The Thermodynamic Analysis of Hydrogen Production from Glycerol Steam Reforming

Hundessa Dessalegn Demsash[1] and Ratan Mohan[2]

[1]Research Scholar, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016
[2]Professor, Department of Chemical Engineering, Indian Institute of Technology Delhi Hauz Khas, New Delhi-110016
E-mail: [1]chz128006@iitd.ac.in, [2]ratan@iitd.ac.in

Abstract—*Biodiesel has been found to be a promising biofuel to the glaringly depleting fossil fuels. It also helps contain mounting environmental damages associated with utilization of fossil fuel. However, the increased production of biodiesel is resulted in a surfeit of crude glycerol as by-product in the market and its price has plummeted over the past few years. As the result, glycerol is currently in an oversupply crisis worldwide. Steam reforming for valorization of glycerol to produce clean fuels such as hydrogen has therefore given a due consideration to tackle this problem. Since steam reforming of glycerol for hydrogen production is accompanied with multiple side reactions, it is highly advisable to carry out thermodynamic analysis in order to identify narrow range of experimentation that favor high hydrogen yield by mitigating undesirable products. For the same, in the current work, with Aspen plus ^{TM} simulator using Gibbs free energy minimization techniques thermodynamic analysis was carried out. Though various thermodynamic analysis were reported, the equilibrium thermodynamic analysis of glycerol steam reforming with comprehensive possible by-products and/or products such as hydrogen, methane, carbon monoxide, carbon dioxide, acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic acid, water, coke and propanediol and unreacted glycerol were considered for first time. Sensitivity analyses were performed for temperatures range of 300°C to 1200°C, pressures 1 to 10 atm. and water to glycerol weight percent 10 to 90. At 650°C temperature, 1atm. pressure and 10 wt. % glycerol feed ratio, high hydrogen yield and low side products was observed.*

1. INTRODUCTION

The continued depletion of fossil fuel reserves and the threat of climate change caused by excessive emissions of anthropogenic greenhouse gases such as carbon dioxide have become vital issues for mankind [1-2]. Consequently, in the past several years the search for alternative renewable energy sources which can decrease the global reliance on fossil fuels has been intensified.

Biodiesel as the biodegradable, non-toxic, near CO_2-neutral and environmentally beneficial fuel has become more attractive recently as alternative diesel fuel to reduce dependency on fossil fuel imports. However, a side problem of making biodiesel is utilization of the large amounts of glycerol produced as a by-product [2-5]. About 10wt. % of glycerol is produced during the production of biodiesel fuel through the catalytic transesterification process [2]. Selembo and coworkers reported that 980 million liters of glycerol per year are produced compared to a demand of only 216 million liters[3].Glycerol production is expected to grow dramatically.Approximately3 megatons of crude glycerol is projected to be generated by the year 2020. The amount of glycerol used in commercial applications each year is less than 500 kilotons [4]. The biodiesel industries are managing the glut of glycerol as a waste because of its impurities and they are also suffering from the impact of the increasing storage and management costs. The accumulation of crude glycerol not only hampers the development of the biodiesel industry, but it also creates economic and environmental problems [3]. To address this glycerol crisis, handful of studies have been attempted reforming of glycerol to valorize high amounts of glycerol to useful products such as hydrogen [2-23]. Hydrogen is an ideal fuel which has the highest combustion energy release per unit weight than any other fuels. Not only this property but also its low weight makes it the fuel of choice for the upper stages of multi-stage rockets. Moreover, its combustion is clean and produces only water.

Currently, almost 95% of the hydrogen is being produced from nonrenewable feedstocks [2]. Not only hydrogen is an essential fuel, it also plays an important role in the conversion of chemical industry towards the increasing use of renewable resources and an essential chemical for important industrial processes such as hydrodesulphurization, the current industrial hydrogen production is essentially based on fossil fuels reforming, its production from cheap and renewable raw materials such as glycerol is a prudent choice. As the result, hydrogen production via glycerol reforming is becoming crucial and significant research topics. Hydrogen can be produced from glycerol through steam reforming, partial oxidation, dry reforming, aqueous reforming and autothermal reforming. Owning to higher hydrogen yield, low side reactions, simplicity, easy control and cost effectiveness for production of hydrogen steam reforming process is favored over the other reforming techniques [2-3] and [5].

