Hydrogen Production form Glycerol Steam Reforming in Supercritical Water with CO_2 Absorption Unit

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Glycerol is expected to be an adequate renewable resource for hydrogen production in the future because it is the by-product of biodiesel production. In this work, crude glycerol containing 80 wt% of glycerol and 20 wt% of methanol is used to perform the thermodynamic analysis of hydrogen production via the glycerol supercritical steam reforming process using the Gibbs free energy minimization method in AspenPlus[TM]. The effects of operating conditions i.e., temperature, pressure and the ratio of supercritical water to crude glycerol (S/G ratio), in the reformer were analyzed. The simulation results show that the suitable operating conditions for the reformer giving 65 mol% H_2 in the gaseous product are at temperature, pressure and S/G ratio of 800 °C, 240 atm and 90. However, the purity of hydrogen is still not suitable for industrial application. Therefore, the hydrogen purification processes including the gas-liquid separation unit and CO_2 absorption process using monoethanolamine (MEA) as an absorption media were also investigated. The results show that the final product of the absorption process using 5-stage absorber can produce approximately up to 99 mol% H_2.

1. Introduction

Biodiesel--a member of biofuel energy has received much attention in the recent year since it is a biodegradable, renewable and non-toxic fuel. In addition, the burning products contains lower amount of ash, carbon monoxide, sulphur dioxide, and incomplete burning carbon, than those of diesel. Although the capital and production costs are still quite high, it is worth noting that the biodiesel production would be a promising option while the crude oil price is in the crisis. With the growth of biodiesel production industry, it leads to large amount of glycerol, the main by-product of biodiesel production in which vegetable oils or animal fats are converted into biodiesel through the transesterification process. Glycerol can be used in many applications that include food, cosmetics and pharmacy. One of effective ways for utilization of glycerol is the conversion of glycerol to hydrogen. This is valuable added of the low-price glycerol without the requirement of glycerol purification unit and reduce the dependent on petroleum source for hydrogen production.

Hydrogen is considered to be an energy source for the future because it causes no harmful to the environment when it is combusted with oxygen. In addition, hydrogen can be used in many different functions including use in chemical production industries and use as a feed for fuel cells. To date, hydrogen production from glycerol can be accomplished by various reforming processes i.e., steam reforming (Authayanun et al., 2011), partial oxidation (Wang, 2010), autothermal reforming (Pairojpiriyakul et at., 2010) and aqueous phase reforming (Wen et al., 2008). Considering the steam reforming reaction, it can be found that this reaction can be used for a commercial production because this process provides the highest yield of hydrogen (up to 70 % on a dry basis). However, this reaction is highly endothermic reaction, therefore; it needs high energy to heat up the feed of water and glycerol to the desired reaction temperature.

Recently, there are some researchers focused on the investigation of supercritical water reforming since this can reduce the energy needed in the reactor. Moreover, the outstanding property of supercritical water is that

it can dissolve in the non-polar organic compound which can reduce the reaction time. Bennekom et al. (2011) studied hydrogen production from pure glycerol, crude glycerin, and methanol (pure and in the presence of Na_2CO_3) in supercritical water. Their experimental results indicated that glycerol can be completely converted to H_2, CO_2, CH_4 and CO under temperatures of 460 - 650 ^oC, feed concentrations of 5 – 20 wt% and the residence time of 6-173 s. Ortiz et al. (2011) performed thermodynamic calculations of glycerol reforming using supercritical water to identify the operating conditions that maximize hydrogen production from a mixture of water and glycerol.

However, hydrogen product from the reformer always gives considerably content of CO_2. This is not suitable for industrial use and thus, the hydrogen purification unit is required to achieve the final product purity (Collodi, 2010). In general, there are several techniques for CO_2 capture e.g., pressure swing adsorption, temperature-swing adsorption, physical absorption, and chemical absorption. Among these techniques, the absorption process using aqueous solution of monoethanolamine (MEA) has been widely used in the industry (Moioli and Pellegrini, 2013). As a matter of fact that MEA is high reactive and low cost (Mofarahi et al., 2008). However, the absorption process is selected for the CO_2 capture from exhaust gas of power plants, natural gas and refinery gas. Mofarahi et al. (2008) studied the recovery of CO_2 by absorption process from gas turbine exhaust of gas refinery power station. Chavez and Guadarrama (2011) simulated the CO_2 capture by chemical absorption process with MEA from the flue gases of the power plant. The CO_2 capture from synthesis gas has not been reported in the open literature. As a result, the integration of the absorption process with MEA and the steam reformer is seemed to be interesting and challenge task. Significantly, hydrogen produced from reforming in supercritical water has high pressure and thus, it is easily and directly to supply for the absorption process.

