Selective Production of Hydrogen by Steam reforming of Glycerol over Ni/A1$_2$0$_3$ promoted by Cobalt and Magnesium Catalysts

Narasimha Reddy Ravuru[1], Sanjay.S. Patel[2]

[1]*Assistant Professor, Chemical Engineering Department, Institute of technology, Nirma University, Ahmedabad*
[2]*HOD, Chemical Engineering Department, Institute of technology, Nirma University, Ahmedabad*

***Abstract*: The developing interest of hydrogen needs renewable wellsprings of crude materials to create it. Glycerol, by-product of biodiesel blend, could be a bio-renewable substrate to acquire hydrogen. With the increment underway of biodiesel, there would be an overabundance of glycerol on the worldwide market. Glycerol is a potential feed stock for hydrogen generation in fact that one mole of glycerol on steam reforming produces 7 moles of hydrogen. As hydrogen is a perfect vitality transporter, transformation of glycerol to hydrogen is one among the most alluring approaches to make utilization of glycerol. Steam reforming is a promising approach to use the weakened glycerol watery answer for produce hydrogen. Creation of hydrogen from glycerol is ecologically inviting in light of the fact that it increases the value of glycerol produced from biodiesel plants. In this study, the catalytic generation of hydrogen by steam reforming of glycerol has been performed in a fixed bed reactor. The execution of this procedure was assessed on 5wt%, 10wt%, 15wt% Ni/Al2O3 promoted by magnesium and cobalt. The catalyst were prepared by the wet impregnation procedure. For a comparative reason, the steam reforming investigations were led under same working conditions, i.e., response temperature going from 700 0C to 850 0C, atmospheric pressure and 1:9 glycerol to water molar proportion. Additionally the impact of glycerol to water proportion, metal stacking, and the feed stream rate (space speed) was analyzed. The outcomes demonstrated that the hydrogen generation decreases with the decrease in the treatment temperature.**

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

I. INTRODUCTION

Because of lessening of fossil powers it is exceptionally significant to look for option source to recover the vitality interest of the world [1-2, 13]. Glycerol is a side product in biodiesel creation which are imagined by means of vegetable oils. Glycerol containing H_2, CO, CO_2, CH_4 and different traces of hydrocarbons which are utilized as an option fuel [3]. These days glycerol is created by using the amid transformation of vegetable oil into biodiesel [4-6, 14]. There are numerous procedures to generate hydrogen from glycerol yet steam reforming is the most basic and vitality capable. In this paper some investigation work done utilizing catalyst nickel using promoter cobalt and magnesium in view of Al_2O_3. Arrangement of glycerol and water filled in a fixed bed catalytic reactor under atmospheric pressure and around 700 ^{0}C to 850 ^{0}C with distinctive proportions of glycerol and water. In this hydrogen is assume an imperative part in the change of concoction industry towards the expanding utilization of renewable sources [7]. After the generation of hydrogen with greatest yield from glycerol is the new route in the spotless fuel innovation. These days hydrogen produces from cognitive gas however innovation of delivering hydrogen from glycerol is the most financial way in light of the fact that unrefined glycerol is the by-result of biodiesel generation and this is the ideal path for saving cost to use this[8].It is firmly endothermic, and it must be done at high temperatures, low pressure, and high steam to glycerol proportion to accomplish higher transformation [9][14].The steam changing response of glycerin continues as indicated by the accompanying following reactions:

Steam reforming of glycerin:

$$C_3H_8O_{3\,(g)} + 3H_2O_{\,(g)} \leftrightarrow 3CO_{2\,(g)} + 7H_{2\,(g)} \quad (1)$$

Reverse Water gas shift reaction:

$$CO_{\,(g)} + H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + H_{2\,(g)} \quad (2)$$

Methanation reaction:

$$CO_{\,(g)} + 3H_{2\,(g)} \rightarrow CH_{4\,(g)} + H_2O_{\,(g)} \quad (3)$$

The overall reaction given as follows [5,14]:

$$C_3H_8O_{3\,(g)} + 3H_2O_{\,(g)} \leftrightarrow 3CO2_{\,(g)} + 7H_{2\,(g)} \quad (4)$$

ΔH^0_{298}= +346.4kJ/mol.

