Overview of Biodiesel Wastes Utilization for Hydrogen Production

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Nowadays, biodiesel costs more than fuels produced from crude oil due to prices of raw materials. The production cost of biodiesel could be reduced if cheaper raw material is used and utilization of the biodiesel by-product is one of the promising options for lowering the production cost. Hydrogen will play an important role in the world's future. Therefore, hydrogen production from renewable sources such as glycerol, is gaining attention. This article reviews on the latest development on hydrogen production from biodiesel waste. Glycerol reforming and biotransformation are two main routes available for converting crude glycerol to hydrogen. In more recent years, there have been extensive studies, and some encouraging results on processes for utilization of crude glycerol for hydrogen production. However, many of the proposed technologies still need further development to make them cost-effective and operationally feasible processes to directly utilize crude glycerol from biodiesel production on a large scale.

1. Introduction

Biodiesel is gaining global attraction as an alternative fuel because of its biodegradability and environmental friendliness. Biodiesel is typically made by chemically reacting lipids such as vegetable oil with an alcohol. The commercial production of biodiesel has resulted in an increase in crude glycerol as its byproduct. Crude glycerol is the main by-product of biodiesel production which is about 10 % by weight of the starting material (Nartker et al., 2014). The quantity and quality of crude glycerol produced depend on raw material and the process used in biodiesel production. Approximately 10 kg of crude glycerol as by-product will be produced from every 100 kg production of biodiesel (Razaviarani and Buchanan, 2015). Crude glycerol generated by homogeneous base-catalyzed transesterification contains approximately 50-60 % glycerol, 12-16 % alkalis, especially in the form of alkali soaps and hydroxides, 15–18 % methyl esters, 8–12 % methanol, and 2–3 % water. In addition to methanol and soaps, crude glycerol also contains a variety of elements such as Ca, Mg, P, and S as well as other components. To produce high-quality glycerol, these contaminants must be removed which makes it very costly to purify. It was projected that by 2020 the global production of glycerol will reach 41.9 billion L (Nanda et al., 2014). With increased biodiesel production and sharp decrease of glycerol prices, glycerol is expected to become a major chemical feedstock. Efforts have been carried out to utilize excess of glycerol such as seen in the conversion of glycerol to high value compound such as hydrogen via glycerol fermentation process or reforming.

Hydrogen, will play an important role in the world's future as a good alternative renewable fuel in replacing the petroleum-based fuel. This is because hydrogen can offer a clean energy since it produces only water during its combustion. Currently, almost 95 % of hydrogen is industrially produced from fossil fuel-based feedstock which is nonrenewable (Ewan et al., 2005). The catalytic steam reforming of natural gas or coal gasification are current well-established hydrogen production. This paper reviews the state-of-the-art of hydrogen production from biodiesel waste with the main focus on glycerol fermentation and steam reforming. Furthermore, the paper discusses the influence of different process parameters on hydrogen yield. The paper addresses some of the challenges faced in hydrogen production.

2. Bio-hydrogen production by glycerol fermentation

Fermentation is said to be the best approach to produce hydrogen biologically. This is because fermentative production of hydrogen offers several advantages such as simple process (Cardoso et al., 2014) with high production rate; thus favoured by industry because simpler process means lower cost. In addition, the process is stable and efficient (Azwar et al., 2014), can use various types of microorganisms as producer depending on the substrates (Vendruscolo, 2015), and wider choice of substrate, especially from waste makes the process a waste to wealth process.

There are few microbes that have the ability to convert glycerol into H_2 by fermentation under anaerobic conditions; each with their own advantages and disadvantages. Strict anaerobes (*Clostridia*, methylotrophs, rumen bacteria, methanogenic bacteria, archaea), facultative anaerobes (*Escherichia coli*, *Enterobacter*, *Citrobacter*), some aerobes (*Alcaligenes*, *Bacillus*) (Rittmann et al., 2015), and algae are among the microorganisms that have been reported to have the potential to produce hydrogen. Above all, clostridia are the most studied (Abdeshahian et al., 2014). This may be because Clostridia have a robust and diverged fermentative metabolism, stable, easily isolated, form spore, and secrete hydrogenases, the enzyme responsible for the hydrogen production (Jame et al., 2011). However, Clostridia are commonly used with other types of wastes and less literature reported on combination of Clostridia and glycerol. Furthermore, clostridia are best-known as producer in acetone-butanol-ethanol (ABE) production (Ezeji et al., 2014).