Interest in glycerol steam reforming is rising adjudicating from the amassed number of review articles and recent investigations [2-23]. Even though it is well-known that steam reforming of glycerol is strongly endothermic, and ideally, it must be carried out at high temperatures, low pressure, and high steam to glycerin ratio to achieve higher conversion, what sets of parameters favor maximum yield must be known with thermodynamic analysis [2-5]. Thermodynamic analysis forms an essential part of reaction engineering while catalysts play a role in facilitating or suppressing product formation rates. From the thermodynamic analysis, appropriate strategies can be formulated to maximize desired products through the optimization of the reaction conditions, such as reactant ratio, pressure and temperature. The selection of appropriate reaction conditions is then very important. In current work, for this purpose, an equilibrium thermodynamic analysis of glycerol steam reforming with comprehensive possible side products was done with Aspen plus ^{TM} simulator for the first time. The effects of operation parameters such as temperature, pressure, water-to-glycerol feed ratio on hydrogen production and product composition were evaluated. As possible products and byproducts hydrogen, methane, carbon monoxide, carbon dioxide, acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic acid, water, coke, propanediol and unreacted glycerol were considered in our thermodynamic simulation.

2. METHODOLOGY

Thermodynamic equilibrium product composition of steam reforming of glycerol for different parameters sensitivity were calculated based on the minimization of the Gibbs free energy technique. Commercial Aspen Plus software along with its physical property models was used for calculations. The procedure available in the subroutine of RGIBBS was used to determine the thermodynamic equilibrium composition of each phase present. The Soave–Redlich–Kwong model was selected as the equation of state to correct the ideal Gibbs energy value. Equations (1)-(3) were used for conversion, selectivity(S_{H2}) and yield (Y_{H2}) calculations respectively [2], [7] and [22].

$$\text{Conversion}\ (\%) = \frac{\text{glycerol fed} - \text{glycerol out}}{\text{Glycerol fed}} \times 100 \qquad (1)$$

$$S_{H2}(\%) = \frac{\text{Hydrogen produced}}{\text{Carbon atoms in products}} \times \frac{1}{\text{RR}} \times 100 \qquad (2)$$

RR is the reforming ratio (7/3), defined as the ratio of moles of H_2 to CO_2 formed.

$$Y_{H2}(\%) = \frac{\text{Hydrogen produced}}{7(\text{Glycerol mole feed})} \times 100 \qquad (3)$$

Table 1: Plausible competing side reactions

Plausible Reactions	Nos.
$C_3H_8O_3(g)+3H_20\ (g) \rightarrow 7\ H_2\ (g) + 3CO_2(g)$	(1)
$C_3H_8O_3(g) \leftrightarrow C_3H_6O_3(g) + H_2(g)$	(2)
$C_3H_8O_3(g) \leftrightarrow C_3H_6O_2(g) + H_2O(g)$	(3)
$C_3H_6O_3(g) \leftrightarrow C_3H_4O_2(g) + H_2O(g)$	(4)
$C_3H_6O_2(g) \leftrightarrow C_3H_4O(g) + H_2O(g)$	(5)
$C_3H_8O_3(g) \leftrightarrow 3CO(g) + 4H_2(g)$	(6)
$C_3H_8O_3(g) \leftrightarrow C_2H_4(g) + CO(g) + 2H_2O(g)$	(7)
$C_3H_4O_2(g) \leftrightarrow C_2H_4O(g) + CO(g)$	(8)
$C_2H_4O(g) \leftrightarrow CH_4(g) + CO(g)$	(9)
$CO(g)+3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$	(10)
$CH_4(g) + 2H_2O(g) \leftrightarrow CO_2(g)+4H_2(g$	(11)
$C_2H_4\ (g)+ H_2(g) \leftrightarrow C_2H_6(g)$	(12)
$CO(g)+H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$	(13)
$C_2H_4\ (g) \leftrightarrow 2C(s) + 2H_2(g)$	(15)
$CH_4\ (g) \leftrightarrow C(s) + 2H_2(g)$	(16)
$2CO\ (g) \leftrightarrow C(s) + CO_2(g)$	(17)
$CO\ (g)+ H2(g) \leftrightarrow C(s) + H_2O(g)$	(18)
$CO_2\ (g)+ 2H_2(g) \leftrightarrow C(s) + 2H_2O(g)$	(19)

