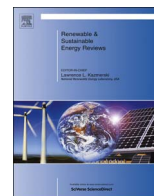




ELSEVIER

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

Conversion of crude and pure glycerol into derivatives: A feasibility evaluation



Pei San Kong, Mohamed Kheireddine Aroua*, Wan Mohd Ashri Wan Daud

Chemical Engineering Department, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:

Received 4 April 2015

Received in revised form

26 January 2016

Accepted 13 May 2016

Keywords:

Crude glycerol

Pure glycerol

Biodiesel

Derivatives

Feasibility

ABSTRACT

The transformation of glycerol to derivatives has been widely investigated because of the demand to enhance the value of crude glycerol produced by biodiesel and oleochemical industries. Intensive research has focused on the conversion of pure glycerol (PG) to different valuable derivatives. Nevertheless, the feasibility of the direct conversion of crude glycerol (CG), which is a waste byproduct of biodiesel production, through chemical processes has been rarely reported because this application is limited by the impurities of CG. Therefore, this review evaluates the feasibility of the direct transformation of CG to value-added derivatives, supplemented with the performance comparison of both PG and CG. This review also demonstrates that the relevant approaches to transform CG into value-added derivatives mainly rely on the following factors: acceptable production cost, advanced process technology, convenient final product separation and purification, excellent product specification, appropriate CG feedstock quality, and minimum catalyst deactivation problem.

© 2016 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	534
2. Glycerol production routes and quality	534
2.1. High-pressure splitting	534
2.2. Soap production (saponification)	535
2.3. Biodiesel production	535
2.4. Comparison of glycerol impurities	535
3. Biodiesel as a major source of glycerol	536
3.1. Advancement of the methyl ester route in the oleochemical industry	538
3.2. Basic glycerol derivative routes	538
4. Strategies to transform CG and PG	538
4.1. Hydrogen	538
4.2. Propylene glycol	540
4.3. Acrolein	541
4.4. Dihydroxyacetone (DHA), glyceric acid (GA), and mesoxalic acid (MA)	542
4.4.1. DHA	542
4.4.2. GA	542
4.4.3. MA	543
4.5. Epichlorohydrin (ECH)	543
4.6. Glycerol ethers	545
4.7. Polyglycerols	546
4.8. Glycerol ester	546
4.8.1. Triacetin	546
4.8.2. Monoglycerides	548
4.9. Dioxolane and dioxane	548

* Corresponding author. Tel.: +603 79674615; fax: +603 79675319.

E-mail address: mk_aroua@um.edu.my (M.K. Aroua).

4.10. Polyesters.....	549
4.11. Glycerol carbonate.....	549
5. Alternative applications of CG.....	550
5.1. Solvent for reaction.....	550
5.2. Co-substrate for liquefaction.....	550
5.3. Biopolyols for polyurethane foam.....	550
6. Feasibility of the direct conversion of CG to glycerol derivatives.....	551
7. Conclusion.....	553
Acknowledgments.....	553
References.....	553

1. Introduction

Glycerol is a colorless, odorless, viscous, and hygroscopic liquid substance with a slightly sweet taste. It is the simplest trihydric alcohol that can be reacted as an alcohol but can remain stable under most conditions. Glycerol was first discovered by C.W. Scheele in 1779 through the saponification of olive oil with lead oxide. The name “glycerol” was first used by M.E. Chevreul in 1813; until the 1930s, glycerol was mainly produced via a fat-splitting process. Pasteur (1857) showed that glycerol, together with succinic acid, can be produced from sugars via a biochemical pathway called alcoholic fermentation. In World War I and II, glycerol was also produced through fermentation or carbohydrate hydrogenolysis [1–4]. Glycerol has also been synthetically produced from petrochemical feedstock since 1943 (I.G. Farben); synthetically produced glycerol accounted for approximately 60% of the total market in 1965 [3]. However, the use of synthetic glycerol has lost popularity over renewable-derived glycerol because of cost-ineffective production [5]. Three common pathways have concurrently generated excess agriculture-based glycerol: hydrolysis, saponification, and biodiesel transesterification [6,7].

