Hydrogen Production from Glycerol via Steam Reforming Process using Nickel Catalyst using Promoters 2% La, And 2% Ce

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***Abstract*: Biodiesel production by transesterification of vegetable oil, large amount of Glycerol is produced as byproduct. Which is available at very low cost. Hydrogen is a clean energy carrier, and production of Hydrogen from glycerol is most attractive way to use of byproduct glycerol. In this study, experiments are done for the catalytic production of hydrogen by glycerol via steam reforming. The performance of this process evaluated over Nickel supported on aluminum oxide promoted by lanthanum and cerium. Ni is impregnated on aluminum oxide over wide range of temperature range of a 600 0C to 850 0C. Same operating conditions preferred for the comparative study. i.e., atmospheric pressure, operating temperature 600 0C and 1:9 glycerol to water molal ratio. In which we are getting 90% of glycerol conversion in all experiments. As we increases reaction temperature increase in hydrogen production was seen. 10% Ni supported on aluminum oxide is best catalyst which give highest production of hydrogen at 850 0C. Wet impregnation method is used for devolvement of support.**

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

I. INTRODUCTION

Due to the decrement in energy supply reserves, nowadays researcher pay their attention to find out new energy sources. Utilizing of biomass resources to useful energy is one of the most prominent way. Use of renewable energy sources is that reduction in carbon-dioxide which is harmful for environment. Which is used by the growth of biomass [1]. Biomass is an alternative which can be used in production of hydrogen. It can provide useful energy in fuel cell by which demand of hydrogen has wide market [2]. From the available different renewable resources glycerol is having very low cost which can be feedstock for hydrogen production. Nowadays it can be obtained as a byproduct of biodiesel via transesterification of vegetable oils [3]. From the production of 9Kg of biodiesel 1Kg of glycerol is obtained [4]. There are so many process used for the production of hydrogen from glycerol. But steam reforming process is one of best process which utilize glycerol for hydrogen production [5]. In catalytic steam reforming process there are so many catalyst used supported on Al_2O_3, ZrO_2, MgO, SiO_2, La_2O_3[6]. Coke formation on active sites of catalyst is one most important problem which deactivates the catalyst [5]. Steam reforming reactions for production of hydrogen from glycerol are summarized as follows:

Steam reforming of glycerol:
$C_3H_8O_{3(g)} + 3H_2O_{(g)} \leftrightarrow 3CO_{2(g)} + 7H_{2(g)}$ (1)
Reverse Water gas shift reaction:
$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$(2)
Methanation reaction:
$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$(3)
The overall reaction given as follows:
$C_3H_8O_{3(g)} + 3H_2O_{(g)} \leftrightarrow 3CO_{2(g)} + 7H_{2(g)}$ (4)
$\Delta H^0_{298} = +346.4$kJ/mol.

Catalyst effectiveness is one of most important aspect in this process. Catalyst activity majorly depend on method of preparation of catalyst, supports thermal stability, nature of metal used [7]. There are many process used in catalyst preparation in reforming process. Wet impregnation is most used process in steam reforming process [1, 2, 8-11]. In this work wet impregnation method was used for impregnation of nickel over cerium oxide. Main purpose of using this technique is achieving high surface area.

II. EXPERIMENTAL WORK

A.Catalyst Preparation

Wet impregnation method used for catalyst preparation. For the catalyst Nickel metal nickel nitratehexahydrate($Ni(NO_3)_2.6H_2O$)(Sigma-aldrich) used as metal precursor by CDH and lanthanum nitrate hexahydrate ($La(NO_3)_2.6H_2O$) andcerium nitrate hexahydrate ($Ce(NO_3)_2.6H_2O$) both from CDH as promoter. Support used was aluminum oxide(99.99% pure by CDH Company). In this procedure calculated amount of metal precursor was taken and dissolved in distilled water as per the dilution factor. This prepared solution was impregnated on catalyst. For well mixing of solution and impregnation of catalyst on support shaking is provided for 6 hours. After dry it at 110 ^{0}C for 12 hours to remove water. Calcined at 973^{0}C to remove oxide form in it. Different catalyst prepared such as 5%, 10%, 15%

Ni/Al_2O_3 for both promoter. Table 1 shows the different catalyst prepared used in steam reforming process.