Plausible reactions during steam reforming of glycerol were shown in table 1. Reaction No. (1) represents overall glycerol steam reforming while reaction Nos. (2)-(19) are plausible side reactions. So far literature considered hydrogen, methane, carbon monoxide, carbon dioxide, acrolein, ethane, ethylene, coke, water and unreacted glycerol as product and/or byproducts [2], [5], [7], [22] and [23]. Apart with these species, for the first time we have considered ethylene oxide, propanoic acid, acrylic acid, methoxyacetic acid, and propanediol in current analysis. The thermodynamic analysis was performed for temperatures range of 300°C to 1200°C, pressures between 1 and 10 atm. and water to glycerol weight percent between 10 and 90. It has to be noted that all analysis were done on dry basis.

3. RESULTS AND DISCUSSION

The amount of unconverted glycerol observed in product streams in all sensitivity analysis was almost nil. This implies that there was complete conversion of glycerol over range of temperatures, pressures and water to glycerol ratio analyzed. This results is in agreement to what had been reported [6], [7]. Hence, steam reforming of glycerol is not limited by thermodynamics. Hence, in the subsequent analysis Eq. (1) was taken into account as it was completely shifted towards reaction products.

4. EFFECT OF TEMPERATURE

The effect of temperature variation on product composition, yield and selectivity are shown in Figs. 1 and 2. During this temperature sensitivity analysis other reforming parameters were held constant.(10 wt. % glycerol feed ratio and 1 atm. pressure) As can be seen from Fig.1 the amount of hydrogen produced appreciably increased along with increment of temperature from 300°C to 650°C in the product stream. Upon further increment of temperature from 650°C to 1200 °C hydrogen concentration in the product stream has shown negligible variation with tendency of reduction 650°C onwards. In the same manner the hydrogen yield and selectivity had shown significant raise with increment of temperature. This is primarily attributed to thermal decomposition of glycerol, steam reforming of methane and water gas shift reaction. (reaction Nos. (6), (11) and (13)). In fact, dehydrogenation of glycerol also contributed in generation of some amount of hydrogen. The negligible change in concentration of hydrogen observed above 650°C might be the result of the reticence of the exothermic water gas shift reaction. On the other hand, the concentration of methane in product stream was found to be decreasing with increasing temperature. Substantial reduction in methane concentration was observed in temperature range of 300°C to 650°C. Upon further increment of temperature this reduction in methane concentration drops to zero. This implies that the steam reforming of methane has occurred considerably between 300°C to 650°C. Meanwhile, the concentration of carbon dioxide in the outlet gas mixture gradually decreased with increasing temperature. This might be an implication of reversed water gas shift reaction (No. (13)) and carbon dioxide methanation (No. (11)). On the other hand, the concentrations of carbon monoxide was showing an increasing trend along with the temperature rise. In the whole range of temperatures analyzed, it was observed to be increasing with the increase of temperature. This indicates that the conversion of carbon dioxide and methane through reversed water gas shift reaction.

Minor byproducts such as acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic acid, coke, propanediol and unreacted glycerol were observed in less than order of magnitude of parts per million. Therefore for convenience it was totaled and plotted in Fig.1. The formation of this byproducts was found to be negligible. However, their effects will be analyzed separately in section 3.4 The hydrogen selectivity is found to be in a range of 13.4 to 66.6%.The highest selectivity yield was obtained at temperature of 650°C which is 85.4% .

