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Challenges in the production of hydrogen from glycerol-a biodiesel byproduct via steam reforming process

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Abstract

The depleting fossil fuels with their ever increasing prices have paved ways for alternative fuels. Biodiesel is one of those alternative fuels which have picked up keen interest of the people due to its similar properties to diesel. However due to biodiesel being costlier than diesel in the present scenario, it has not been preferred to diesel. However if the cost of biodiesel is reduced then its effective usage can be made, either by blending with conventional diesel or by utilizing its byproduct (glycerol) effectively. One way is to use glycerol to produce hydrogen. Hydrogen, being another source of renewable energy, is also seen as a clean fuel for transportation purpose. Hydrogen can be prepared through glycerol via various routes namely steam reforming, auto-thermal reforming, partial oxidation, etc. The paper here focuses on the steam reforming process. This process is used widely used in the industries and it would not require much change in the system if the feedstock is changed to glycerol from naphtha or natural gas. However like every process this process also has some limitations which hinder the effective production of hydrogen. The paper throws light on these challenges, along with few possible solutions which can be used in order to avoid or eliminate these challenges and help in efficient production of hydrogen.

Keywords: *Glycerol, Steam reforming, Hydrogen production, Biodiesel, Challenges*

1. Introduction

The ever increasing prices of crude oil, which leads to the increase in prices of fuels from it, and the limiting reserves of conventional fossil fuels along with ever growing population and pollution has led the people to come up with alternative fuels which would be cheaper, efficient and causing less pollution. As a result, new technologies requiring the use of renewable feedstock have been the focus of intense process development within the past decade [1].

In this respect, green catalytic processes which utilize renewable feedstock for the conversion into commodity chemicals and clean biofuels have attracted considerable attention. So, alternative bio-based fuels are emerging as the long-term solution. The Biofuels have become alternate to fossil-based fuels because they are renewable and theoretically, carbon dioxide (CO_2) neutral.

Many researchers have been doing research on biofuels and Bio-diesel is one of them. Today, Biodiesel has become more competitive against petroleum diesel due to the higher prices of crude oil and increased demand for environmentally

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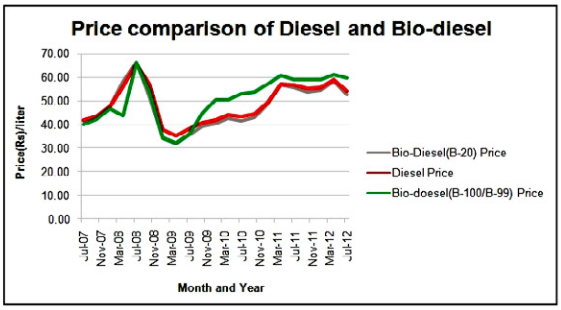
acceptable fuels [2]. However, the popularity of bio-diesel among the world has not picked up much due to its competitive nature with diesel in terms of price per liter (Table 1)[3]. Figure 1 (a) and (b) shows the graphs of comparison in prices of diesel and bio-diesel. Hence it is important, for effective usage of Bio-diesel; the price has to be lowered.

Table 1. Comparison between the prices of diesel and biodiesel in USA for past five years

