

Experimental Investigation of Steam Reforming of Glycerol over Alumina Supported Nickel Catalysts

Narasimha Reddy Ravuru

Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad, Gujarat, 382481, India

Abstract:- The growing demand of hydrogen needs renewable sources of raw materials to produce it. Glycerol, by-product of biodiesel synthesis, could be a bio-renewable substrate to obtain hydrogen. Momentous amount of glycerol is produced as a by-product during bio-diesel production by the transesterification of vegetable oils, which are available at low cost in large supply from renewable raw materials. As hydrogen is a clean energy carrier, conversion of glycerol to hydrogen is one among the most attractive ways to make use of glycerol. Production of hydrogen from glycerol is environmentally friendly because it adds value to glycerol generated from biodiesel plants. In this study, the catalytic production of hydrogen by steam reforming of glycerol has been experimentally performed in a fixed-bed reactor. The performance of this process was evaluated over 5wt%, 10wt%, and 15wt% Ni/Al₂O₃. The catalysts were prepared by the wet impregnation technique. For a comparative purpose, the steam reforming experiments were conducted under same operating conditions, i.e., reaction temperature ranging from 700°C to 900°C, atmospheric pressure and 1:9 glycerol to water molar ratio. Also the effect of glycerol to water ratio, metal loading, and the feed flow rate (space velocity) was analysed. The results showed that the hydrogen production increased with the increase in the treatment temperature. The highest amount of hydrogen produced was attained over 15wt% Ni/Al₂O₃ at 850 °C at 1:9 glycerol to water molar ratio. The catalyst Co/Al₂O₃, Cu/Al₂O₃ were prepared by wet impregnation technique and need to do activity test and compare the results with Ni/Al₂O₃.

Keywords: Biodiesel, Hydrogen, Glycerol, Steam reforming, Ni/Al₂O₃, Wet impregnation

I. INTRODUCTION

There is an increasing energy demand, because of limitation of fossil oil reserves and pollution. In search of alternative energies, many scientists, due to low price, less pollution, pay more attention on the renewable energy sources [1, 2]. Fuel cell technology is an attractive alternative lately, for transportation and producing electricity. The growth in fuel cell technology has improved the demand for hydrogen (H₂), which is the simplest and most abundant element [3]. Hydrogen production process and technology, has been improving and changing. However, hydrogen is mostly produced from natural gas and oil fractions, which are still abundant and economically feasible. Nevertheless, hydrogen production by these methods, produce high amount of carbon monoxide [1]. Glycerol, which is the by-product of biodiesel production, is non-toxic, non-volatile and has high energy density. Theoretically, after the transesterification process, 10

kg biodiesel and as by-product, 1 kg glycerol can be produced [4]. Increasing energy demand will cause the need for clean energy technologies, like biodiesel, and this will effect glycerol production. Using glycerol for hydrogen production, more effective and clean energy can be produced.

The overall reaction of glycerol steam reforming reaction is showed in equation below:

$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$ (1) Steam reforming of glycerol includes a lot of complex reaction series. For that reason, operation conditions like temperature, pressure, feed ratio and catalysts effect are very important to produce desirable product [1]. In researches for glycerol steam reforming, various catalysts are investigated and especially, noble-metal based catalysts and nickel based catalysts' activities are studied [4]. Noble-metal catalysts activities are well known, on the other hand, more researches are focused on nickel based catalysts which have a relatively low cost and high selectivity. In this study, we have investigated the performance of Ni based catalysts on Al₂O₃ with different metal loading metal loading (5, 10, and 15%) and catalyst preparation method parameters have been investigated. Catalyst performance was analysed at four different temperatures between 700, 800, 850, and 900°C. The conversion of glycerol and the selectivity of hydrogen in the steam reforming conditions were investigated.

$$\%H_2\text{selectivity} = \frac{H_2 \text{ moles produced}}{C \text{ atoms produced in gas phase}} \times \frac{1}{RR} \times 100$$

Where RR is H₂/CO₂ reforming ratio is 7/3 in the case of glycerin steam reforming process

$$\%H_2\text{selectivity of } i = \frac{C \text{ atoms in species } i}{C \text{ atoms produced in gas phase}} \times 100$$

Where species i = CO, CO₂, and CH₄.

$$\%Conversion = \frac{C \text{ atoms in gas products}}{Total C \text{ atoms in feedstocks}} \times 100$$