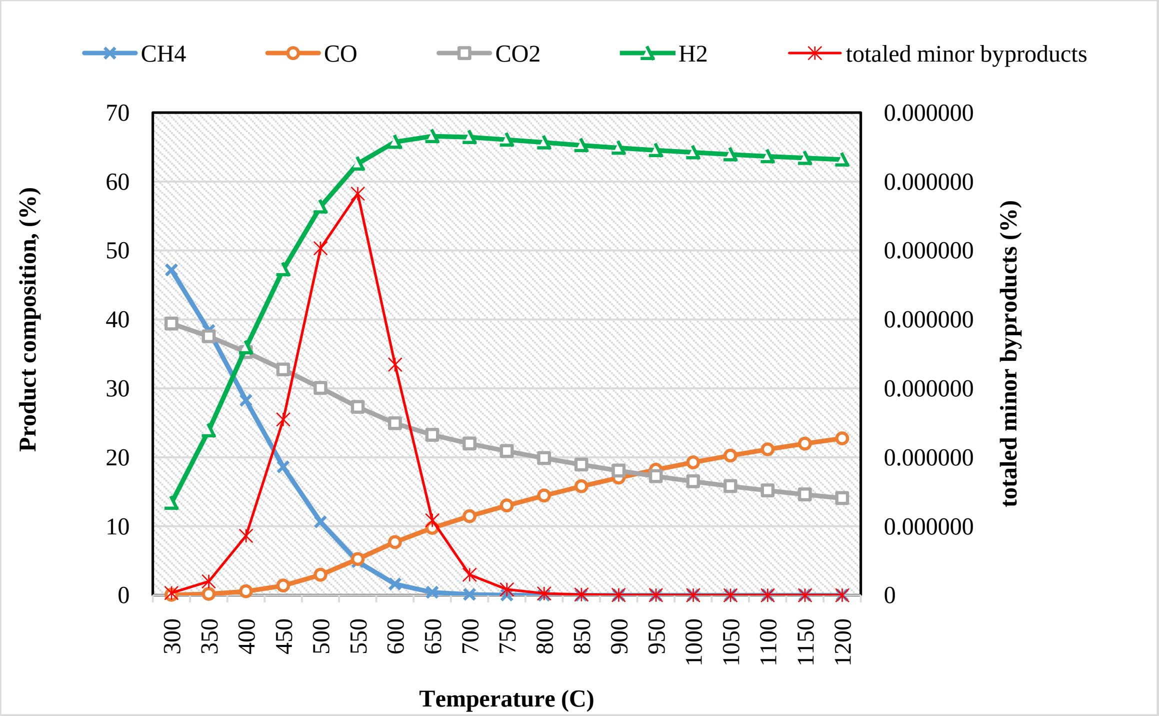

Fig. 1: Effect of temperature on product distribution

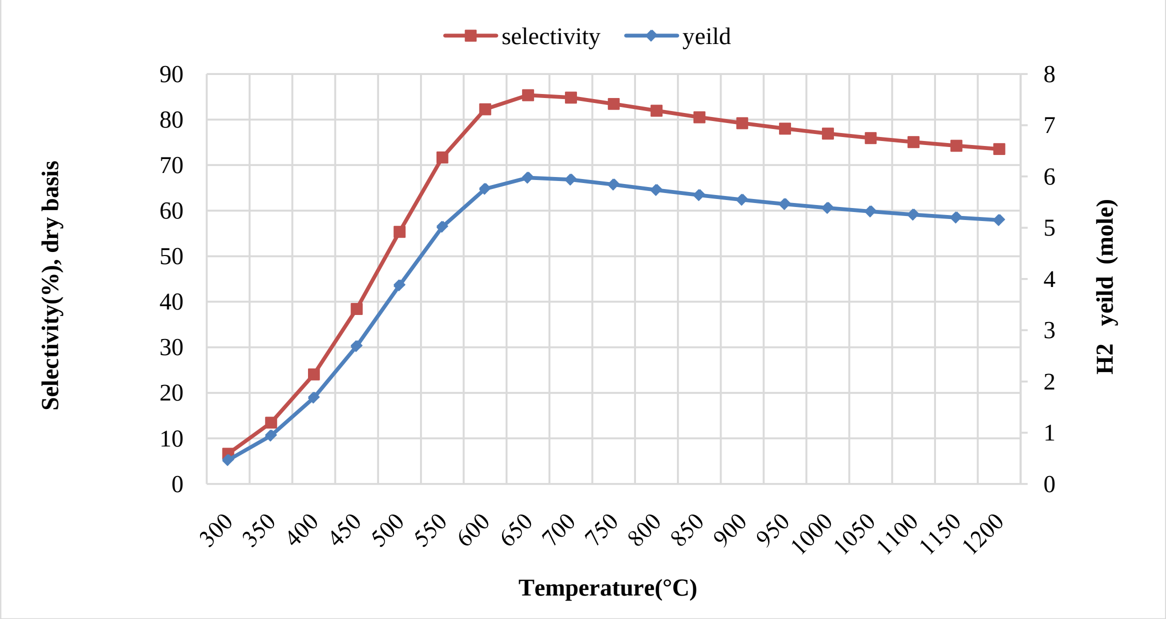

Fig. 2: Temperature effect on yield and selectivity

5. EFFECT OF GLYCEROL FEED RATIO

To see the effect of water to glycerol feed ratio on product composition, yield and selectivity, feed ratio has been varied from glycerol 10%wt. to 90wt%. The results are shown in Figs. 3 and 4. Lower glycerol weight percent than 10 were not considered because this would imply, in practice, too much costs for water vaporization. At low concentration of glycerol in the feed (higher water to glycerol ratio), the amount of hydrogen produced was found to be high. In the range of glycerol feed percent from 10 to 30wt%, products mole percent of hydrogen produced was almost constant. As shown in Fig. 4, the highest hydrogen yield was found at 10wt% glycerol which is 96.9%. Upon further increment of glycerol feed weight percent, the concentration of hydrogen in the product stream was found to be appreciably reducing. Moreover, the selectivity and yield of hydrogen were decreasing whereas, the concentrations of carbon monoxide and methane were increasing. This indicates that lower water to glycerol ratios favor the reverse water–gas-shift reaction and methanation. On the other hand the concentration of carbon dioxide in the product stream was found to be decreasing with increasing glycerol feed percent. Totaled minor byproducts namely acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic acid and coke was found to be increasing in a general trend. This suggests that higher glycerol feed concentration favors coke formation and other byproducts. The hydrogen concentration in the product stream was found to be highest at 10 percent by weight glycerol concentration feed with selectivity of 96.9% on a dry basis at 650°Cand 1 atm.

