Production of Hydrogen from Glycerol via Steam Reforming Process Using Ni/Sio2 Catalyst

Parth Desai[1]
Department of Chemical Engineering
Sal Engineering and Technical Institute, Sola Road, Ahmedabad, India

Abstract— Because of hiking price and depleting source of fossil fuels demand of bio-diesel is increased. Hydrogen is the most energy proficient fuel nowadays. Glycerol is the byproduct of bio-diesel production so it is very energy proficient process when we exploit glycerol as a reactant. Steam is the best medium for reforming of biodiesel byproducts which subsuming hydrocarbons at high pressure with minimal time. Water imparts as a source to produce steam. Experiments carried out in atmospheric condition with solid-gas phase tubular reactor at a temperature ambit of about 750 ◦C to 950 ◦C. Theoretically 7 moles are obtained but practically it is hardly about 4.5 to 6 moles. This paper focuses on the conversion of glycerol to hydrogen using nickel based catalyst supported on SiO2 with different composition of nickel.

Keywords: Hydrogen, Glycerol, Steam Reforming Process, Ni/Sio2 Catalyst

I. Introduction

Due to diminution of fossil fuels it is very crucial to search for alternative source to redeem the energy demand of the world [1-2]. Glycerol is a byproduct in biodiesel production which are contrived via vegetable oils. Glycerol containing H_2, CO, CO_2, $CH_4$and other traces of hydrocarbons which are used as an alternative fuel [3].Nowadays around 10 % wt. of glycerol is generated during conversion of vegetable oil or animal fats into biodiesel[4-6]. There are many processes to generate hydrogen from glycerol but steam reforming is the most simple and energy proficient. In this paper some experiment work done using catalyst nickel based on SiO_2. Solution of glycerol and water filled in a fixed bed catalytic reactor under atmospheric pressure and about 700 ˚C to 1000 ˚C with different composition of glycerol and water.

In this context hydrogen is asked to play an important role in the conversion of chemical industry towards the increasing use of renewable sources[7]. After the production of hydrogen with maximum yield from glycerol is the new way in the clean fuel technology. Nowadays hydrogen produces from natural gas but technology of producing hydrogen from glycerol is the most economic way because crude glycerol is the by- product of biodiesel production and this is the perfect way for saving money to utilize this[8].

II. Experimental procedure

A. Steam Reforming Reaction

$$C_3H_8O_{3(g)} + 3H_2O_{(g)} \rightarrow 7H_{2(g)} + 3CO_{2(g)}$$

Steam reforming is the most ubiquitous method of converting glycerol into hydrogen and syngas. This process is the combination of glycerol pyrolysis with the water-gas shift reaction(WGS).

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

The overall steam reforming process is an endothermic process. So, it favors high temperature and low pressure[9]. The main product of steam reforming process is H_2 and CO_2 and CH_4 and CO are the side products in low concentrations [10].

B. Catalyst preparation

If the catalysts are prepared using Nobel metals like platinum and pelledium then it gives higher activity, higher conversion and yield. Also using this metals the coke formation is drastically decreased other then Nickel metal. So, it is desired to make a catalyst using non-nobel metals like nickel which gives the similar yield as nobel metals. It will also affect on the overall cost also[11].All the catalysts have been supported on SiO_2 powder. There are so many catalysts available for steam reforming process. In this paper there is discussion about nickel precursor on SiO_2 based catalyst.

Select a precursor of nickel as nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) which is available in crystal form. Select a wet impregnation method for prepare a catalyst. In this method take a required quantity of salt and dissolve in to a required quantity of water. This solution is added drop-wise from burette on the support. Then put it into shaker for 6 hours for shaking. After shaking put it in to dryer at 110 ˚C for 12 hours to evaporate water. Thus metal from salt is impregnated on the support. Then do a calcination process for 4 hours at 600 ˚C for increasing the porosity. We can make variety of catalysts by changing the compositions of metal. Here in the below table some copper metal catalysts with different compositions are given[12].

Sr. No.	Weight of catalyst (g)	% Weight of Ni	Weight of Ni (g)	Weight of SiO_2(g)	Weight of salt $Ni(NO_3)_2.6H_2O$ (g)
1	10	5	0.5	9.5	1.9023
2	10	10	1	9	3.805
3	10	15	1.5	8.5	5.707
4	10	20	2	8	7.6094

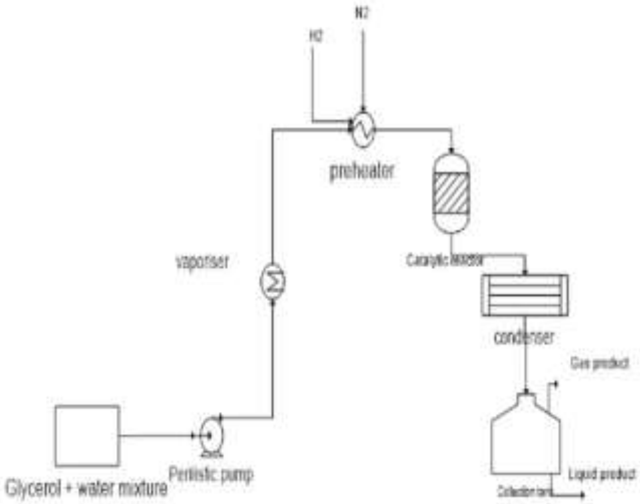
C. Experimental

1) Reaction condition

The best thermodynamic condition for hydrogen production by steam reforming of glycerol is at a temperature above 627°C.[13]

Operating Pressure	1 atmosphere
Operating Temperature	500 ˚C to 900 ˚C
Weight of catalyst	1 gram
Flow rate of (glycerol + water) mixture	3 ml/minute
Possible molar ratios of water to glycerol	9:1, 12:1, 15:1, 18:1
H_2 : N_2 (flow rates)	15:85
Flow rate of H_2	50 ml/minute
Flow rate of N_2	283 ml/minute