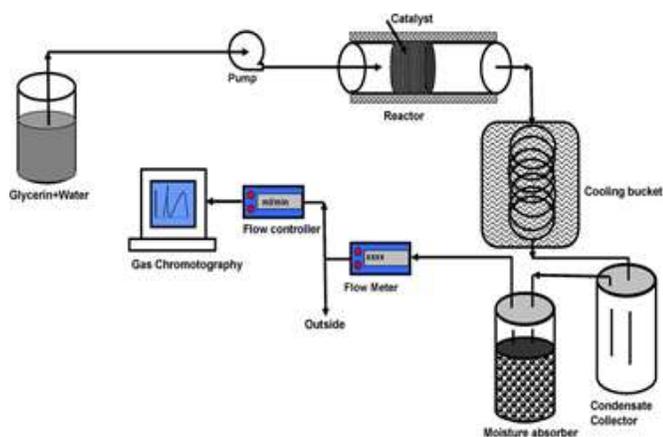


Fig.1. Schematic of glycerin steam reforming setup

II. RESULTS AND DISCUSSION

2.1 Effect of Temperatures on Conversion

The effect of temperature on glycerol conversion and hydrogen yield was studied using 5, 10 and 15 wt% Ni/Al₂O₃ for water to glycerol ratio 9:1 at a feed rate of 1ml/min. The temperature was varied from 700-900 °C. The glycerol conversion increased from 46.19% to 68% as the temperature was increased from up to 900°C. Thermodynamic data clearly shows that the product gas yield increases with temperature.

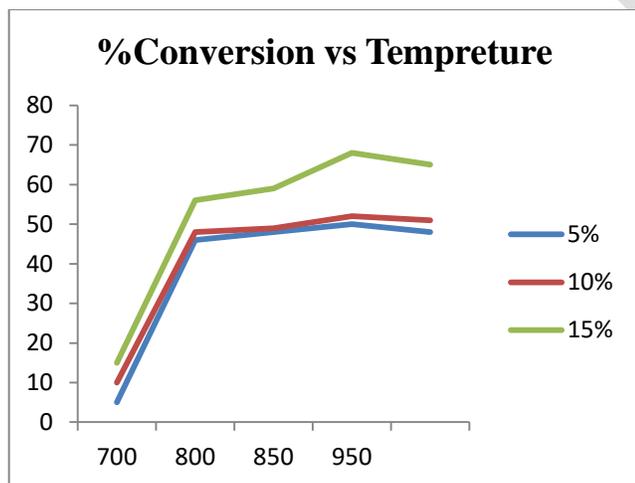


Fig 2 shows the effect of temperature on hydrogen yield.

2.2 Effect of metal loading

Catalysts with three different metal loadings (5, 10, and 15 wt %) were prepared for Ni/Al₂O₃ to see the effect of the metal percentage on selectivity of H₂ and other gases, and glycerin conversion. With the increase in metal loading the glycerine conversion increased. At 5 wt%, the glycerine conversion was 46.19% and increased to 68% with the metal loading of 15 wt%. Although glycerin conversion increased with the metal loading, H₂ selectivity as well as the selectivity of CO, CH₄,

and CO₂ was found to be almost stable at different metal loadings investigated under this study.

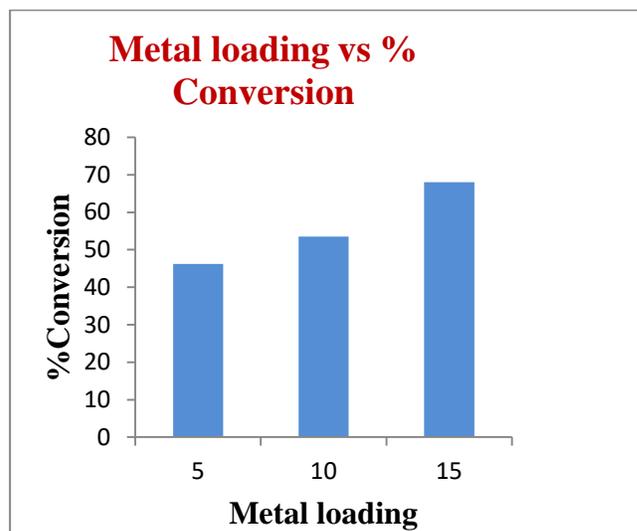


Fig.3 shows the effect of the metal loading in terms of glycerin conversion

2.3 Effect of water to glycerin ratio

With increase in WGRs, the glycerin conversion increased monotonously in case of Ni/Al₂O₃. Although glycerin conversion increased with increase in WGR from 6:1 to 9:1. Glycerin conversion was almost 68% at WGR 9:1 with Ni/ Al₂O₃. With the increase in WGR, the H₂ selectivity increased. H₂ selectivity of about 71.5% (5 moles of H₂) was obtained with Ni/Al₂O₃. At the same time, with the increase in WGR from 6:1 to 9:1, the production of CH₄ was completely inhibited in the case of Ni/Al₂O₃ at 900°C and FFR 1ml/min. Similarly, with the increase in WGR, the selectivity towards H₂ and CO₂ were increased. The increase in H₂ and CO₂ selectivity could be attributed to the water gas shift reaction.