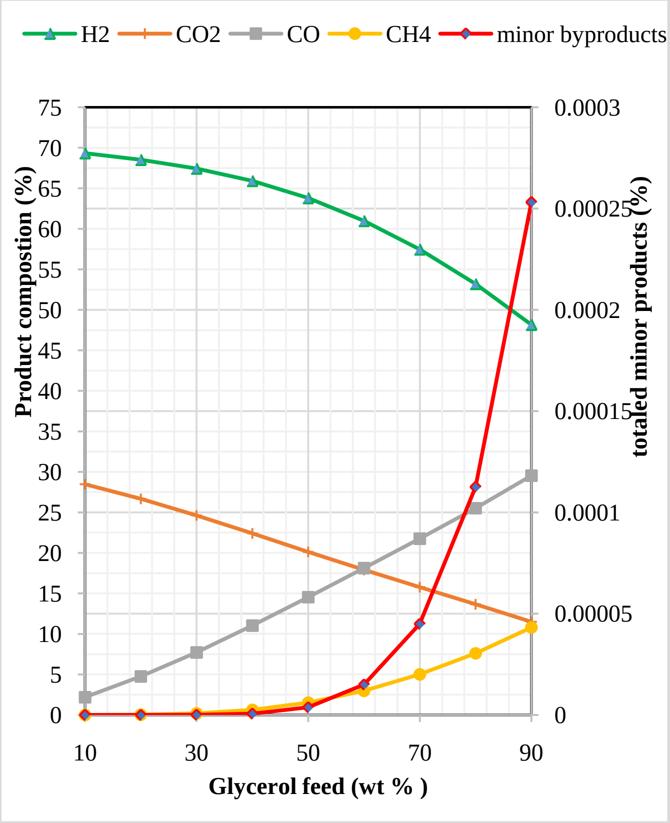

Fig. 3: Feed ratio effect on product distribution

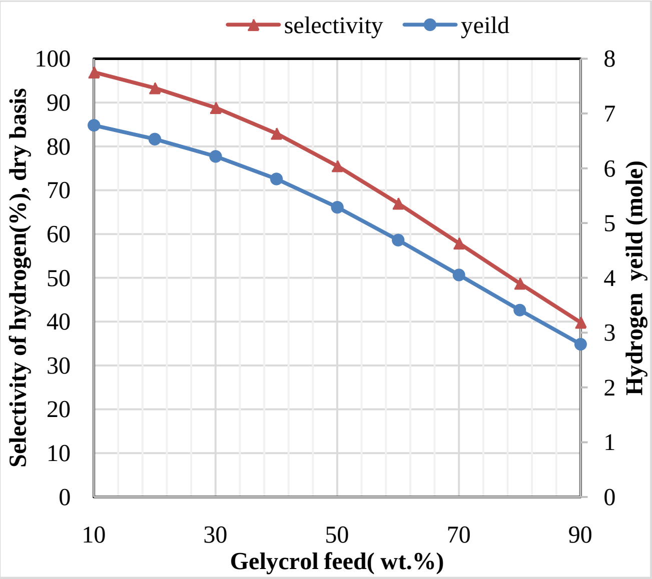

Fig. 4: Feed ratio vs yield and selectivity

6. EFFECT OF PRESSURE

Since pressure significantly affects the thermodynamic equilibrium of steam reforming, the consequence of pressure variation was also examined at 10wt% glycerol feed and 650°C. As can be observed from Fig. 5 and 6, the higher pressures the lower the yield and selectivity of hydrogen. According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change.

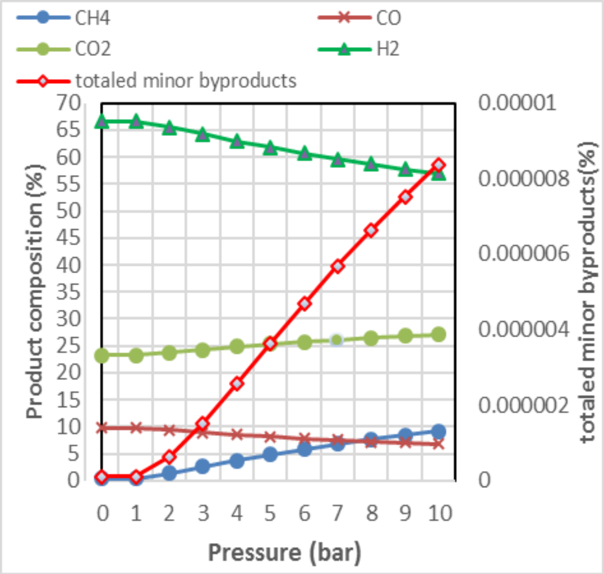

Fig. 5: Effect of pressure on product distribution

That means when higher pressures are applied, the thermodynamic equilibrium will be shifted towards the production of a lower total number of moles. However, once the glycerol conversion was complete for all the range of pressures used, the decrease of the hydrogen yield cannot be associated to reforming reaction. Instead, it is associated to the enhancement of the methanation reaction (No. (10)), which consumes hydrogen and favors methanation reaction. Upon increase of pressure over a range of 1atm to 10atm. the concentrations of hydrogen and carbon monoxide were observed to be decreasing, while the methane and carbon dioxide concentrations was increasing with the increase. This was so because the increase of pressure facilitates methanation.

