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Review

The potential of glycerol as a value-added commodity

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HIGHLIGHTS

- Glycerol offers a wide range of new opportunities based on its transformation.
- Thus this paper is a comprehensive review of the utilization of glycerol as a value-added commodity.
- In the future, glycerol expected to be a promising renewable feedstock in biorefineries.

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ABSTRACT

Glycerol is a by-product of biodiesel, soap and fatty acid manufacturing plants, which are now facing sustainability threats and a reduction in prices in the market due to its oversupply as a result of the rapid expansion of biodiesel plants all over the world. The global production and consumption of glycerol, as well as demand and supply, are evaluated here. Glycerol offers a wide range of new opportunities based on its transformation in many applications due to its unique properties, renewability and availability in the current market. This paper is a comprehensive review of the utilization of glycerol as a value-added commodity, including in the synthesis of chemicals, in the production of hydrogen gas, as a fuel additive, as a fermentation substrate, in the co-pyrolysis and co-gasification of glycerol, in methanol production, in the development of fuel cells, in wastewater treatment and in many other applications. In the future, glycerol definitely will become a promising renewable feedstock in biorefineries to synthesize fuel, chemicals and power.

Contents

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1. Introduction

Current energy crisis issues due to the depletion of fossil-based fuels, high petroleum prices, and the drastic effects on the environment caused by the emission of hazardous substances and chemicals into the atmosphere have necessitated a search for alternatives to substitute for fossil fuels. Biodiesel production from vegetable oil, animal tallow, oil and fats had been a promising biofuel to be blended with gasoline or used directly. Generally, for every 3 mol of methyl esters produced, 1 mol of glycerol is synthesized, which is nearly 10 wt.% of the total product [1].

One of the major obstacles to the commercialization of biodiesel is its inevitable co-product glycerol's market has become saturated, causing a dramatic reduction in prices and consequently affecting the biodiesel economy adversely. This was evidenced when synthetic glycerol producer Dow Chemical shut down their production plant in Texas in 2007 and Procter & Gamble Chemicals closed its glycerol refinery in England in 2006 [2,3].

Glycerol is currently produced from the transesterification process during biodiesel production and the saponification and hydrolysis processes in fatty acid and soap manufacturing plants. The crude glycerol generated from biodiesel plants includes many impurities and other chemicals, for instance, methanol, organic and inorganic salts, water, vegetable colours, mono and diglyceride traces and soap [4,5]. The purification of crude glycerol is an expensive process, requiring expensive processing equipment [6,7]. Hence, large-scale biodiesel producers can refine the crude glycerol into a refined form with purities up to 95.5% and 99% to be used in the pharmaceutical, food or cosmetic industries [2,8]. However, small-scale producers are looking for alternatives to allow use of the unrefined glycerol in beneficial and profitable applications.

A promising avenue would be to transform glycerol into more economically valuable end-products, which will find applications in many industrial fields, including chemicals, fuels, plastics, heat generation and many more. This review discusses the possible application of glycerol as a commodity, both for commercialization and to sustain the biofuel and glycerol market on a global scale.

2. Glycerol market overview

2.1. Global glycerol production, supply driver and price fluctuations

The glycerol market is comparatively small on global basis; worldwide glycerol production is approximately 2 billion pounds and its yearly value is $1 billion [9]. Glycerol is predominantly produced from biodiesel, fatty acid and soap manufacturing, and the demand for these products drives the glycerol market price. In 1999, most glycerol was produced from fatty acid and soap manufacturing (Fig. 1). Over the decades, the glycerol supply has increased as interest shifted to biodiesel production, where, in 2011, over 65% of glycerol was produced from biodiesel plants and approximately 23% was produced from fatty acid production.

Fig. 2 displays the production of biodiesel by region from 2005 to 2011. In the last decade, the rapid upsurge in the biodiesel industry due to the increase in oil prices and concern over energy security has been prominent; this issue contributed greatly to the surfeit of glycerol in the global market. The earlier synthetic mechanisms for glycerol manufacturing were swapped with the transesterification process in biodiesel production [12]. Hundreds of tonnes of crude glycerol were headed for an already saturated market for every million tonnes of biodiesel produced [13].

Nationally, the current average biodiesel (B99–B100) fuel price is $3.77, while biodiesel (B20) is $2.92 [15]. Over the past few years, the pure glycerol and crude glycerol prices dropped to $0.50 from $1.50 per pound and to $0.04 from $0.33 per kg, respectively [16]. Fig. 3 illustrates the crude glycerol price fluctuations from the year 2001–2011. After the development of the biodiesel industry in the United States, the crude glycerol price was at its nadir in 2007, when the price fell from $0.25 to $0.05 per pound while the refined glycerol price decreased from $0.70 to $0.30 per pound [5]. Ayoub and Abdullah [17] claimed that the reduction of crude glycerol prices would continue in an over-abundant market. The volatility of the glycerol market is due to its dependence on the global supply and demand and its dependence on the production of petroleum and biodiesel [18].

The European Union (EU) produced 503,432 tons of refined glycerol in 2010, which was an increase of 32% year-over-year, and the consumption of refined glycerin in the EU had increased

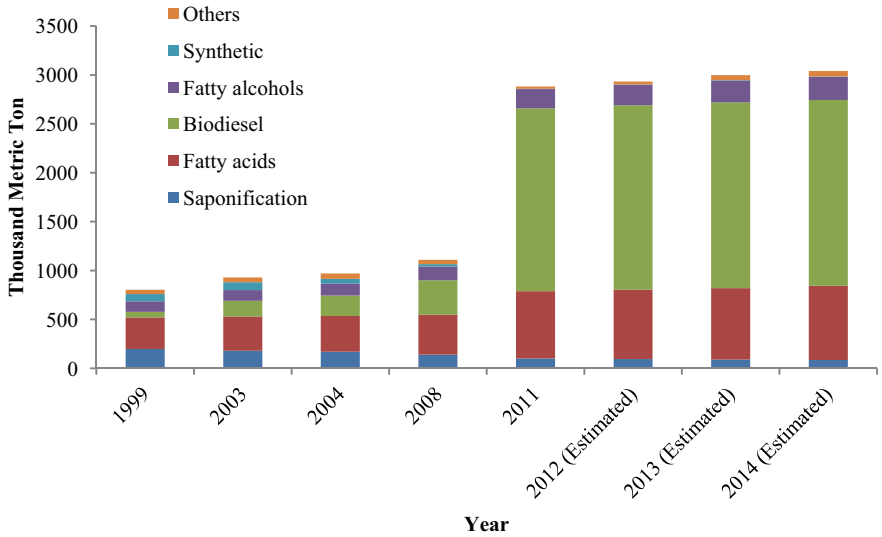

Fig. 1. World glycerol supply driver [10,11].