III. CONCLUSION

The study on glycerin steam reforming for hydrogen production over 5%, 10%, 15% Ni/ Al₂O₃ supported catalysts was performed. Under the reaction conditions investigated, 15% Ni/Al₂O₃ were found to be the best performing catalysts in terms of H₂ selectivity and glycerin conversion. Effects of the glycerin to water molar ratio, feed flow rate, and metal loading were also Investigated. It was found that with the increase in the WGR, H₂ selectivity and glycerin conversion increased. About 72% of H₂ selectivity was obtained with 15% Ni/Al₂O₃, WGR 9:1 at 850°C and feed flow rate 1ml/min.

REFERENCES

- [1]. S. Adhikari, S. Fernando, S.R. Gwaltney, S.D. Filip To, R.M. Bricka, P.H. Steele, A. Haryanto, Int. J. Hydrogen Energy 32 (2007) 2875–2880.
- [2]. X. Wang, S. Li, H. Wang, B. Liu, X. Ma, Energy Fuels 22 (2008) 4285–4291.

- [3]. A. Iriondo, V.L. Bario, J.F. Cambra, P.L. Arias, M.B. Guemez, R.M. Navarro, M.C. Sanchez-Sanchez, J.L.G. Fierro, *Top. Catal.* 49 (2009) 46–58.
- [4]. S. Adhikari, S. Fernando, A. Haryanto, *Catal. Today*. 129 (2007) 355–364.
- [5]. I.N. Buffoni, F. Pompeo, G.F. Santori, N.N. Nichio, *Catal. Commun.* 10 (2009) 1656–1660.
- [6]. N. Luo, X. Fu, F. Chao, T. Xiao, P.P. Edwards, *Fuel* 87 (2008) 3483–3489.
- [7]. T. Hirai, N. Ikenaga, T. Miyake, T. Suzuki, *Energy Fuels* 19 (2005) 1761 – 1762.
- [8]. F. Frusteri, S. Freni, L. Spadaro, V. Chiodo, G. Bonura, S. Donato, S. Cavallaro, *Catal. Commun.* 5 (2004) 611–615.
- [9]. N. Palmeri, V. Chiodo, S. Freni, F. Frusteri, J.C.J. Bart, S. Cavallaro, *Int. J. Hydrogen Energy* 33 (22) (2008) 6627–6634.
- [10]. S. Adhikari, S. Fernando, A. Haryanto, *Catal. Today* 129 (2007) 355–364.
- [11]. S. Cavallaro, V. Chiodo, S. Freni, N. Mondello, F. Frusteri, *Appl. Catal. A* 249(2003) 119–128.
- [12]. W. Buhler, E. Dinjus, H.J. Ederer, A. Kruse, C. Mas, *Supercrit. Fluid* 22 (2002) 37–53.
- [13]. S. Adhikari, S. Fernando, A. Haryanto, *Renew. Energy* 33 (2008) 1097.
- [14]. R.D. Cortright, R.R. Davda, J.A. Dumesic, *Nature* 418 (2002) 964.
- [15]. J.R.H. Ross, M.C.F. Steel, A. Zeini-Isfahani, *J. Catal.* 52 (1978) 280.
- [16]. R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic, *Appl. Catal. B* 43 (2003) 13–26.
- [17]. J.W. Shabaker, J.A. Dumesic, *Ind. Eng. Chem. Res.* 43 (2004) 3105–3112.
- [18]. M.R. Nimlos, S.J. Blanksby, X. Qian, M.E. Himmel, D.K. Johnson, *J. Phys. Chem. A* 110 (2006) 6145–6156
- [19]. C.C.R.S. Rossi, C.G. Alonso, O.A.C. Antunes, R. Guirardello, L. Cardozo-Filho, *International Journal of Hydrogen Energy.* 34 (2009) 323.
- [20]. K.H. Lin, W.H. Lin, C.H. Hsiao, H.F. Chang, A.C.C. Chang, *International Journal of Hydrogen Energy.* 37 (2012) 13770.
- [21]. S. Adhikari, S. D. Fernando, A. Haryanto, *Energy Conversion and Management.* 50 (2009) 2600.
- [22]. X. Wang, M. Li, S. Li, H. Wang, S. Wang, X. Ma, *Fuel Processing Technology.* 91 (2010) 1812.
- [23]. S. Adhikari, S. Fernando, S.R. Gwaltney, S.D.F. To, R.M. Bricka, P.H. Steele, A. Haryanto, *Int. J. Hydrogen Energy*, in press.
- [24]. B. Zhang, X. Tang, W. Cai, Y. Xu, W. Shen, *Catal. Commun.* 7 (2006) 367
- [25]. S. Adhikari et al. / *Catalysis Today* 129 (2007) 355–364 Publication, 2006, New Jersey, USA, 2nd edition, Chapter 2, pp. 90-117.