Month and Year	$/gallon			Rs/liter		
	Diesel	Biodiesel		Diesel	Biodiesel	
		B-20	B-99/B-100		B-20	B-99/B-100
Jul-12	3.75	3.83	4.23	52.86	53.99	59.63
Apr-12	4.12	4.18	4.35	58.08	58.92	61.32
Jan-12	3.86	3.95	4.2	54.41	55.68	59.20
Oct-11	3.81	3.91	4.18	53.71	55.12	58.92
Jul-11	3.95	4.02	4.19	55.68	56.67	59.06
Apr-11	4.04	4.05	4.32	56.95	57.09	60.90
Jan-11	3.45	3.50	4.05	48.63	49.34	57.09
Oct-10	3.07	3.14	3.82	43.28	44.26	53.85
Jul-10	2.95	3.06	3.75	41.58	43.13	52.86
Apr-10	3.02	3.12	3.57	42.57	43.98	50.32
Jan-10	2.87	2.96	3.59	40.46	41.72	50.61
Oct-09	2.79	2.88	3.19	39.33	40.60	44.97
Jul-09	2.54	2.69	2.55	35.80	37.92	35.95
Apr-09	2.27	2.49	2.28	32.00	35.10	32.14
Jan-09	2.44	2.67	2.45	34.39	37.64	34.54
Oct-08	3.65	4.04	3.85	51.45	56.95	54.27
Jul-08	4.71	4.66	4.69	66.39	65.69	66.11
Apr-08	4.14	3.98	3.09	58.36	56.10	43.56
Jan-08	3.40	3.37	3.31	47.93	47.50	46.66
Oct-07	3.11	3.08	2.99	43.84	43.42	42.15
Jul-07	2.96	2.96	2.84	41.72	41.72	40.03

(a)


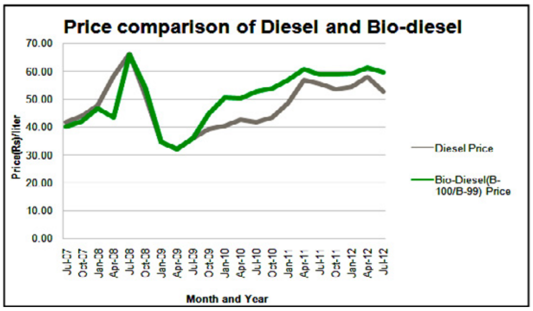
(b)


Fig. 1. Graphical presentation of prices of diesel and biodiesel (a) Graph showing the comparison of diesel and bio-diesel (B-20, (B-99/B-100)) and (b) Comparison of prices of diesel and bio-diesel (B-99/B-100)

With the production of Biodiesel, glycerol (1,2,3-propanetriol), a carbohydrate ($C_xH_yO_z$), is obtained as byproduct during biodiesel production from vegetable oil and bioethanol. By utilizing this by-product of bio-diesel efficiently the cost of biodiesel can be reduced (as shown in Fig 2) [4]. Glycerin is produced about 10% of the total quantity of the biodiesel produced, i.e. for 10 kg of total production 9kg would be biodiesel and 1 kg would be glycerol.

1.1. Biodiesel Byproduct: Glycerol

Currently, almost two third of the industrial uses of glycerol are in food and beverage (23%), personal care (13%), oral care (20%), tobacco (12%), etc (Fig 3)[5]. The purification of crude glycerin from the biodiesel plants is a major issue. Also the disposal of glycerol by the emerging biodiesel industry is therefore a new engineering challenge in order to make it more competitive with the conventional fossil diesel [6]. With the ever-increasing production of biodiesel, a glut of glycerin ($C_3H_8O_3$) is expected in the world market [7]. Hence it is necessary to explore alternative uses of glycerin.

One promising way is to use glycerin to produce hydrogen or synthesis gas via steam reforming. Hydrogen is a clean energy source with uses including ammonia production, petroleum processing, and power generation in fuel cells [8]. Also it is known that, demand for hydrogen is expected to greatly increase globally in the future, due to the increasing environmental concerns.