Literature has proven that bioconversion of glycerol into a high energy and clean hydrogen is the best option in replacing the progressively depleted petroleum-based fuel and excess of glycerol. However, study on the conversion of the crude glycerol into hydrogen is still low because most substrates used are carbohydrate-based feedstocks. In addition, those using crude glycerol claimed that pretreatment is needed for bioconversion of crude glycerol since the crude glycerol contains impurities, which may become toxic to the microorganisms.

Recent glycerol bioconversion by Laxman et al. (2015) reported 1.5 mol H_2 / mol glycerol without sparging the nitrogen but only 1.2 mol H_2 / mol glycerol with the sparged of nitrogen. Maru et al. (2013), in their comparison study of hydrogen yield produced using the combination of *Enterobacter* spH1, *Enterobacter* spH2, and *Citrobacter freundii* H3 (in 1:1:1 ratio), found that single culture of *Enterobacter* spH1 produced the highest yield of 0.85 mol H_2/mol glycerol compared to the mixed culture. Kivistö et al., (2010) reported to obtain the highest hydrogen yield at 1.6 mol H_2 / mol glycerol by halophilic bacteria *Halanaerobium saccharolyticum* subspecies senegalensis. Theoretically, depending on the end-product of fermentation (acetate or butyrate and ethanol) the hydrogen yield can be 3 mol, 2 mol or 1 mol per mole of glycerol (Maru et al., 2013). Thus, be it pure culture or mixed-culture microorganisms, newly isolated or genetically modified microorganisms - via batch or continuous methods or even by the hybrid methods of biological approaches the yields claimed are still lower.

Physico-chemical factors like pH, temperature, and head space, and carbon to nitrogen ratio can affect the hydrogen production and yield as well as the growth of the microbes. pH is one of the most crucial factors for microbial environment that can influence metabolic pathways, hydrogenase activity and hydrogen yield. Most literature reported that maximum yield of hydrogen can be obtain at pH lower than 6 (Oliveira and Ferreira-leitão, 2016). Their claims has been proven by (Varrone et al., 2012) who obtained 0.96 mol H_2 / mol glycerol at initial pH of 7.9. It is said that methanogenic activity only occurs at pH between 6.5 and 7 while pH dropped from 7.0 to 6.45 during the fermentation due to the production of organic acids acid also been reported in Markov et al. (2011). Thus, it is important also to control pH during the fermentation because the productions of organic acids can supressed the production of hydrogen by lowering the pH to acetogenic condition (Lee et al., 2013).

Temperature is another affecting factor. It can affect the growth rate of bacteria of all cellular reactions. A study on the effect of temperature was done by Qin and Li (2012) under batch fermentation and found that 35 °C was the optimum temperature for maximum production of hydrogen. Wang and Wan (2011) studied on the effect of combined effect of temperatures and pH on hydrogen production under batch fermentation of mixed cultures. They found that maximum hydrogen yield was achieved at 37.4 °C, pH 6.9. Thus it can be concluded that the optimum temperature so far is between 34 to 37 °C; higher temperature may inhibit the production of hydrogen (Abdeshahian et al., 2014).

In the hydrogen production, volumes of head space can also affect the yield of hydrogen by influencing the hydrogen gas pressure and affect the metabolic pathway of hydrogen. The effect of head space on the yield of hydrogen was studied by Abdeshahian et al. (2014). In their work, the production of hydrogen was compared in different Schott Duran bottles containing a total culture medium of 500 mL with three headspace percentage (volume of culture headspace/total volume of bottle × 100) including 15 %, 57 %, and 78 %. From the results, 78 % of head space gave higher yield of hydrogen indicates that larger headspace influence the performance by decreasing the partial pressure of hydrogen in liquid and gas phase. The same finding was found by

Junghare et al. (2012) and Xia et al. (2016) also reported that low volume of headspace will cause the shift in metabolic pathway thus cause the cells to further synthesis reduced products such as lactate, acetone, ethanol and butanol.