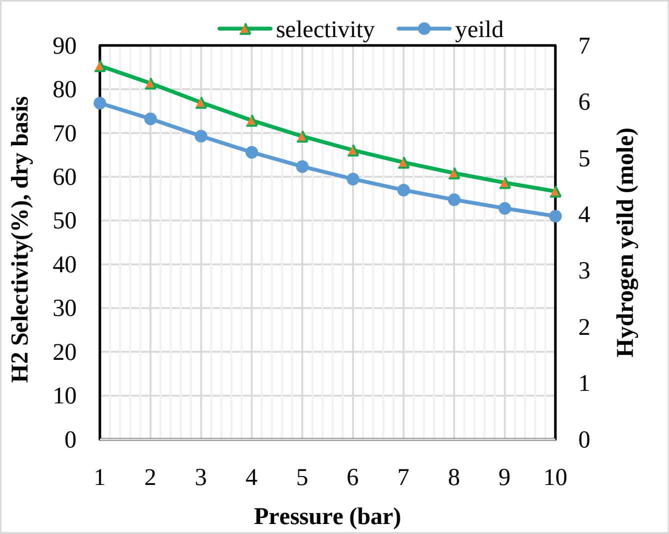

Fig. 6: Effect of pressure on yield and selectivity

7. COKING AND FORMATION OF MINOR PRODUCTS

Since glycerol steam reforming is a catalytic process, the formation of coke affects the performance of the catalyst during actual operation. Coke formation during the catalytic steam reforming could lead to deactivation of catalysts, resulting in low operation durability and activity loss. It is interesting to regulate the reaction settings that eliminates coke and other side products. Besides to formation of coke, acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic were also undesirable as they lower yield of the process.Even though they are at ppm level in this thermodynamic analysis they might be produced significantly during actual process. When there is insufficient steam supply, there is formation of solid carbon, due to methane decomposition. The concentrations of acrolein, ethane, ethylene, ethylene oxide, propanoic acid, acrylic acid, methoxyacetic thermodynamically approach zero in in temperature range of 600°C-1200°C, pressure 1atm-2atm and glycerol percent feed from 10%-50%. This result is in agreement with our previous work “to be published” [1]. Consequently, it may be concluded that coke forming reactions (Nos. (15)- (19)) were suppressed in temperature of

600°C to 1200°C, pressure 1atm to 2atm. and glycerol percent feed from 10% to 50%.

8. CONCLUSION

The thermodynamic analysis of glycerol steam reforming was studied with the Aspen plus^{TM} software over wide range of parameters such as pressure, temperature and water to glycerol feed ratios. Sensitivity analyses of these parameters were done to know what narrow range of parameters favor maximum hydrogen yield and eliminates coke and other side products. At 700°C temperature, 10wt% glycerol feed ratio and 1 atm. pressure maximum hydrogen yield and minimum disastrous side product such as coke were obtained for this particular study. With the basis of this thermodynamic analysis, it is suggested that the development of new catalyst is highly desired for the glycerol reforming to overcome the kinetic limitation and regulate disastrous side product such as coke for actual catalytic operation.

REFERENCES

[1] H. Dessalegn, C. Accharya and R. Mohan “Hydrogen Production from glycerol steam reforming—Accepted for oral presentation,” CHEMCON-2014, 67th Annual Session of Indian Institute of Chemical Engineers, Chandigarh, INDIA.

[2] S. Adhikari, S. Fernando and A. Haryanto, “Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts,” Catalysis Today, vol. 129, no.3, pp. 355-364, 2007

[3] P. A. Selembo, J. M. Perez, W. A. Lloyd, and B. E. Logan,“High hydrogen production from glycerol or glucose by electrohydrogenesis using microbial electrolysis cells,” Int. J. of Hydrogen Energy, vol. 34no 13, pp. 5373-5381, 2009.

[4] K. H. Lin, W. H. Lin, C. H. Hsiao, H. F. Chang, and A. C. C. Chang, “Hydrogen production in steam reforming of glycerol by conventional and membrane reactors,” Int. J. of Hydrogen Energy, vol. 37 no. 18 pp. 13770-13776, 2012

[5] E. A. Sanchez, and R. A. Comelli, “Hydrogen by glycerol steam reforming on a nickel–alumina catalyst: Deactivation processes and regeneration,” Int. J. of Hydrogen Energy, vol. 37 no.19, pp. 14740-14746, 2012.

[6] B. .Zhang, X. Tang, Y. Li, Y. Xu, and W. Shen, “Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts,” Int. J. of Hydrogen Energy, vol. 32, no. 13, pp. 2367-2373, 2007

[7] C. D. Dave and K. K. Pant, “Renewable hydrogen generation by steam reforming of glycerol over zirconia promoted ceria supported catalyst,” Renewable Energy, vol. 36, no.11, pp. 3195-3202, 2011.