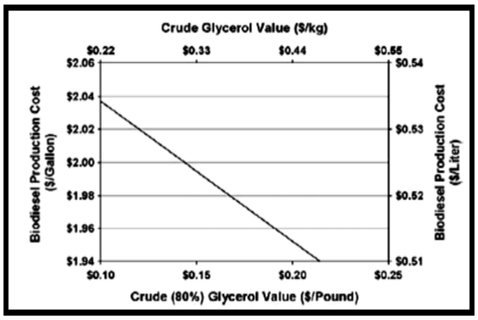


Fig. 2. Respective change in the biodiesel cost with the change in crude glycerol value

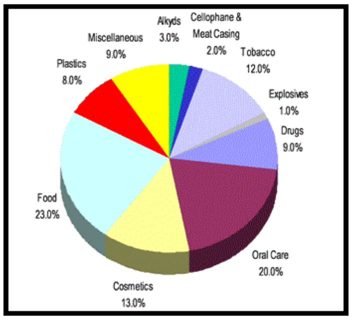


Fig. 3. Pie chart showing various uses of glycerol

2. Why Glycerol for hydrogen production?

Fossil fuels are the dominant source of industrial hydrogen. Today approximately 80% of hydrogen can be generated from natural gas or from other hydrocarbons, here the steam (H_2O) reacts with methane (CH_4) to yield syngas, at a high temperatures (700–1100 °C),

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = +\,191.7 \text{ kJ/mol} \tag{1}$$

In a second stage, the hydrogen is generated at the lower temperature due to water shift gas reaction, at about 130 °C.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -\,41 \text{ kJ/mol} \tag{2}$$

There are certain side reactions which includes the oxygen atom to oxidize CO to CO_2. This oxidation reaction helps in maintaining the energy balance of the reaction. Additional heat required to the system is generally provided by burning some portion of the methane. As per stochiometry the moles obtained by steam reforming of natural gas is 4. While hydrogen obtained from steam reforming of glycerol is 7 as per equation (3). So as per stochiometric study, glycerol provides most number of moles of hydrogen and hence can be preferred over the fossil fuels.

$$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 7H_2(g) + 3CO_2(g) \qquad \Delta H = 128 \text{ kJ/mol} \tag{3}$$

Though more amount of glycerol is required in terms of weight as compared to methane in order to get just double the amount of hydrogen, but in steam reforming of natural gas (methane), a fuel is burnt off to make another fuel while this is not the case in glycerol steam reforming and hence it would be advisable to use glycerol instead of methane.

3. Hydrogen production from glycerol through different routes.

Today due to the technological advancements in the fuel cell industry, the demand of hydrogen is increasing. At present, almost 95% of the world's hydrogen is being produced from fossil fuel based feed stocks. Renewable resources based technologies for hydrogen production are attractive options for the future due to carbon neutral nature of these technologies with lesser effects to the environment. A great interest in utilizing glycerol for hydrogen production is seen over the last few years. Most of the studies on hydrogen production are focused on thermo-chemical routes [6].

Hydrogen can be produced from glycerol by the following ways

- Steam reforming process
- Partial oxidation gasification process
- Auto-thermal reforming process
- Aqueous-phase reforming process
- Supercritical water reforming process

3.1. Steam reforming process

The steam reforming of hydrocarbons has been the preferred method for many decades for industrial scale hydrogen production. Reforming process mainly involves splitting of hydrocarbons in the presence of water and water–gas shift reaction as given below.

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)\ H_2 \qquad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41\ kJ/mol \qquad (5)$$

The first step is highly endothermic, taking more heat than it evolves from water–gas shift reaction. Therefore, overall steam reforming is an endothermic process. Thermodynamically, steam reforming process favors high temperatures and low pressures.

3.2. Factors affecting the steam reforming process

The factors affecting the production of hydrogen from steam reforming process are

- Temperature
- Pressure
- Water to Glycerol Feed Ratio (WGFR)
- Feed reactants to inert gas ratio
- Feed gas rate

It has been observed that these factors hold a key role in order to have a high hydrogen yield and a good glycerol conversion. As per various researches [2], [9-19], it has been found that for optimum results the process of glycerol steam reforming requires a high temperature (800K-1000K), a atmospheric pressure (~ 1 atm), the feed reactants to inert ags ratio and feed gas rate should be low. It has also been suggested that the water to glycerol ratio (WGFR) should be around 9:1, i.e. Steam to carbon ration should be around 3:1. The glycerol conversion is a strong function of water to glycerol ratio, but a weak function of other parameters over the conditions of the process.