B. Experimental Setup

Schematic representation of experimental setup is necessary for analysis of experiment. Figure 1 shows experimental setup which majorly consist of a peristaltic pump by Raval pumps ltd. (RP- V120), the major part catalytic reactor by Shimazdu, also consist of vaporizer, condenser and gas liquid separator. The whole arrangement of experimental setup was shown in figure 1. There are majorly 4 steps of whole experiment. i.e. a) preparation of catalyst and loading, b) reduction of catalyst, c) final reaction and d) analysis of generated product in gas chromatography.

a) Preparation of Catalyst and Loading:

In this step preparation of catalyst was done by wet impregnation method and after that it was loaded in reactor supported by a quartz wool which can withstand catalyst in center of reactor.

b) Reduction of Catalyst:

Reduction of catalyst was done with the help on supplying hydrogen with flow of 50ml/min. and nitrogen is continuously supplied at rate of 280 ml/min at constant temperature of reactor was 450 ^{0}C. The reduction was carried out for 2 hours and after which supply of hydrogen was closed and nitrogen continuously supplied till the end of complete experiment.

c) Final Reaction:

After the completion of reduction of catalyst the vaporizer and preheater was set at 250 ^{0}C and 450 ^{0}C respectively. The feed which is mixture of glycerol and water as 1:9 molal ratio had been feed with the help of a peristaltic pump. Whereas at the same time reactor temperature was set to 600 ^{0}C and increases up to 850 ^{0}C. And continuously sampling of generated product gas was done.

d) Analysis of Generated Product in Gas Chromatography:

Analysis of generated product from gas liquid separatorwas send to gas chromatography equipment of an Shimazdu 2010 from which moles of hydrogen generated can be find out.*B.Reaction condition*

C. Reaction Conditions
:

Table 2. The operating parameters for hydrogen generation by steam reforming of glycerol is best above the temperature 600 ^{0}C[12].

Operating Pressure	Atmospheric pressure
Operating Temperature Range	600 ^{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_2flowrate	50ml/minute
N_2 flowrate	280 ml/minute

Table 1. Prepared catalyst calculation table.

Catalyst	Percentage	Percentage of Promoter	Amount of Promoter	Amount of Precursor	Amount of ɣ-Al_2O_3
Ni/Co	5%	2%	0.6197	1.8497	4.65
Ni/Co	10%	2%	0.6197	3.0797	4.4
Ni/Co	15%	2%	0.6197	4.31	4.1
Ni/La	5%	2%	0.627	1.857	4.65
Ni/La	10%	2%	0.627	3.087	4.4
Ni/La	15%	2%	0.627	4.317	4.1

III. EQUTIONS USED IN CALCULATION OF PRODUCT ANALYSIS:

1) $\% \text{ Hydrogen yield} = \frac{\text{Hydrogen moles produced} * 100}{\text{Moles of glycerol in feed} * 7}$

2) The average conversion of glycerol within interval of time(X)

$$X = \frac{(\text{Moles of glycerol feeded} - \text{moles of glycerol in liquid}) * 100}{\text{moles of glycerol feeded}}$$