The objective of this work is to study the hydrogen production via the supercritical water reforming of crude glycerol based on the thermodynamic principle. The Gibbs free energy minimization procedure in AspenPlus^{TM} is used to calculate the equilibrium composition. The effects of key operating conditions i.e., temperature, pressure, supercritical water to glycerol ratio were examined. The CO_2 absorption process integrated with the reforming process is also proposed in this study. The effect of design and operating parameters on the H_2 purification is analysed.

2. Process description

2.1 Hydrogen production from glycerol supercritical water reforming process

The glycerol supercritical water reforming process is composed of two main reactors i.e., supercritical water reformer and water gas-shift reactor. This process is shown in Figure 1. The reactants are crude glycerol (GLYCEROL) and supercritical water (W1). Generally, crude glycerol contains impurities for example methanol, ethanol, water and catalyst. In this work, we assume that crude glycerol is pretreated to reduce its effect on reactors and equipment. Pretreated glycerol is composed of 80 wt% of glycerol and 20 wt% of methanol. At standard condition, glycerol is fed to the reformer with the molar feed rate of 100 kmol/h at 25 ^oC, 1 atm. Supercritical water is fed with the rate of 9,900 kmol/h at 500 ^oC, 240 atm. Therefore, the ratio of supercritical water to glycerol (S/G) is 99. The mixture of supercritical water and glycerol is mixed in the mixer (MIX) and then is fed to the compressor (COMP) and heater (HEAT) to adjust the temperature and pressure before entering to the reformer (SWREFORM). The reactions occur in the reformer are shown in Table 1. The operating conditions for the reformer and equipment, i.e., mixer, compressor, heater, turbine, water gas-shift reactor, separator are shown in Table 2. Gaseous products from the reformer will be sent to turbine (TURBINE) and cooler (COOLER1) for reduction of pressure and temperature to 1.4 atm. and 20 ^oC, respectively. This mixture is then fed to the water gas-shift reactor (WSHIFT) where the CO reacts with steam to produce additional H_2 and CO_2 at 200 ^oC. The synthesis gas from water gas-shift reactor will be cooled before it is separated in the separator (SEP) where the liquid water and gases i.e., CO and H_2 will be split.

2.2 CO_2 absorption process with monoethanolamine absorption media

Because the purity of hydrogen obtained from the supercritical steam reforming is not suitable for industrial application, the next step of hydrogen production is to eliminate the impurity in the mixture of gas containing hydrogen and carbon dioxide. In this work, CO_2 will be removed by absorption process using the MEA solution. This solution can be regenerated and recycled back to the process. The process diagram is shown in the Figure 2. The gas mixture from the reformer is fed to the 3-tray absorption tower (ABSORBER) where it is in contact with 25 wt% of MEA solution. The CO_2- rich stream flows to the 6-tray stripper tower (STRIPPER) for the purpose of MEA recycling where the H_2-rich steam flows to the flash drum (FLASH) for splitting of water and H_2. The unit model and operating conditions for the absorption process are shown in Table 3.

3. Methodology

This work performs a thermodynamics analysis for the hydrogen production from supercritical steam reforming process using Aspen Plus. The gaseous components from reforming process at equilibrium can be calculated
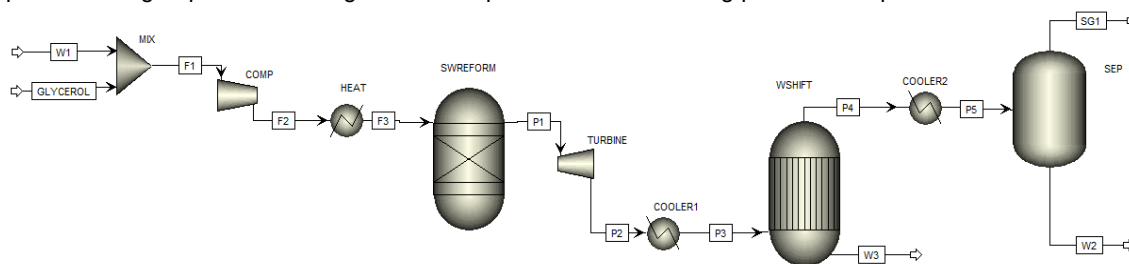