2) Experimental setup



3) Procedure for carrying out experiment

First of all set a catalyst of 1 g between the bed of ceramic wool in a fixed bed catalytic reactor. Before carrying out reaction pass the nitrogen gas (N_2) as an inert gas in the reactor with a required flow rate. Once set the flow of N_2 gas then close the valve from nitrogen cylinder. After this process open the valve from H_2 gas cylinder with a required flow rate as mentioned above and simultaneously again start the nitrogen gas in to the reactor and set the flow rates of both the gases. Rise the temperature of reactor step by step with 50 ˚C. After 2 hour reduction stop the supply of hydrogen into the reactor. After this procedure start the pump, flow of water in condenser and collect liquid and gas sample from collector as shown in figure for every increase of 50 ˚C. Temperature of reactor is increased upto 900 ˚C.

III. RESULTS AND DISCUSSIONS

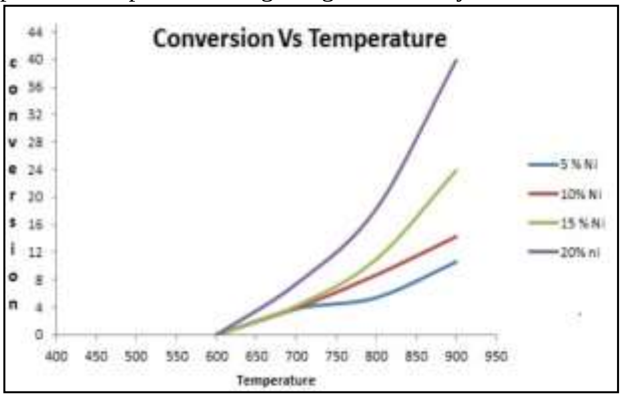
A. Conversion and product analysis at different temperature at desired glycerol to water feed ratio for different composition of metal

Catalyst	Ni %	Temperature (^{0}C)	H_2 yield (mole%)
Ni/SiO$_2$	5	800	5.40
		900	10.61
	10	800	8.7
		900	14.27
	15	800	10.98
		900	23.88
	20	800	18.28
		900	39.88
	50	900	38.58

From the experiments it seems that the desired temperature for getting maximum conversion is around 850 ^{0}C to 900 ^{0}C.Here glycerol to water mole ratio in the feed is 1:9. If we increase this ratio up-to 1:12, 1:15 or 1:18 then hydrogen production is going to be increased because as per le-chetelier principle if we increase the concentration of one of the reactant then reaction goes towards the forward direction.

B. Effect of Temperature

From the above table it seems to be that as the temperature increased, the conversion of glycerol and yield of hydrogen also increased. We can get maximum yield of hydrogen at 900 ^{0}C for all the catalysts. From the experiments the optimum temperature for getting maximum yield is 880 ^{0}C.



C. Effect of water to glycerol feed ratio

Generally the steam reforming process is reversible and endothermic. Therefore, product formation is very less because the product is a again converted into reactants. So, as per le-chetelier principle if we increase the concentration of one of reactant means add one of the reactant in to excess mole percentage other than required. So, if we increase the concentration of glycerol or water then there is no byproduct formation and conversion is going to be increased. Here the water is add as an excess reactant because compare to glycerol water is too cheaper. The unreacted glycerol in product is going to be decreased and we can get maximum conversion of glycerol.

D. 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. If feed flow rate of glycerol water mixture is minimum then mixture is passed very slowly from the reactor tube and residence time is going to be increased. If the residence time is going to be increased then collision frequency between molecules of glycerol and water is increased and reaction going towards forward direction and by-product formation or amount of unreacted glycerol is going to be decreased.

E. Effect nickel percentage in yield of hydrogen

From the experimental results shown in above table it seems that if the mole percent of nickel in catalyst increases the hydrogen yield increased. So, for better yield it is desired to increase the amount of nickel in catalyst.

IV. CONCLUSION

Steam reforming of glycerol has been studied using different temperature conditions and different composition of Nickel. From the experimental studies it was conclude that as compositions of nickel increased in catalyst, yield of hydrogen will be increased. Maximum yield of hydrogen and 100 % conversion of glycerol was obtained at between 850˚ C to 900˚ C. From the experimental studies the optimum temperature is 900˚C and WGFR is 9: 1 at feed flow rate of 2.8 to 3 ml/minute. The best catalyst for getting maximum hydrogen yield is 20% Ni/SiO$_2$.From the experimental studies it seems to be clear that high temperature, low pressure and high water to glycerol feed ratio is the best conditions for getting higher yield 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. 10804.
[2] Saxena RC, Adhikari DK, Goyal HB. Biomass-based energy fuel through biochemical routes: a review. Renewable Sustainable Energy Rev 2009;13:167e78.
[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;19:1761e2
[5] Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, Chen H, et al. Hydrogen production by sorption-enhanced steam reforming of glycerol. Bioresour Technology 2009;100:3540e7.
[6] Douette AMD, Turn SQ, Wang W, Keffer VI. Experimental investigation of hydrogen production from glycerin reforming. Energy & Fuels 2007; 21:3499e504.
[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 – 382 481, 08-10 December, 2011
[10] Cortright 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] http://www.impco-inc.com/technical/impregnation-methods
[13] Adhikaria S., Fernandoa S., Steven R. G., Filip Toa S. D., Brickac R. M., Philip H. S., Haryantoa A., (2007), Athermodynamic Analysis of Hydrogen Production by Steam Reforming of Glycerol.International Journal of Hydrogen Energy, 32(14), p.2875 – 2880.