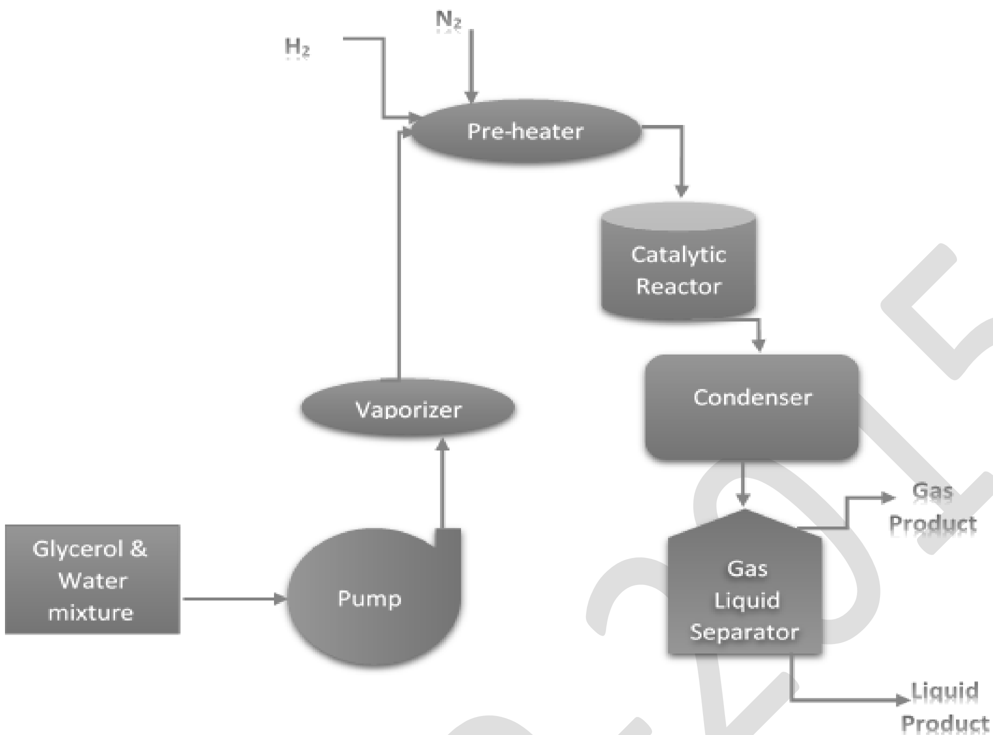

Fig.1. Schematic of glycerol steam reforming setup

IV. RESULTS AND DISCUSSIONS

Table3.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%La	32.00	25.75	24.58	24.03
10%Ni/2%La	30.53	25.54	26.21	20.14
15%Ni/2%La	22.54	22.61	21.74	20.07
5%Ni/2%Ce	16.30	15.74	11.80	11.33
10%Ni/2%Ce	18.20	17.15	15.96	16.66
15%Ni/2%Ce	10.04	12.34	16.13	24.32

From the results experiments it was seen that the desired temperature for maximum hydrogen yield is around 680^{0}C to 700^{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 movein forward direction.

A. Effect of Temperature

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 700^{0}C for the different concentration of nickel catalyst and for both promoter.

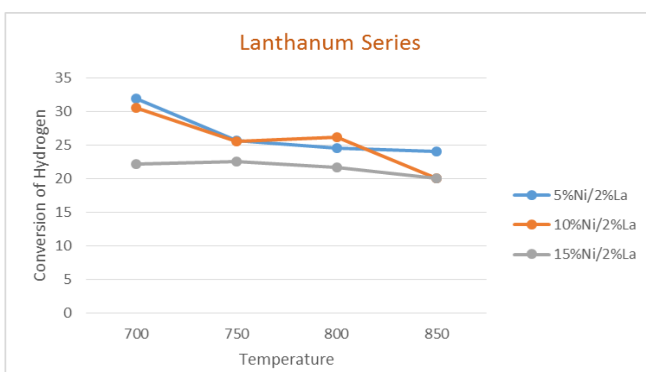

Fig 2 shows the effect of temperature on hydrogen yield for lanthanum series.

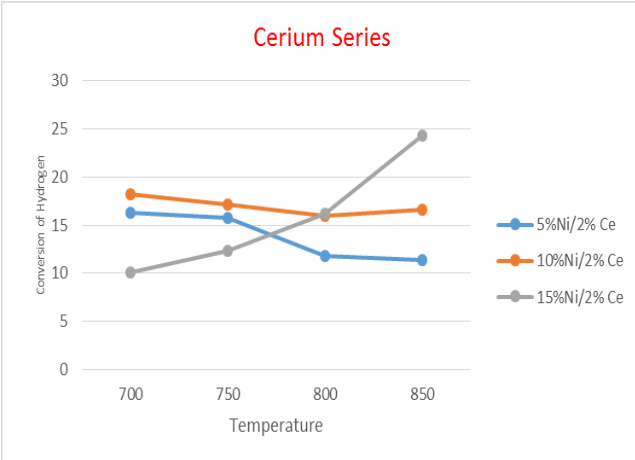

Fig 3 shows the effect of temperature on hydrogen yield for cerium series.

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 more 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 product 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 decreases or vice-versa.So,for better conversion it is recommended to decrease the weight of nickel in catalyst.

V. 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 fixing the same composition of promoter cerium and lanthanum. 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 80% conversion of glycerolcan be obtained in between the temperature range of 680^{0}C to 700^{0}C. From the experiments done it can be concluded thatoptimum temperature is 700^{0}C and WGFR is 9:1 with feed flow rate of 2.75 ml/minute. The catalyst by which we can get maximum hydrogen yield is 15% Ni/Al_2O_3promoted by cerium.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.

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