4. Challenges in the process of steam reforming of glycerol and their possible solution

4.1. Steam reforming process

The process for production of hydrogen from glycerol is a very good option for producing a renewable source of energy. However like every process, there are few loop-holes or challenges in the effective production of hydrogen through steam reforming of glycerol. The challenges need to be overcome for the effective commercializing of the process.
Following are the few problems which have been observed from the literature survey.

- Stochiometrically the glycerol steam reforming reaction states that for one mole of glycerol there should be 7 moles of hydrogen formed. However, when it comes to the practical operation, it has been observed that the production/yield of hydrogen limits to 5.8 to 6 moles while the minimum amount of hydrogen obtained is 4 moles.

- The steam reforming process is endothermic reaction and hence requires a high temperature. Also it is been observed that the yield of hydrogen increases with the increase in temperature, however this yield starts to decrease after a critical temperature. The temperature range for the process is around 800 K – 1000 K. The control of this high temperature is a difficult task and it adds to the operational cost. Moreover high temperature would increase the capital cost of the reactor in terms cost of material of construction

- Very few studies have been performed using crude glycerol. The crude glycerol consists of water, ash, methanol and few of the fatty materials, the effective usage of crude glycerol may lead to the decrease in the overall cost of the process, as the refining stage of glycerol would be eliminated.

- The steam reforming of glycerol apart from producing hydrogen produces 3 moles of carbon dioxide stochiometrically. It is well known that release of carbon dioxide is an environmental concern, and hence effective utilization of carbon dioxide is required.

- The glycerol steam reforming process sometimes has to face certain side reactions which hinder the production as well as the purity of hydrogen. One such side reaction is the formation of methane. This methane is either formed through the reaction of carbon dioxide and hydrogen (eq (5)) or reaction between carbon monoxide and hydrogen (eq (6)) or through hydrogenolysis of glycerol (eq (7)). These reactions need to be subsidized inorder to have higher and purer yield of hydrogen.

$$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g) \quad (5)$$

$$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g) \quad (6)$$

$$C_2H_8O_3(g) + 2H_2(g) \leftrightarrow 2CH_4(g) + CO(g) + 2H_2O(g) \quad (7)$$

- The process also deals with the formation of coke/ carbon during the process. This carbon/coke acts as a poison and clogs the pores of the catalyst and hence deactivates the catalyst thus affecting the process as well as the yield and purity of hydrogen. It is also observed that the coke formation increases with temperature increase. If the temperature could be lowered down the coke formation may decrease but this also may affect the yield of hydrogen.

4.2. Possible solutions to the challenges

There have been some studies which deals with the optimization of the process for increasing the productivity as well as the purity of hydrogen from the glycerol reforming. Few of these methods that can be used have been mentioned here.

1) Decreasing the pressure of the system

It is been observed that the decrease of pressure below 1 bar could enhance the hydrogen production. However, an operating pressure below the atmospheric pressure is difficult to achieve. Also a lower operating temperature is also critically important for industrial application which leads to the reductions of energy usage, catalyst sintering [20][21]. An alternative way is use of the carrier gas, to decrease the partial pressure of reactants and the desired temperature range.

2) Increase of feeding steam ratio.

If the inert gas is replaced by steam, It is observed that the hydrogen production was enhanced considerably. This option will not only decrease the partial pressure of glycerol but also, increases the reactant water. As per the equation and Le Chatelier's principle, both the two effects could enhance the forward reaction.