II. EXPERIMENTAL WORK

A. Catalyst preparation

On the off chance that the catalyst are readied utilizing Nobel metals like platinum and palladium then it gives higher activity, higher conversion and yield. Likewise utilizing this metals the coke generation is radically diminished other than Nickel metal. So, it is wanted to make a catalyst utilizing non-nobel metals like nickel which gives the comparative yield as nobel metals. It will likewise influence on the general cost additionally [11].All the catalyst have been based on Al_2O_3 balls. There are such a large number of catalyst accessible for steam reforming procedure. In this paper there is discourse about nickel precursor with cobalt and magnesium as promoter on Al_2O_3 based catalyst. Selected precursor is nickel nitrate ($Ni(NO_3)_2.6H_2O$) in crystal particles. A wet impregnation method [12] used for preparation a catalyst. In this procedure take calculated amount of metal precursor and dissolve in water according to dilution factor. This solution is impregnated on the support. Then used shaking for 4 hours of well mixing. After dry it at 110 ^{0}C for 12 hours to remove water. By which nickel from metal precursor and promoter was impregnated on the Al_2O_3. Calcined for 5 hours at 973 ^{0}C for increasing the activity. Prepare different catalysts by varying amount of nickel. Following table shows different Nickel catalysts with different weight percentage of nickel are given.

Catalyst	Percentage	Percentage of Promoter	Amount of Promoter	Amount of Precursor	Amount of γ-Al_2O_3
Ni/Ce	5%	2%	0.6197	1.8497	4.65
Ni/Ce	10%	2%	0.6197	3.0797	4.4
Ni/Ce	15%	2%	0.6197	4.31	4.1
Ni/Mg	5%	2%	0.933	2.16	4.65
Ni/Mg	10%	2%	0.933	3.393	4.4
Ni/Mg	15%	2%	0.933	4.623	4.1

Table 1 Catalyst preparation table

B. Experimental setup

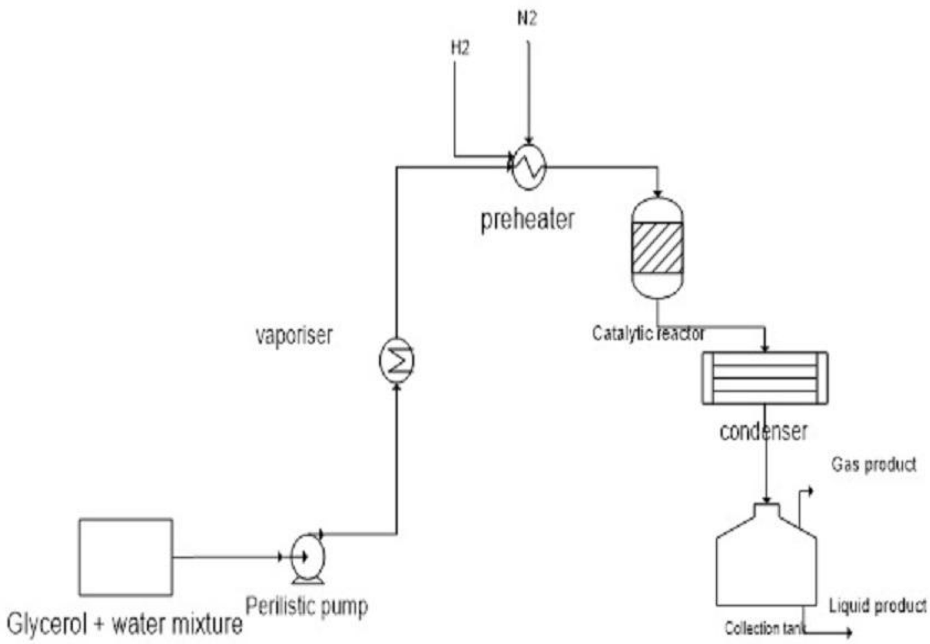

Fig.1. Schematic of glycerol steam reforming setup

B. Reaction condition

Table 2. The operating parameters for hydrogen generation by steam reforming of glycerin is best above the temperature 600 ^{0}C [13,14].

Operating Pressure	Atmospheric pressure
Operating Temperature Range	700 ^{0}C to 850 ^{0}C
Amount of catalyst	1 gram
Flow rate of (glycerol + water) mixture	3 ml/minute
Molar ratios of water to glycerol	9:1
H_2 flowrate	55 ml/minute
N_2 flowrate	280 ml/minute

III. RESULTS AND DISCUSSIONS

Table 3. Conversion and product yield at different temperature at for different proportions of metal is given in following table.

Catalyst	700 ^{0}C	750 ^{0}C	800 ^{0}C	850 ^{0}C
5%Ni/2%Mg	24.01	22.02	21.90	20.29
5%Ni/2%Mg	26.13	29.91	25.04	20.67
5%Ni/2%Mg	33.79	33.54	30.77	38.13
5%Ni/2%Co	10.9	35.53	23.20	27.18
10%Ni/2%Co	8.62	22.33	23.82	26.20
15%Ni/2%Co	27.44	25.76	20.00	11.11

From the results experiments it was seen that the desired temperature for maximum hydrogen yield is around 700 ^{0}C to 750 ^{0}C. In our experiments glycerol to water mole ratio in the feed was 1:9. As per le-chetelier principle if we increase the feed ratio to 1:12, 1:15, 1:18 then hydrogen yield can be increased. Because concentration of one of the reactant is increases then reaction move in forward direction.