Figure 1: Process flow diagram of hydrogen production from glycerol via supercritical steam reforming

Table 1: Reactions in the supercritical steam reformer

Reactions		
Glycerol reforming:	$C_3H_8O_3 + 3H_2O \rightleftharpoons 3CO_2 + 7H_2$	(1)
Glycerol decomposition:	$C_3H_8O_3 \rightleftharpoons 3CO + 4H_2$	(2)
Methanol reforming:	$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2$	(3)
Methanol decomposition:	$CH_3OH \rightleftharpoons CO + 2H_2$	(4)
Reverse water gas-shift:	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	(5)
Methanation:	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	(6)
Water gas-shift:	$CO + H_2O \rightleftharpoons CO_2 + H_2$	(7)

Table 2: The operating condition of reforming process

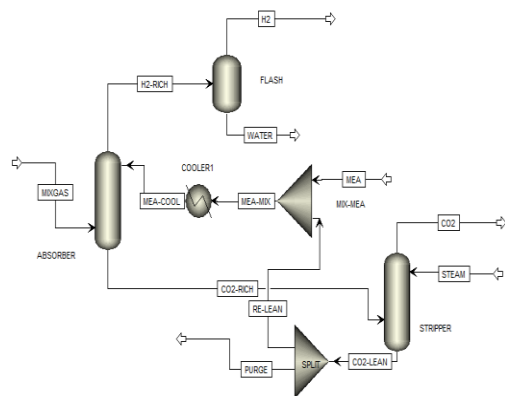| Code	Unit Model	Standard Condition	Operational range
COMP	Compressor	-	200 – 300 atm
HEAT	Heater	-	500 – 1,000 $^\circ$C
SWREFORM	RGibbs Reactor	500 $^\circ$C	500 – 1,000 $^\circ$C
		240 atm	200 – 300 atm
TURBINE	Turbine	1.4 atm	-
COOLER1	Heater	200 $^\circ$C	-
WSHIFT	REquil Reactor	200 $^\circ$C	-
		1.4 atm	-
COOLER2	Heater	60 $^\circ$C	-
SEP	Flash Separator	60 $^\circ$C	0 – 60 $^\circ$C
		1.4 atm	1.4 – 50 atm

Figure 2: Process flow diagram of CO$_2$ absorption

Table 3: The operating condition of CO$_2$ absorption process

Code	Unit Model	Standard Condition
ABSORBER	Rad Frac Columns	stage = 3
		10 atm
FLASH	Flash Separator	0 $^\circ$C
		10 atm
STRIPPER	Stripper	stage = 6
		1.4 atm
COOLER1	Heater	101 - 25 $^\circ$C
SPLIT	SSplit	Split fraction 0.2
MIX-MEA	Mixer	-

from the minimisation of Gibbs free energy using RGibbs Model. The Soave-Redliche-Kwong Equation of State is used. The effects of supercritical water to glycerol ratio, reaction temperature, pressure and operating condition for separator in the reforming process were analyzed. In the absorption process, the electrolyte-NRTL was used to analyse the absorption process of MEA. The effects of MEA concentration, number of trays, pressure and the MEA feed rate on the performance of CO_2 absorption were analysed.

4. Model validation

To confirm the validation of the Aspen Plus model calculation, this work compared the simulation results with the experimental results of Adam et al. (2008). It was found that the simulation results of the hydrogen production from the supercritical reforming process and the experimental results on Ru/Al_2O_3 catalyst under the same operating conditions were in a good agreement.

5. Results and discussions

5.1 Hydrogen production
The simulation starts with calculation of the hydrogen production in the reformer. According to the standard operating conditions shown in the Table 2, the gaseous products from the reformer contain 12.48 % H_2O, 42.73 % H_2, 23.29 % CO_2, and 21.29 % CH_4 with glycerol conversion around 100 %. In order to improve the efficiency of the reforming reaction, the effects of key operating conditions were analysed in the following section.

