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Biodiesel by-product glycerol and its products

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Abstract

Due to the increase in human population as well as industrialization, the worldwide consumption of petroleum also increases during the past decades, which has led to the depletion of fossil fuel reserves and high petroleum price. Furthermore, fossil fuels combustion contributes to the emissions of greenhouse gases that lead to global warming and atmospheric pollution. Biodiesel is considered as best alternative to petroleum diesel in transport section. Biodiesel is produced by the chemical reaction of vegetable oil with the alcohol like methanol or ethanol etc. Moreover, glycerol is obtained as byproduct in this reaction. Naturally, with increase in production of biodiesel, crude glycerol production has been increasing. Many impurities are present in crude glycerol due to its use in pure form is difficult and need expensive refining process. So, there is need for this crude glycerol to transform into other value added products. Crude glycerol consumption is of prime importance due to its use for reducing negative effects on environment and also increases the biodiesel production economic importance. This review described comprehensively the consumption of glycerol as development of fuel cell, production of hydrogen gas, synthesis of chemicals, methanol production, waste water treatment and many other applications. In future, glycerol will definitely become renewable feedstock in chemicals, power and in biorefineries for fuel synthesis.

Key words: Glycerol, Biodiesel, Methanol, Gasification, Transesterification

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1. Introduction

There is serious energy crisis due to extra use of natural resources such as fossil fuel and increased industrialization. World is facing serious energy crisis in this century due to increased industrialization. Fossil fuel consists of 88% of total global energy consumption. It was estimated that about 53% energy demands will be increased up to 2030. Petroleum is very important resource for many applications like agriculture, household products, clothing, for chemicals and synthetic material. By 2030 only in USA petroleum demand may escalate up to 116.00 million [1]. As the dependence on non-renewable resources is increasing so, there is great need for utilization of alternate energy source. So, the sources should have the trait of green economy and sustainability. In this view, biofuels can be used as potential alternative resources [2]. In this perspective, great opportunities have created to replace petroleum materials with bio-fuel alternatives. In search of alternative energy source to fossil fuel, researchers have focused on biodiesel (BD) which is one of the promising and renewable fuel [3]. Generally, monoalkyl esters of long chain fatty acids derived from transesterification of renewable or no8n renewable oil with alcohol is referred as biodiesel [4-5]. Biodiesel is considered as attractive source for many reasons: (1) it is biodegradable and has less toxicity (2) it is renewable fuel that is sustainable (3) it appears to improve the economic rural potential [6]. There are several feed stocks to produce biodiesel [7-8] and can be categorized as first, second and third generation feed stocks. First generation feed stocks include edible oils i.e. rapeseed, soyabeans [9], palm oil [10] and sunflower [11]. Biodiesel which is produced from edible oil has negative impact to economy because it could bring imbalance to food market [12]. Energy crops such as jatropha [13], mahua [14], jojoba oil [15], tobacco seed [16], salmon oil [17] and seamango [18] represent second generation of biodiesel feed stocks [19]. However microalgae are referred as third generation feedstock and are appeared as most encouraging substitute source of lipid for benefit in biodiesel production [20]. One of the major obstacles to the production of the biodiesel at large scale is its price which is greater than that of the petro diesel. However, this price can be controlled by the proper use of its by product (glycerol) in number of industries [21]. But the problem is that the produced glycerol have impurities and other chemicals, for example, inorganic salts, organic salts, methanol vegetable colors, soaps, mono and diglyceride [22-23]. Crude glycerol purification is an expensive process which requires expensive processing equipment [24].

2. Biodiesel as major source of glycerol

Market statistics has shown that high amount of glycerol production is attributed during biodiesel production. When biodiesel production is increases, glycerol production is also increases. Glycerol contains about 10 wt.% of the total production of biodiesel, this research revealed that 11,500 t of 99.9% pure glycerol (PG) is produced annually by a plant with a capacity of 30 million gallons of glycerol [25].

3. Impact of glycerol price on biodiesel cost

One of the major obstacles in the commercialization of biodiesel is that it is manufactured by raw materials which are not cost effective. Biodiesel cost is over US$0.5/L and it is 1.5 times more than that of petroleum-based diesel depending upon the nature of feedstock oils [26]. However, the appropriate separation and purification of glycerol after the completion of transesterification reaction for biodiesel production can also help to decrease the biodiesel cost by improving the market of good grade glycerol.

4. Transesterification reaction for glycerol production

In transesterification reaction, fat and oil react with any alcohol in the presence of catalyst to produce methyl esters fatty acid and glycerol (by product) [27]. The reaction of transesterification can be carried out in continuous or batch equipment [28].

5. Purification of crude glycerol

Glycerol which is derived from biodiesel has poor quality. The purpose of refining is to convert the crude form of glycerol into utilizable state in order to its use in number applications. Purification of glycerol involved distillation, chemical treatment, filtration, adsorption decanation, ion exchange and crystallization processes [29].

6. Potential application of glycerol

As the biodiesel production is increasing day by day so glycerol availability will be more. Due to increase in production of biodiesel the accommodation of glycerol is in excess within market [30]. Thus due to excess amount of glycerol, it would be used in value added products. Glycerol is more functional than hydrocarbons which are produced petrochemically. So, by various reactions, more value added chemicals could be produced [31]. Catalytical oxidation produce various compounds such as glyceraldehyde, dihydroxy acetone [32]. Wide range of application of glycerol is reported like from boat coating and energy bars to cough syrups (You *et al.* 2007).