A. Effect of Temperature on conversion:

From the experimental results it seen to be that as the temperature increased, the conversion of glycerol and yield of hydrogen also decreases. We will have maximum yield of hydrogen at 750 ^{0}C for the different concentration of nickel catalyst in both promoter cobalt and magnesium.

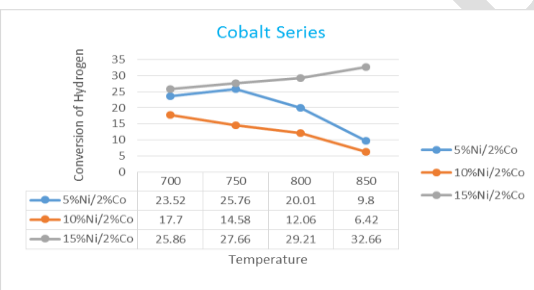

Fig 2 shows the effect of temperature on hydrogen conversion for cobalt series.

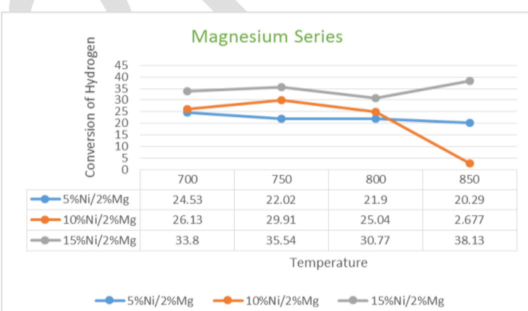

Fig 3 shows the effect of temperature on hydrogen conversion for magnesium series.

B. Effect of water to glycerol feed ratio

For the most part the steam reforming procedure is reversible and endothermic. In this manner, hydrogen generation is less that the product is an again changed over into reactants. So, as per Le-Chetelier standard on the off chance that we build the convergence of one of reactant means include one of the reactant into overabundance mole rate other than required. Along these lines, in the event that we build the convergence of glycerol or water then there is no side effect development and yield will be expanded. Here the water is include as an abundance reactant in light of the fact that contrast with glycerol water is excessively less expensive. The unreacted glycerol in item will be diminished and we can get most extreme conversion of glycerol.

C. Effect of feed flow rate and residence time

For the steam reforming process it is desired that the feed flow rate must be minimal and for all the reactions residence time must be increased. It means that if we have to increase the residence time then we have to provide feed with very low flowrate. If the flowrate is low then residence time is increased then collision frequency between the all molecule of glycerol and water is increased and reaction cannot move in backward direction. And by-product formation or measure of unreacted glycerol will be diminished.

D. Effect nickel percentage in yield of hydrogen

From the experiment result table shown in above it was seen that if the mole percent of nickel in catalyst increases the hydrogen yield decreased or vice-versa. So, for better conversion it is recommended to decrease the weight of nickel in catalyst.

E. Temperature effect on Selectivity:

Cobalt as promoter:

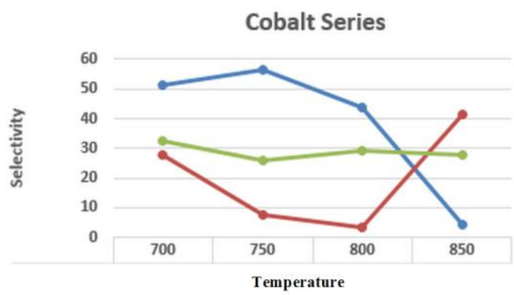

Fig 4 shows the effect of temperature on selectivity of hydrogen for cobalt series.

Magnesium as promoter:

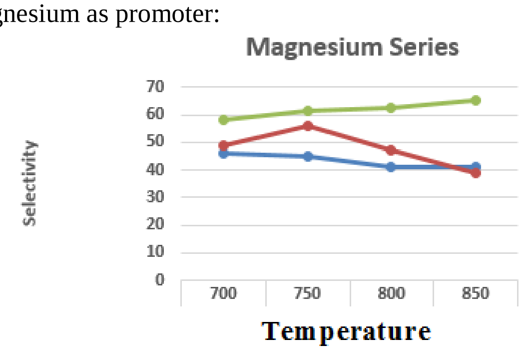

Fig 4 shows the effect of temperature on selectivity of hydrogen for magnesium series.