5.1.1 Effect of temperature on the supercritical reforming reaction
Figure 3 reveals the effects of the temperature of heater and reformer on the mole fraction of gaseous products. It can be seen that high operating temperature provides more H_2 mole fraction. It increases from 42.73 mol% at 500 $^\circ$C until it reaches constant value of 65 mol% at temperature more than 800 $^\circ$C. This is because the glycerol reforming is endothermic, therefore; high temperature will shift the equilibrium to the H_2. However, the mole fraction of H_2 reaches constant value at temperature more than 800 $^\circ$C due to the fact that the reforming reaction is reversible and is controlled by the chemical equilibrium at this temperature. The simulation results also show that 1 mole of glycerol produces 6 mole of hydrogen which is close to the stoichiometric of reforming reaction (1 mole of glycerol to 7 mole of hydrogen). Nevertheless, mole fraction of CH_4 is reduced when temperature is raised because the reverse reaction of methanation reaction produces more hydrogen.

5.1.2 Effects of supercritical water to crude glycerol ratio
The effect of supercritical water to crude glycerol ratio (S/G ratio) was studied at temperature and pressure of 800 $^\circ$C and 240 atm, respectively. The results show that increasing in S/G ratio causes higher mole fraction of hydrogen while mole fraction of methane is lower (Figure 4). However, at S/G of 90, mole fraction of gaseous products becomes almost constant with 65 mol% H_2 and 0.1 mol% CH_4. The mole fraction of other products i.e., CO, CO_2, H_2O are insignificantly changed. The increasing of S/G ratio at constant glycerol feed rate is the increasing of supercritical water feed to the reformer. This shifts the reaction equilibrium of the reforming reaction to the product side while it also shifts the equilibrium of the methanation to the reactant side, therefore; more hydrogen products can be produced from reforming and reverse methanation reactions.

5.1.3 Effects of pressure on the supercritical reforming reaction
As discussed in the previous section, the suitable temperature for glycerol supercritical reforming reaction is 800 $^\circ$C. Consequently, this temperature is selected for studying the effect of pressure. The simulation results indicate that the change in pressure (pressure of compressor and reformer) has insignificant effect on the mole fraction of the gaseous products. Mole fraction of hydrogen is almost constant at 65 mol%.

5.1.4 Effect of gas-liquid separation operating conditions.
The suitable operating conditions of glycerol supercritical steam reforming at 800 $^\circ$C, 240 atm and S/G ratio = 90 can provide only 65 mol% H_2. To improve the efficiency of the process, the effects of gas-liquid separator operating conditions were analysed. Figure 5 indicates that increasing of operating pressure in gas-liquid separator causes better separation of water from gas mixture which results in lower in mole fraction of H_2O and higher mole fraction of H_2 and CO_2 in the gaseous products. This is because high operating pressure can condense more steam. As shown in Figure 6, the simulation results show that low temperature improves the water separation because more steam is condensed. From the simulation results, it can be found that the optimal operating conditions of separator are pressure of 20 atm and temperature of 20 $^\circ$C. Under these conditions, the gaseous product consists of 1 % H_2O, 74 % H_2 and 25 % CO_2. Although the highest purity of H_2 from the reforming and separation is 74 mol%, this is not suitable for using in both industry and laboratory.

Therefore, the CO_2 absorption process with MEA solution is implemented for production of higher purity hydrogen.
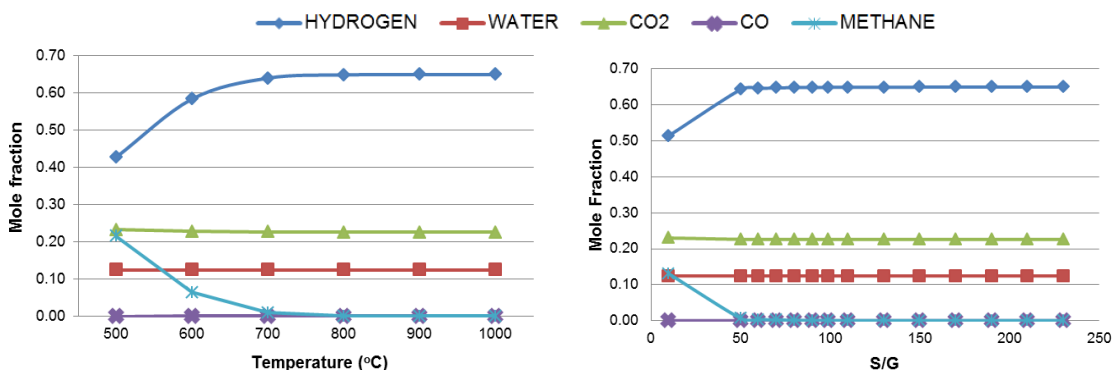