Another important factor that can influence the production of hydrogen is carbon to nitrogen ratio (C / N ratio). C/N ratio is important because nitrogen itself is an important element in the proteins, nucleic acids and enzymes; and also in the growth of hydrogen producing bacteria. However until now, there may be less or no research mentioned about C/N ratio when dealing with glycerol alone. Unless the reaction is an integration of glycerol and other biomass or sugar, then the C/N ratio must be considered (Sen et al., 2013). Sen et al. also reported that, for 0.15 m^3 fermenter, a C/N ratio of 10 to 30 can give the optimal value of hydrogen yield.

3. Hydrogen Production by Glycerol Reforming

There are several methods to produce hydrogen using glycerol as a raw material such as steam reforming, partial oxidation, dry reforming, autothermal reforming, aqueous reforming, pyrolysis and photocatalysis reforming. The conversion of glycerol to hydrogen via steam reforming gives some advantages since the steam reforming of hydrocarbons process is a known, mature, and efficient technology (Iriondo et al., 2009). Thermodynamically, steam reforming process favours high temperatures and a low pressure.

In steam reforming, five main reactions can be expressed as Eq(1-5) for glycerol conversion into hydrogen production. Firstly, glycerol decomposition occurs as Eq(1) and followed by the water-gas shift reaction as Eq(2). The desired overall reaction or steam reforming of glycerol can be summarized as Eq(3). Unfortunately, some hydrogen is lost via methanation of carbon monoxide (CO) and carbon dioxide (CO_2), which presented in Eq(4-5).

$$C_3H_8O_3 \overset{H_2O}{\longleftrightarrow} 3CO + 4H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \tag{3}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{4}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{5}$$

Based on the reactions, it shows that there will be some side products of carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4) while producing hydrogen. With the excessive of water (H_2O) presents in the water-gas shift reaction, hydrogen production will increase due to the carbon monoxide conversion. At the same time, hydrogen will also react with carbon monoxide and carbon dioxide to produce methane. This situation will result in the decreasing of hydrogen production. Therefore, several reaction parameters which can affect the hydrogen production should be focused to prevent unnecessary hydrogen conversion into side products. The reaction parameters which can affect the hydrogen production include reaction temperature, glycerol feed concentration, and feed flow rate.

Pompeo et al. (2011) has observed that it is possible to achieve a complete glycerol conversion using Ni/SiO$_2$ catalyst at minimum temperature of 450 °C. Hakim et al (2016) studied on the steam reforming of glycerol at different temperatures of 400, 500, and 600 °C; and they reported that the hydrogen yield among the three temperatures used, 600 °C showed a high hydrogen production of over 50 %. This is because at high temperature, the process of breaking C-C and O-H bonds from glycerol is easy to achieve. Furthermore, the presence of steam at high temperature can assist the movement of OH groups towards the catalyst surface and hence facilitates the reaction process. Similar finding was observed by Chiodo et al. (2010) where the hydrogen yield increased with higher temperature for temperature ranges from 450 to 650 °C. However, at higher temperature above 650 °C, a sudden decreased of hydrogen production occurred due to side reactions. CH_4 selectivity is the only side products which were decreased due to the increasing temperature while CO and CO_2 will keep increasing with the increasing temperature. Temperature optimization must also be focused to achieve a higher hydrogen production with lower side products (CO, CO_2, and CH_4) (Dave and Pant, 2011).

Wang et al. (2010) has found that the hydrogen selectivity and glycerol conversion increased with the increasing in water / glycerol molar ratio (WGMR). Similar finding were reported by Dave and Pant (2011). They also found that the increasing of WGMR will reduce the selectivity of CO and CH_4 only, but selectivity for CO_2 will increase. This is because the excess steam improved the conversion of glycerol into gaseous

products through water gas shift process. The excess steam will reduce the formation and accumulation of CO on the catalyst surface by converting it into CO_2 and H_2 (Hakim et al., 2016).

