Renewable and Sustainable Energy Reviews 39 (2014) 327–341

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Dealing with the surplus of glycerol production from biodiesel industry through catalytic upgrading to polyglycerols and other value-added products

Zahra Gholami, Ahmad Zuhairi Abdullah *, Keat-Teong Lee

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form
19 May 2014
Accepted 7 July 2014
Available online 31 July 2014

Keywords:
Glycerol surplus
Biodiesel industry
Catalytic conversion
Etherification
Polyglycerols

ABSTRACT

An increase in glycerol production is expected because of the increasing use of fuel additives such as methyl esters. This increase can enhance the importance of glycerol as a cheap raw material for producing value-added products. Future scenarios for worldwide glycerol market will mostly be related to the supply and demand of glycerol and its application in other industries. Much research have been developed and continuously investigated to convert low-value glycerol using different strategies and approaches. Due to the unique structure of glycerol, properties and renewability feature of it, new opportunities for the transformation of glycerol into high-valued chemicals have merged in recent years. This paper provides a review on glycerol, global market of glycerol and conversion of glycerol to value-added products. Catalytic etherification of glycerol to value-added products such as polyglycerols is particularly reviewed.

Contents

1. Introduction

An increase in glycerol production is expected because of the increasing use of fuel additives such as methyl esters. This increase

* Corresponding author. Tel.: +60 4 559 6411; fax: +60 4 594 1013.
E-mail address: chzuhairi@usm.my (A.Z. Abdullah).

http://dx.doi.org/10.1016/j.rser.2014.07.092
1364-0321/

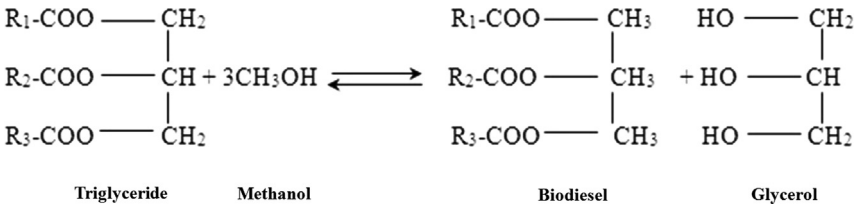

Fig. 1. Glycerol as a by-product of the methanolysis of vegetable oils.

Table 1
Typical elemental analysis results of crude glycerol from biodiesel industries [10].

Element	Weight %
Carbon (C)	52.8
Hydrogen (H)	11.1
Nitrogen (N)	< 0.0001
Sulfur (S)	–
Balance oxygen (O)	36.2

Table 2
Differences between types of glycerol [12].

Parameter	Crude glycerol	Purified glycerol	Refined/commercial glycerol
Glycerol content (%)	60–80	99.1–99.8	99.20–99.98
Moisture content (%)	1.5–6.5	0.11–0.8	0.14–0.29
Ash (%)	1.5–2.5	0.054	< 0.002
Soap (%)	3.0–5.0	0.1–0.16	0.04–0.07
Acidity (pH)	0.7–1.3	0.10–0.16	0.04–0.07
Chloride (ppm)	ND	1.0	0.6–9.5
Color (APHA)	Dark	34–45	1.8–10.3

can enhance the importance of glycerol as a cheaper raw material for new products used in surfactants, lubricants, cosmetics, food additives, etc. [1]. To deal with the major excess of glycerol and develop the "green" credentials of the compound, innovative and greener catalytic processes should be developed to convert glycerol into higher value products. The synthesis of value-added molecules from crude glycerol is an attractive replacement to disposal by incineration [2]. Fig. 1 shows the schematic of the biodiesel production through vegetable oil (triglyceride) methanolysis. Homogeneous acid and base solutions are commonly used as catalysts. In a stoichiometric reaction, 1 mole of glycerol is obtained for every 3 mole of fatty acid methyl esters (biodiesel) produced.

It is anticipated that the development of crude glycerol biorefineries benefit the economy of overall biodiesel industry through the reduction of the disposal costs of residues and increase in production of high value chemicals [3]. The process of biodiesel production starts with the purification of crude vegetable oil. The refined oil then undergoes transesterification to produce biodiesel with glycerol as the waste by-product. In a typical process, the glycerol layer (containing about 80% glycerol) [4] must be removed to enable the use of the esters as fuel. Selling of the waste glycerol solution can reduce the production cost of biodiesel by 6% [5].

Recently, biodiesel has been promoted as a means toward energy independence, rural development, and reduction of greenhouse gas emission. Biodiesel can be produced through the reaction between feedstock oil with either methanol or ethanol. The solubility of oil in methanol is less than that in ethanol. Its rate of reaction is mass transfer-limited, and methanol enables higher equilibrium conversion because of the higher reactive intermediate i.e. methoxide. Most of the biodiesel production processes use methanol, which is obtained from the petrochemical industry. This dependence on methanol can be considered a non-renewable one [6–9].

The objective of this work is to provide a review catalytic upgrading of glycerol to value-added products through etherification reaction. An overview to the relevant research topics is given in Section 1. The formation of glycerol as main by-product of biodiesel industry, investigation of the impact of this glycerol over the biodiesel production cost and glycerol market is reviewed in Section 2. This study also provides a view of transformation of this low value glycerol to upgraded products such as diglycerol using various heterogeneous catalysts as discussed in Section 3. Polyglycerols are biodegradable and biocompatible products that can be used in various industries. Various catalytic routes to produce

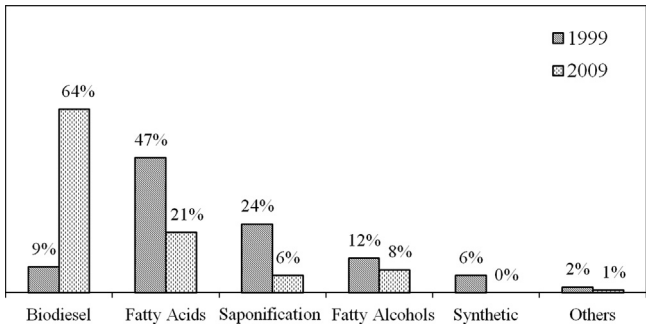

Fig. 2. Changes in glycerol supply drivers from 1999 to 2009 [14].

polyglycerols and the performance of catalysts reported in literature so far are reviewed in Section 4. Section 5 provides a review on the reaction mechanism involved in base-catalyzed etherification process.

2. Glycerol

Glycerol is a material which has numerous uses mainly because of its physical and chemical properties. Table 1 shows typical the elemental analysis results of crude glycerol produced in biodiesel industries, indicating that C, H, and O are the main elemental contents of this material [10]. Glycerol is a good renewable energy source for various applications which might be due to its high carbon content (52.8%). Furthermore, its high oxygen content (36.2%) to indicate that it is a valuable compound [11].

Glycerol can be classified into three main categories: crude, purified/refined, and commercially synthesized. Table 2 shows the major differences between these three types of glycerol from biodiesel industries. This table shows that the differences between purified and commercial glycerol are insignificant, while considerable differences can be observed between crude and purified glycerol. Actually, purified or refined glycerol is often prepared with qualities nearly equivalent to that of commercially synthesized glycerol because of its applications in sensitive fields, such as medicine, food, and cosmetics. Furthermore, Table 2 shows that