Figure 3: Effect of operating temperature on reformer

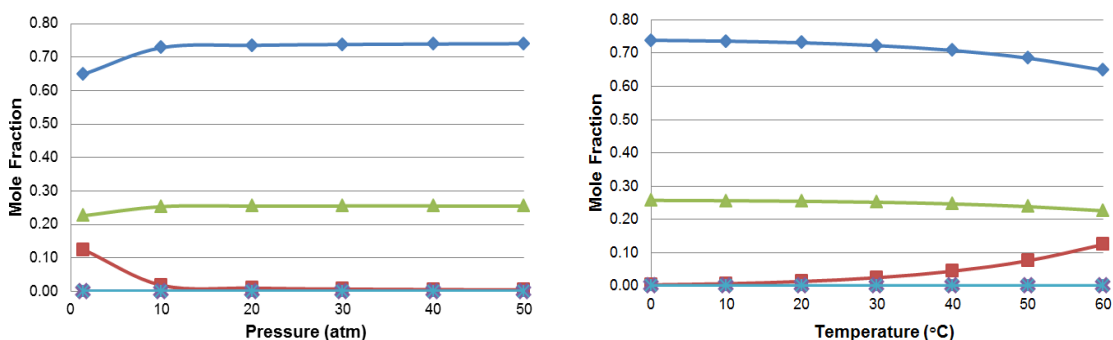*Figure 4: Effect of S/G ratio on reformer*

Figure 5: Effect of pressure on separation

Figure 6: Effect of temperature on separation

5.2 Integration of glycerol supercritical water reforming process with CO_2 absorption process

According to the previous study, the amount of CO_2 in the gaseous products is 24 mol%, this can be reduced by the CO_2 absorption process. The CO_2 absorption process considered in this work uses MEA solution as an absorption media. The key operating conditions were analysed as shown in the following section.

5.2.1 Effect of number of stage and operating pressure of absorber tower

From Figure 7, the simulation results suggest that at constant pressure, CO_2 in the gaseous products will be reduced as more stages are used. This is because better contact has been established when more stages have been used. However, the maximum absorption capacity is reached at 5 stages because the equilibrium of CO_2 and MEA is reached. An increase in pressure causes better absorption due to the fact that high pressure is a driving force that promotes the mass transfer between phases. This enables the better CO_2 dissolution into the MEA.

It can be concluded that 5 stages and 20 atm is the most suitable operating condition for absorption tower. Although, the pressure of 25 atm provides better capacity of absorption but the feed stream from process is in the pressure of 20 atm. If the condition of 25 atm is used, this will cause the additional work load to the process. The final product from the absorption process contains 99.1 mol% H_2 and 0.9 mol% CO_2.

5.2.2 Effect of MEA concentration

The concentration of MEA used in the study is varied in the range of 5-60 wt%. The absorption capacity increases with the MEA concentration because more solution is available for CO_2 absorption. As seen in Figure 8, at 50 wt% of MEA, the absorption capacity is 99.9 %. Therefore, CO_2 impurity is in the content of 50 ppm and the hydrogen concentration is 99.99 mol%. However, MEA is a corrosive material; high concentration would reduce the reactor life time. This work considers that 40 wt% of MEA which gives the absorption capacity of 98 % and 99.3 mol% of hydrogen product is the better option.