6.1. Gasification products

Gasification process is the thermochemical decomposition under high temperature which produces carbon monoxide hydrogen, carbon dioxide which is termed as producer gas or syngas. For the gasification of biomass, crude glycerol is used which improves hydrogen fraction and gas yield [33]. It is used in chemical industry as by product for example formic acid, hydrochloric acid, ammonia, cyclohexane, acetic acid, urea, and methanol. Although hydrogen is advantageous for the solution of sustainable energy solutions, its methods of production for commercial implementations are under developed. Conventional methods of the production are thermochemical and electrolysis [34-35].

6.2. *Precursor for the synthesis of chemicals*

Glycerol has wide range of applications and is used as chief feedstock for many chemicals production. Three hydroxyl groups present in glycerol structure give benefit for the chemical and biological transformation of glycerol into the profitable commodity chemical. By highly functionalized molecule of glycerol, more value added products can be made than that of hydrocarbon which are derived petrochemically [31].There are wide range of researches and literature which are available on glycerol valuable chemical production to valorization [36]. Figure 1 representing glycerol conversion to different useful chemicals.

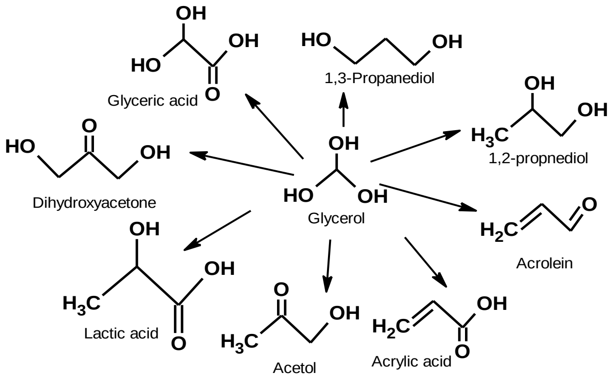

Fig.1. Glycerol conversion into useful chemicals [36]

Table 1.Studies on the gasification of crude glycerol to produce syngas

Method	Crude glycerol properties	Conditions	Yield
Air gasification with oil kernel	85.4% glycerol, 8.4% water, 6% other	49% glycerol, 850^{0}C, air ratio 0.4	Increased from 0.4 to 1.2 Nm^3/kg, 19 to 33% (v/v) H_2 increase Tar decrease 19.5 to 2.4%

Hydrothermal continuous gasification by supercritical water	68.53–71.18% glycerol, 2.62–4.19% methanol, 25.91–29.71% MONG,1.49–2.51% ash, 0.01–0.04% water	650°C, 5% glycerol, continuous tubular reactor,	26.44–35.85 mmol/g
Gasification with hardwood chips	–	–	Up to 20% glycerol produce most significant gases within ICE standards, HHV of 18.71 MJ/Kg
Gasification by supercritical water	–	500°C, 7% glycerol, 45 MPa	H_2 mole fraction yield 27.9 mol%,
Steam gasification	60% glycerol, 31% methanol, 7.5% water, 1.05% KOH	Liquid hourly space velocity of 0.77/h, 800°C, Ni/Al_2O_3catalyst, 1:3 steam to glycerol	15% mol increase over pyrolysis 89.4% yield 62 mol% H_2,1.9 L/g total gas
Hydrothermal gasification in supercritical water	–	–	$K_2HPO_4$and K_3PO_4 max H_2 H_3PO_4 and KH_2PO_4 max CH_4
Air/O_2Gasification	60% glycerol, 20% MONG, 15% methanol, 5% ash	Entrained flow gasifier, excess air ration 0.35–0.4	Syngas HV: Air: 1750 kcal/N m_3O_2 : 2300–2500

6.3. Methanol production

One of the renewable sources of energy is methanol that is used widely as intermediate product for the bulk chemical synthesis and it also serves as energy transporter in internal combustion engines. Research studies have shown that 0.270 kg methanol/kg glycerol is produced and overall efficiency was 38%. In the production of biodiesel, the methanol which is produced from the biodiesel derived glycerol can be reused into the process of transesterification. In this way biodiesel operation cost could be reduced considerably [37].

6.4. Conversion to glycerol ester

Esterification of glycerol with carboxylic acid can generate mono, di, or tri-acyl glycerols and these derivatives are also known as triglycerol ester [38].

6.4. Glycerol ethers

Glycerol tertiary butyl ether is an oxygenated fuel that have a tendency to take place of methyl tertiary butyl ether that is very poisonous [39]. Use of glycerol tertiary butyl ether in biofuel as additive decreases the biodiesel cloud point and fume contents, particulate matters, carbonyl compounds and carbon oxides during combustion. This addition of glycerol also has positive effects on the final quality of diesel [40].

7. Conclusion

In recent years, advance developments in the search of renewable energy sources cause a rapid growth in the biodiesel industry. During the biodiesel production, glycerol is produced as a by-product in huge amounts. Low cost of glycerol has a great effect on the biodiesel production cost and have adverse effect on economy. Therefore, glycerol can be used as an alternative energy source in a wide range of applications, for example, for the production of chemicals, in the fuel industry for the production of hydrogen gas and also used as an additive to increase the efficiency of the fuel, for the fuel cells development, glycerol gasification, for the production of methanol and for the treatment of the waste water. However, still there are some uncertainties but glycerol looks propitious. If glycerol is well-marketed into important and advantageous products, its demand will increase and in near future a stable market will be established that will help the biodiesel producers to counterpoise their costs.

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