F. Kinetics:

Causing of Numerous Gaseous Products (H_2, CO, N_2, CH_4 and CO_2) and different Liquid phases (Acetaldehyde, Acetonitrile, Ethanol, Methanol, un-converted Glycerol-Water) in varying Compositions it becomes extremely difficult to obtain the Equilibrium Constants.

$$R_3 = (K_1.K_2.K_3.P^{*}_{C3H8O3.Ni}.P^{2*}_{H2O.Ni})/(K_1.P_{C3H8O3} + K_2.P^{2*}_{H2O.Ni} + K_4.P^{2*}_{H2.Ni} + K_4.P^{2*}_{H2.Ni})$$

$$C_3H_8O_3.\ Ni^* + 2H_2O.\ Ni^* \rightarrow CO_2. + 2H_2.\ Ni^* + CH_4 + CO.\ Ni^* + O_2$$

Theory Proposed: Three Active sites are made available. The Five gases (Carbon Dioxide, Hydrogen, Methane, Carbon Monoxide and Oxygen) that are produced are the result of Five Step Mechanism (Adsorption, Reaction, and Desorption). The Production of this gases depends upon the "affinity" of the Catalyst with the reactant at a given temperature and pressure. The affinity of Production of Hydrogen is comparatively less when compared with carbon Monoxide.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Favouring High Temperature, may obtain higher Conversion but will drastically reduce the Selectivity and vice-versa. Thus an optimum Temperature must be obtained to balance conversion and Selectivity.

II. CONCLUSION

Steam reforming of glycerol has been studied by varying different temperature ranges in between 700^{0}C to 850^{0}C and with varying different composition of Nickel with magnesium and cobalt as promoter. From the experimental result data it was concluded that as compositions of nickel increased in catalyst, mole percentage of hydrogen will be decreased. Highest yield of hydrogen and 100% conversion of glycerin can be obtained in between the temperature range of 700 ^{0}C to 750 ^{0}C in both the promoter. Out of which cobalt is best promoter coupled with nickel for production of hydrogen compared to magnesium. From the experiments done it can be concluded that optimum temperature is 660 ℃ and WGFR is 9:1 with feed flow rate of 2.88 ml/minute. The catalyst by which we can get maximum hydrogen yield is 10% Ni/2%Co Al_2O_3.From the experimental studies it seems to be clear that low pressure and high water to glycerol feed ratio is the best conditions for getting higher moles of hydrogen.

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. 108.
[2]. Saxena RC, Adhikari DK, Goyal HB. Biomass- based energy fuel through biochemical routes: a review. Renewable Sustainable Energy Rev 2009; 13:167.
[3]. 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.
[4]. Hirai T, N-o Ikenanga, Miyake T, Suzuki T. Production of hydrogen by steam reforming of glycerin on Ruthenium catalyst. Energy & Fuels 2005; 19:1761.
[5]. Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, Chen H, et al. Hydrogen production by sorption-enhanced steam reforming of glycerol. BioresourTechnology 2009; 100:354.
[6]. Douette AMD, Turn SQ, Wang W, Keffer VI. Experimental investigation of hydrogen production from glycerin reforming. Energy & Fuels 2007; 21:499,504.
[7]. Andreas, R. (2007). Hydrogen as a Future Energy Carrier.WILEY-VCH Verlag GH & Co. KGA.Weinheim.
[8]. Anggoro, D. D. and Amin, N. A. S. (2006). Methane to Liquid Hydrocarbons over Tungsten-ZSM-5 and Tungsten Loaded Cu/ZSM-5 Catalysts. Journal of Natural Gas Chemistry.15: 340 - 347.
[9]. R. N. Reddy, S. S. Patel, Sai Kumar Nair and Y.V.N.S. Suvikram "Preparation of Hydrogen from Glycerol via Steam Reforming Process"Institute of technology, Nirma university, Ahmedabad–382481, 08-10 December, 2011
[10]. R.D.,Davda, R.R.,DumesicJ.A."Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water", Nature, 2002; 418, 964–967.
[11]. Jun K.W., Roh H.S., Chary K.V.R., Structure and Catalytic Properties of Ceria-based Nickel Catalysts for CO2 Reforming of methane, Catal. Surv. Asia, 2007; 11, 97–113.
[12]. www.impcoinc.com/technical/impregnation
[13]. Ebshish, Ali, Zahira Yaakob, Binitha Narayanan, Ahmed Bshish, and Wan Ramli Wan Daud."Steam Reforming of Glycerol over Ni Supported Alumina Xerogel for Hydrogen Production",Energy Procedia, 2012.
[14]. Adhikari, S."Production of hydrogen by steam reforming of Glycerine over alumina supported catalyst",Catalysis301-07