3) Carbon dioxide removal

As per Le Chatelier's principle, a possible way to promote the steam reforming is to remove carbon dioxide as soon as it is formed from the reaction zone. This is the so-called in-situ adsorption enhanced steam reforming for hydrogen production and has been widely accepted as an effective method to improve the reforming process for hydrogen production There have been researches [22-29] been carried out for the solution of these problems, many of these researches suggest of using an adsorbent like calcium oxide (CaO) for the adsorption of CO_2 during the process. Even alkali enhanced reforming can be one of the options where alkali (NaOH) is used along with feed, the alkali reacts with CO_2 to form sodium carbonate (Na_2CO_3), which is similar to the method above.

It is observed that the adsorption of CO_2 during the process enhances the yield of hydrogen along with the purity of hydrogen by reducing the production of methane (CH_4), carbon monoxide (CO). However the increase in the yield of hydrogen is the function of fraction of CO_2 removed or adsorbed.

It is also observed that the temperature range of the process is also lowered with the in-situ sorption of CO_2. This may help in reducing the energy input and hence the operating cost. The use of sorbent also helps in the reduction of carbon formation as the production of CH_4 and CO.

4) Hydrogen in-situ separation

Few of the researches [7],[30] also suggests that instead of adsorption of CO_2 the in-situ separation of hydrogen may be a better option. However the separation of hydrogen needs to be done by using a membrane reactor. The separation of hydrogen deals with lower temperature range and lower production of methane carbon monoxide and carbon as compared to CO_2 adsorption.

Summary

It can be seen that the production of hydrogen from glycerol is a very good option, keeping into mind that hydrogen as well as biodiesel are said to be the future fuels of the world. Also, it is been observed that the amount of hydrogen produced is comparatively though stochiometrically more than the conventional method. However the glycerol steam reforming possesses some challenges which needs to be irradicated or avoided in order to have higher productivity as well as purity of hydrogen.

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References

[1]. Chin C., Say F., and Adesoji A., 2010. Glycerol Steam Reforming over Bimetallic Co-Ni/Al_2O_3, Ind. Eng. Chem. Res., 49, p. 10804.
[2]. Adhikari S, Fernando S, Haryanto A, 2007. A comparative thermodynamic and experimental analysis on hydrogen production by steam reforming of glycerin. Energy Fuel 21(4), p. 2306.
[3]. http://www.afdc.energy.gov/publications/search/keyword/?q=alternative%20fuel%20price%20report, 23/09/2012, 8:30 PM.
[4]. Haas M., McAloon A., Yee W., Foglia T., 2006. A process model to estimate biodiesel production costs, Bioresource Technology 97, p. 671.
[5]. http://www.natchemconsumer.com//information.html, 23/09/2012, 9:30 PM
[6]. Adhikari S., Fernando D., Haryanto A., 2009. Hydrogen production from glycerol: An update, Energy Conversion and Management 50, p. 2600.
[7]. Chen H, Zhang T, Dou B, Dupont V, Williams T, Ghadiri M, 2009. Thermodynamic analyses of adsorption enhanced steam reforming of glycerol for hydrogen production. Int J Hydrogen Energy 34, p. 7208.
[8]. Luo X., Zhao X., Cao F., Xiao T., and Fang C., 2007. Thermodynamic Study on Hydrogen Generation from Different Glycerol Reforming Processes, Energy & Fuels 21, p. 3505.
[9]. Wang X., Li S., Wang H., Liu B., and Ma X., 2008, Thermodynamic Analysis of Glycerin Steam Reforming, Energy & Fuels 22, p. 4285.
[10]. Czernik S., French R., Feik C., Chornet E., 2002, Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion process. Ind Eng Chem Res 41, p. 4209.
[11]. Adhikari S, Fernando S, Haryanto A, 2007, Production of hydrogen by steam reforming of glycerin over alumina supported metal catalysts, Catal Today 129 (3–4), p. 355.
[12]. Douette A., Turn S., Wang W., Keffer V., 2007, Experimental investigation of hydrogen production from glycerin reforming, Energy & Fuels 21, p. 3499.
[13]. Chiodo V., Freni S., Galvagno A., Mondello N., Frusteri F., 2010, Catalytic features of Rh and Ni supported catalysts in the steam reforming of glycerol to produce hydrogen, Applied Catalysis A: General 381, p. 1.
[14]. Iriondo A., Barrio V., Cambra J., Arias P., Guemez M., Sanchez M., Navarro R., Fierro J., 2010, International Journal Of Hydrogen Energy 35, p. 11622.
[15]. Buffoni I., Pompeo F., Santori G., Nichio N., 2009, Nickel catalysts applied in steam reforming of glycerol for hydrogen production, catalysis Communications 10, p. 1656.
[16]. Pompeo F., Santori G., Nichio N., 2011, Hydrogen production by glycerol steam reforming with Pt/SiO_2 and Ni/SiO_2 catalysts, Catalysis Today, p. 183.
[17]. Sa´nchez E., D'Angelo M., Comelli R., 2010, Hydrogen production from glycerol on Ni/Al_2O_3 catalyst, International Journal Of Hydrogen Energy 35, p. 5902.
[18]. Cheng C., Foo S., Adesina A., 2011, Steam reforming of glycerol over Ni/Al_2O_3 catalyst, Catalysis Today 178, p. 25.
[19]. Dieuzeide M., Iannibelli V., Jobbagy M., Amadeo N., 2012, Steam reforming of glycerol over Ni/Mg/gamma-Al2O3 catalysts. Effect of calcination temperatures, International Journal Of Hydrogen Energy, p. 1.
[20]. Cong T., He Y, Chen H, Ding Y, Wen D, 2007, Heat transfer of gas-solid two-phase mixtures flowing through a packed bed under constant wall heat flux conditions, Chem Eng J 130, p. 1.
[21]. Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, Chen H, 2009, Hydrogen production by sorption-enhanced steam reforming of glycerol, Bioresour Technol 100, p. 3540.