5.2.3 Effect of MEA feed rate

The simulation results indicate that the absorption capacity is increased with an increase in MEA feed rate. Higher feed flow rate enable the better mass transfer. At the MEA feed rate of 4,823 kg/h, CO_2 absorption capacity is 99.98 %. This provides 50 ppm of CO_2 or 99.99 mol% of hydrogen.
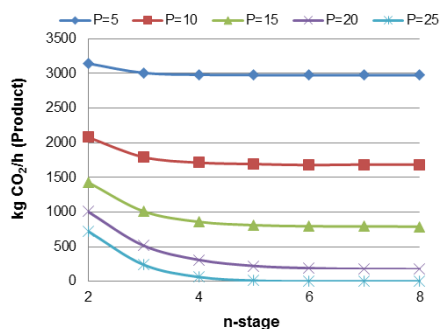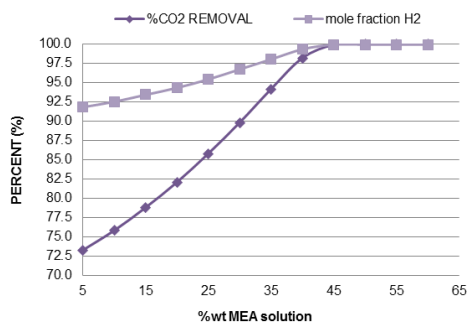
Figure 7: Effect of stage and pressure of absorber

Figure 8: Effect of MEA concentration

6. Conclusions

This work conducted a thermodynamic analysis of the glycerol supercritical steam reforming process with CO_2 absorption process. The Gibb free energy minimization method in the AspenPlus^{TM} was used for computing equilibrium composition. The simulation results at standard condition of the reformer (temperature = 800 °C, pressure = 240 atm and S/G ratio = 99) indicated that the gaseous product composition contain 64.84 % of hydrogen which is not suitable for use. Although the change in operating conditions such as increasing in temperature and S/G ratio can improve the content of hydrogen production, this process is thermodynamically limited by chemical equilibrium. Thus, the separation conditions were also investigated. It is found that increasing in pressure and reduction of the separator would improve the hydrogen concentration in the gaseous product up to 74 mol%. Further, the CO_2 absorption unit is integrated with reforming process to improve the hydrogen purity. The simulation results showed that the integrated process can produce the ready-to-use hydrogen with the concentration of 99 mol%. The optimal operating conditions of CO_2 absorption process are the absorber pressure = 20 atm, number of stages in absorber = 5, MEA content = 40 wt% and MEA solution flow rate = 4,823 kg/h.

References

Byrd A.J., Pant K.K., Gupta R.B., 2008, Hydrogen production from glycerol by reforming in supercritical water over Ru/Al$_2$O$_3$ catalyst, Fuel, 87, 2956-2960

Authayanun S., Arpornwichanop A., Patcharavorachot Y., Wiyaratn W., Assabumrungrat S., 2011, Hydrogen production from glycerol steam reforming for low- and high-temperature PEMFCs, International Journal of Hydrogen Energy, 36, 267-275.

Bennekom J.G.V., Venderbosch R.H., Assink D., Heeres H.J., 2011, Reforming of methanol and glycerol in supercritical water, Journal of Supercritical Fluids, 58, 99– 113.

Chavez R.H., Guadarrama J.J., 2011, Optimized process from post-combustion CO_2 capture in thermoelectric power plant using structured packing, Chemical Engineering Transactions, 25, 69-74.

Collodi G., 2010, Hydrogen production via steam reforming with CO_2 capture, Chemical Engineering Transactions, 19, 37.

Pairojpiriyakul T., Kiatkittipong W., Wiyaratn W., Soottitantawat A., Arpornwichanop A., Laosiripojana N., Croiset E., Assabumrungrat, S., 2010, Effect of mode of operation on hydrogen production from glycerol at thermal neutral conditions: Thermodynamic analysis, International Journal of Hydrogen Energy, 35, 10257-10270.

Mofarahi M., Khojasteh Y., Khaledi H. and Farahnak A., 2008, Design of CO_2 absorption plant for recovery of CO2 from flue gases of gas turbine, Energy, 33, 1311– 1319.

Moioli S., Pellegrini L.A., 2013, Regeneration Section of CO_2 Capture Plant by MEA Scrubbing with a Rate-Based Model, Chemical Engineering Transactions, 32, 1849-1854.

Ortiz F.J.G., Ollero P., Serrera A., Sanz A., 2011, Thermodynamic study of the supercritical water reforming of glycerol, International Journal of Hydrogen Energy, 36, 8994-19013.

Wang W., 2010, Thermodynamic analysis of glycerol partial oxidation for hydrogen production, Fuel Processing Technology 91, 1401–1408.

Wen G, Xu Y, Ma H, Xu Z, Tian Z., 2008, Production of hydrogen by aqueous phase reforming of glycerol, International Journal of Hydrogen Energy, 33, 6657-66.