACT

The demand for petroleum has been rising rapidly due to increasing industrialization and modernization. This economic development has led to a huge demand for energy, most of which is derived from fossil fuel. However, the limited reserve of fossil fuel has led many researchers to look for alternative fuels which can be produced from renewable feedstock. Increasing fossil fuel prices have prompted the global oil industry to look at biodiesel, which is from renewable energy sources. Biodiesel is produced from animal fats and vegetable oils and has become more attractive because it is more environmentally friendly and is obtained from renewable sources. Glycerol is the main by-product of biodiesel production; about 10% of the weight of biodiesel is generated in glycerol. The large amount of glycerol generated may become an environmental problem, since it cannot be disposed of in the environment. In this paper, an attempt has been made to review the different approaches and techniques used to produce glycerol (hydrolysis, transesterification, refining crude glycerol). The world biodiesel/glycerol production and consumption market, the current world glycerin and glycerol prices as well as the news trends for the use of glycerol mainly in Brazil market are analyzed. The technological production and physicochemical properties of glycerol are described, as is the characterization of crude glycerol obtained from different seed oil feedstock. Finally, a simple way to use glycerol in large amounts is combustion, which is an advantageous method as it does not require any purification. However, the combustion process of crude glycerol is not easy and there are technological difficulties. The news and mainly research about the combustion of glycerol was also addressed in this review.

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1. Introduction

Biofuels arose as a sustainable source of fuel in the search for new energy resources and are considered an important form of technological progress in limiting greenhouse gas emissions and diminishing pollution, improving air quality [1]. Biofuels are a source of renewable energy; they are produced from natural material (biologically based). Among the most common biofuels is ethanol generated from maize, wheat or beets and biodiesel from oily seeds and/or animal fat [2]. At present, biofuels are used as a source of energy as a substitute for fossil fuels because they are biodegradable, much cleaner and generate an acceptable level of emissions gases [3,4].

Biodiesel stands out among biofuels. It is a liquid fuel that's obtained from natural lipids such as vegetable oil or animal fat using industrial processes of esterification or transesterification. Biodiesel is superior to diesel oil for health and the environment (it is low in sulfur, emits a low level of noxious particles like HC and CO, and is better in the CO_2 cycle in reducing global warming), as well as for engine performance (better lubrication, high cetane number and more complete combustion) [5–7]. Biodiesel is biodegradable, renewable and non-toxic. It has a high flash point, better viscosity and caloric power similar to fossil fuels [7]. These advantages have convinced Asian countries to utilize biodiesel as an alternative fuel as one of the innovative solutions to reduce global air pollution generated by the growing number of vehicles [8]. Mixtures are the most viable way to increase biodiesel usage, elevating biodiesel's share of the fuel market, benefitting producers, guaranteeing competitive pricing for end users, and requiring less incentives and tax exemptions [9]. It has been reported that from 75 to 95% of the end price of biodiesel is influenced by the cost of the raw material [10].

On the other hand, production of biodiesel has a by-product: glycerol. Generally, 10 to 20% of the total volume of biodiesel produced is made up of glycerol [11–15]. The production of bioethanol also generates glycerol as a by-product, up to 10% of the weight of the sugar consumed [16]. Lately an intense debate has focused on this important problem in biodiesel production: the inevitable production of glycerol as a by-product with a low commercial value [12,17]. Growing biodiesel production will lead to large surpluses of glycerol. A fundamental question soon arises: What can be done with the glycerol? This is one of the main reasons that research at present is focused on developing technology to convert or use the glycerol in order to improve the biodiesel business and drastically improve its economic viability [12,18]. Though glycerol is a raw material and there are over 2000 industrial uses, incessant biodiesel production is leading glycerol to be dealt with as a waste product. Specific concerns about the social and environmental impacts of biodiesel production have been growing [19,20].

This manuscript is a review of the different approaches and techniques used to produce glycerol (hydrolysis, transesterification, refining crude glycerol), the world biodiesel/glycerol production and consumption market, the current world glycerin and glycerol prices and the news trends for the use of glycerol mainly in Brazil. Though it is not an ideal fuel, one option (other than its use in the pharmaceutical or chemical industries) could be to burn it (glycerol combustion) locally in a combined heat and energy generation process (cogeneration), replacing fossil fuels, and optimizing the efficiency of the process as well as reducing the impacts of this byproduct. The news and mainly research about the combustion of glycerol was also investigated in this review.

2. Glycerol

Glycerol is the main component of triglycerides, found in animal fat, vegetable oil, or crude oil. Glycerol is derived from soap or from biodiesel production [18,21]. It's been known since 2800 BCE, when it was isolated by heating fat mixed with ashes to produce soap [22]. However, it is considered to have been discovered in 1779 by Swiss pharmacist K. W. Scheele, who was the first to isolate this compound when he heated a mixture of litharge (PbO) with olive oil. In 1811, French chemist M. E. Chevrel called glycerin a liquid, defining the chemical formulas of fatty acids and the formulas of glycerin in vegetable oil and animal fat. His work was patented. It was known as the first industrial method to obtain glycerin soap by reacting fatty material with lime and alkaline material [23].

2.1. Glycerol's physical properties

Glycerol is the simplest of the alcohols and is known by propane-1,2,3-triol according to IUPAC. It is also commercially known as glycerin, 1,2,3-propanotriol, trihydroxypropane, glyceritol or glycidic alcohol [24]. Glycerol is an oily liquid; it is viscous, odorless, colorless, and has a syrupy-sweet taste. Glycerol is a liquid containing three hydrophilic hydroxyl groups that are responsible for it being hygroscopic and its solubility in water [25,26]. Fig. 1 shows the molecular structure of glycerol, made up of three hydroxyls.

Glycerin is completely miscible in many substances. Among them are: alcohol (methyl, ethyl, isopropyl, *n*-butyl, isobutyl, secondary butyl, and tertiary amyl); ethylene glycol, propylene glycol, trimethylene glycol monomethyl ether and phenol [28,29]. Solubility of glycerin in acetone is 5% by weight; in ethyl acetate it's 9%. It's slightly soluble in dioxane and ethyl, and partially insoluble in superior alcohol, fatty acids and hydrocarbonate, as well as in chlorinated solvents such as hexane, benzene, and chloroform. Glycerin is very viscous: at normal temperatures it remains a viscous liquid even at 100% concentration without crystallizing. At low temperatures, concentrated glycerin solutions tend to super cool as high viscosity fluid. Viscosity rises at first until it quickly becomes vitreous around −89 °C. Aqueous glycerin solutions (at different concentrations) tend to have lower viscosity [30].

At low temperatures glycerin tends to super cool instead of crystallize. Aqueous glycerin solutions resist freezing and are used as antifreeze in cooling systems. Glycerin does not oxidize in the atmosphere in normal conditions, but can be easily oxidized by other oxidants. Glycerin solutions need inhibitors when they are exposed to heat and in contact with ferrous metal or copper since the salts contained in these materials can catalyze oxidation [31]. Glycerol has low volatility and low vapor pressure, which is strictly linked with its hygroscopic property. Between 0 and 70 °C, temperature changes have little effect on the vapor pressure of glycerin solutions. Like other alcohols, glycerin has a lower vapor

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