The three hydrophilic alcoholic hydroxyl groups (–OH) explain the hygroscopicity of glycerol and its solubility in water. Glycerol is characterized by a density of 1.261 kg/l, a melting point of 18.2 °C, and a boiling point of 290 °C under pure anhydrous condition and normal atmospheric pressure [3,5,7–9]. In terms of ecological toxicity, the thermal decomposition of glycerol at 280–300 °C can produce poisonous acrolein. Even approximately 2 ppm of acrolein exhibits strong toxicity. The lower exposure limit of acrolein recommended by an ecological report is as low as 0.09 ppm [10]. Table 1 presents the relevant physicochemical properties and toxicity data of glycerol reported in different studies [1,9,11]. Glycerol is a vital solvent in pharmaceutical preparations and flavour extracts; thus, considerable studies have been conducted on the solubility of numerous solvents in glycerol [12]. Furthermore, the solubility of glycerol in various organic solvents is a useful reference of azeotropic distillation and analytical studies on glycerol derivatives. The solubility of glycerol in various organic solvents is summarized in Table 2.

The quantity and quality of glycerol generated from three major commercial productions are elucidated comprehensively in this review. This review reveals that excess crude glycerol (CG) is attributed not only to biodiesel production but also to alternate chemical routes employed in the oleochemical industry. Fig. 1 illustrates the outline constructed in this review. This study also presents further insights into the utilization of CG and pure glycerol (PG) as starting materials of different valuable glycerol derivatives. To the best of our knowledge, studies have rarely investigated the feasibility of the direct conversion of unpurified biodiesel-derived CG form into different valuable derivatives via

chemical pathways. Thus, the effects of impurities on direct conversion from CG and PG in different routes are critically evaluated. Important approaches in the utilization of CG as feedstock are also proposed in this review.

2. Glycerol production routes and quality

Glycerol that has not undergone chemical treatment, purification, or separation is known as CG. The quality of CG strongly depends on processes and materials. Different impurities, such as monoglycerides, diglycerides, alkali metals, fatty esters (FAEs), soaps, salts, or diols are formed with their corresponding processing technologies. Thus, the common processes of glycerol production (hydrolysis, saponification, and biodiesel transesterification) and their operating conditions are presented. The quality of CG produced through different routes are insight studied in this section.

2.1. High-pressure splitting

High-pressure splitting is often used to obtain high-quality fatty acids in oil and fat processing industry [13]. Fig. 2 illustrates the process flow of a splitting column, which is redrawn on the basis of a

Table 1
Physicochemical properties and toxicity data of glycerol.

Description	Value
Molecular formula	C ₃ H ₅ (OH) ₃
Melting point (°C)	17.8
Boiling point (°C)	290
Viscosity (Pa.s)	1.5
Vapor pressure at 20 °C (mm Hg)	< 1
Density at 20 °C (g cm ⁻³)	1.261
Flash point (°C)	160 (closed cup)
Ethylene glycol and diethylene glycol limit (mg/ml)	≤ 0.050
Residue on ignition	< 0.01%
Chloride	≤ 0.001%
Sulfate	≤ 0.002%
Heavy metals (μg/g)	< 5
Chlorinated compounds	≤ 0.003%
Fatty acids and esters	Not more than 1 mL of 0.5 N sodium hydroxide is consumed
Heat of fusion at 18.07 °C (cal/g)	47.49
Auto ignition temperature (°C)	400
Critical temperature (°C)	492.2
Critical pressure (atm)	42.5
Dielectric constant (25 °C)	44.38
Dipole moment (30–50 °C)	2.68 D
LD50 (oral-rat) mg kg ⁻¹	12 600
LD50 (dermal-rabbit) mg kg ⁻¹	> 10,000
LC50 (rat-1 h) mg m ⁻³	570

Download English Version:

<https://daneshyari.com/en/article/8113398>

Download Persian Version:

<https://daneshyari.com/article/8113398>

[Daneshyari.com](https://daneshyari.com)