Controlling the flow rate in the process is a crucial part in hydrogen production. Slinn et al. (2008) studied the effect of glycerol reforming into hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4) by differing flow rates at temperature of 800 °C . They found that H_2 yields begin to decrease and others (CO, CO_2, and CH_4) increase at faster flow rates. Similar results were reported by other researcher (Dave and Pant, 2011).

The variation of process conditions (reaction temperature, T; feed flow rate, FFR; water glycerol molar ratio, WGMR) which could affect the H_2 selectivity and glycerol conversion were evaluated by many researchers. Zamzuri et al. (2016) claimed that water glycerol molar ratio (WGMR) has the greatest effect on the hydrogen selectivity and glycerol conversion compared to reaction temperature and feed flow rate. With increasing WGMR and higher reaction temperature, the production of hydrogen is increased and the production of CH_4 was completely reduced due to water gas shift reaction (Sad et al., 2015).

The aim of application of catalysts in glycerol reforming process is to provide more active reactions, which results in increasing the hydrogen production from reactant. The selection of active metal catalyst for hydrogen production from glycerol is the main problem faced by researchers. The high cost of catalyst is another major constraint to the steam reforming process. Noble metals such as ruthenium, rhodium, palladium, iridium, and platinum provide high hydrogen yield in the reforming reaction (Yurdakul et al., 2016). However, the high cost of noble metals limited their further application. Accordingly, the search for non-noble metal catalysts that with good activity and selectivity in the glycerol steam reforming reaction would receive considerable attention. Nickel are among non-precious transition metals which have shown good performances in glycerol reforming (Senseni, 2016). However, Nickel-based catalysts are prone to deactivation mainly by carbon deposition on its surface (Dieuzeide et al., 2016). Although tremendous attemps have been made and a number of paper have been published, deactivation is still a great challenge for Nickel based catalyst. Another drawback of the glycerol steam reforming is it requires high reaction temperature. This harsh reaction condition usually leads to thermal sintering of the active metal component as well as coke deposition. Many effort have been focused to enhance the performance of Nickel based catalyst in different ways such as using different support or adding a second metal.

The role of support in the catalytic reaction is complex and still not clear. The selection of catalyst support for active metal catalyst in hydrogen production is a major concern since it affects the activity of metal catalyst The properties of support strongly affect the catalyst activity due to metal and support interaction (Huang et al., 2011). Bobadilla et al. (2015) concluded that the activity of bimetallic NiSn / Al_2O_3 catalysts was enhanced by addition of MgO or CeO_2 and coke formation also decreased. Supported Ni catalysts on Al_2O_3, La_2O_3, ZrO_2, SiO_2, and MgO have been investigated for hydrogen production from steam reforming of glycerol (Zamzuri et al., 2016). They reported that Ni supported on Al_2O_3 was found to be the best catalyst with maximum hydrogen selectivity (71.5 %).Another option to improve the activity of the Ni catalyst is by adding second metal such as cobalt. Sanchez and Comelli (2014) studied 4Ni/Al_2O_3, 4Co – 4Ni / Al_2O_3, and 12Co – 4Ni / Al_2O_3 catalysts for glycerol steam reforming. They reported that the introduction of cobalt favours hydrogen and decreases CO_2 production. Another study by Bobadilla et al. (2016) concluded that the addition of stanum increase the catalyst stability and durability by decreasing the coke deposition.

4. Conclusions

There have been extensive studies, either by glycerol reforming or biotransformation, for converting crude glycerol to hydrogen and some encouraging results on the processes for utilization of crude glycerol for hydrogen production. While bioconversion offers a faster production and a cheaper way of hydrogen, the glycerol reforming also offers a great length of technology, especially because the application itself has been long used and established. Compared to other technology such as electrolytic process by splitting water using electricity, photoelectrochemical hydrogen production (by splitting water using direct solar power), or other thermal process, glycerol reforming or biotransformation of crude glycerol is promising because the process is cheaper and it can help in reducing waste, thus making the process itself as a a clean process. However, no successful industrial application for utilizing crude glycerol for hydrogen production in large scale has been reported so far. The major challenge is how to develop an active, selective, and stable process. Further research and development on crude glycerol utilization for hydrogen production is important in order to make biodiesel production more sustainable and profitable in future.

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