[22]. Chen H., Ding Y., Cong N., Dou B., Dupont V., Ghadiri M., Williams P., 2011, A comparative study on hydrogen production from steam-glycerol reforming: thermodynamics and experimental, Renewable Energy 36, p. 779.
[23]. Dou B., Song Y., Liu Y., Feng C., 2010, High temperature CO_2 capture using calcium oxide sorbent in a fixed-bed reactor, Journal of Hazardous Materials 183, p. 759.
[24]. Wang X., Li M., Li S., Wang H., Wang S., Ma X., 2010, Hydrogen production by glycerol steam reforming with/without calcium oxide sorbent: A comparative study of thermodynamic and experimental work, Fuel Processing Technology 91, p. 1812.
[25]. Wang X., Wang N., Wang L., 2011, Hydrogen production by sorption enhanced steam reforming of propane: A thermodynamic investigation, international journal of hydrogen energy 36, p. 466.
[26]. Wang W., Cao Y., 2011, Hydrogen production via sorption enhanced steam reforming of butanol: Thermodynamic analysis, International journal of hydrogen energy 36, p. 2887.
[27]. Chen H., Ding Y., Cong N., Dou B., Duponta V., Ghadiria M., Paul T. Williams, 2011, Progress in low temperature hydrogen production with simultaneous CO_2 abatement, chemical engineering research and design 89, p. 1774 .
[28]. Fermoso J., He L., Chen D., 2012, Production of high purity hydrogen by sorption enhanced steam reforming of crude glycerol, international journal of hydrogen energy 37, p. 14047.
[29]. Alvarado F., Gracia F., 2012, Oxidative steam reforming of glycerol for hydrogen production: Thermodynamic analysis including different carbon deposits representation and CO2 adsorption, international journal of hydrogen energy 37, p. 14820.
[30]. Lin K., Lin W., Hsiao C., Chang H., Chang A., 2012, Hydrogen production in steam reforming of glycerol by conventional and membrane reactors, international journal of hydrogen energy, p. 1.