[8] M. Araque, T. L. M. Martínez., J. C. Vargas and A. C. Roger, “Hydrogen production by glycerol steam reforming over CeZrCo fluorite type oxides,” Catalysis Today, vol. 176, no. 1, pp. 352-356, 2011.

[9] C. K. Cheng, S. Y. Foo and A. A. Adesina, “Steam reforming of glycerol over Ni/Al2O3 catalyst,” Catalysis Today, vol. 178, no. 1, pp 25-33, 2011

[10] R. M. Dell and D. A. Rand, “Energy storage—a key technology for global energy sustainability,” J. of Power Sources, vol. 100 no. 1, pp. 2-17, 2001.

[11] M. El Doukkali, A. Iriondo, P. L. Arias, J. F. Cambra, I. Gandarias, and V. L. Barrio, “Bioethanol/glycerol mixture steam reforming over Pt and Pt-Ni supported on lanthana or ceria doped alumina catalysts,” Int. J. of Hydrogen Energy, vol. 37, no. 10, pp. 8298-8309, 2012.

[12] M. Hook, and X. Tang, “Depletion of fossil fuels and anthropogenic climate change—a review,” Energy Policy, vol. 52, pp. 797-809, 2013.

[13] A. Iriondo, V. L. Barrio, J. F. Cambra, P. L. Arias, M. B. Guemez, M. C. Sanchez-Sanchez, and J. L. G. Fierro, “Glycerol steam reforming over Ni catalysts supported on ceria and ceria-promoted alumina,” Int. J. of Hydrogen Energy, vol. 35 no. 20, pp. 11622-11633, 2010

[14] K. Kamonsuangkasem, S. Therdthianwong, and A. Therdthianwong, “Hydrogen production from yellow glycerol via catalytic oxidative steam reforming,” Fuel Processing Technology, Vol. 106, pp. 695-703, 2013

[15] Y. C. Lin,“Catalytic valorization of glycerol to hydrogen and syngas” .Int. J. of Hydrogen Energy, vol. 38 no. 6, pp. 2678-2700, 2013.

[16] D. Y Leung, X. Wu, and M. K. H Leung, “A review on biodiesel production using catalyzed transesterification,”Applied Energy, vol. 87 no.4, pp. 1083-1095. 2010.

[17] N. Luo, X. Fu, F. Cao, T. Xiao and P. P. Edwards, (2008). “Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst–effect of catalyst composition and reaction conditions,” Fuel, vol. 87 no. 17, pp. 3483-3489, 2008.

[18] A. Midilli, & I. Dincer, “Hydrogen as a renewable and sustainable solution in reducing global fossil fuel consumption. Int. J. of Hydrogen Energy, vol. 33, no. 16, pp. 4209-4222, 2008.

[19] P. Mohanty, M. Patel, and K. K. Pant, “Hydrogen production from steam reforming of acetic acid over Cu–Zn supported calcium aluminate.” Bioresource Technology, vol. 123, pp. 558-56, 2012.

[20] J. A. Posada, C. E. Orrego, and C. A. Cardona, (2009). “Biodiesel Production: Biotechnological Approach.” Int. Review of Chemical Engineering-Rapid Communications vol. 1, pp., 6, 2009.

[21] S. Shao, A. W. Shi, C. L. Liu, R. Z..Yang, and W. S. Dong. “Hydrogen production from steam reforming of glycerol over Ni/CeZrO catalyst,” Fuel Processing Technology, vol. 125, pp. 1-7, 2014.

[22] P. D.Vaidya, and A. E. Rodrigues, “Glycerol reforming for hydrogen production: a review” Chemical Engineering & Technology, vol. 32, no. 10, pp. 1463-1469, 2009.

[23] X. Wang, N. Wang, M. Li, S. Li, S. Wang and X. Ma, “Hydrogen production by glycerol steam reforming with in situ hydrogen separation: A thermodynamic investigation” Int .J. of Hydrogen Energy, vol. 35 no. 19, pp. 10252-10256, 2010.