International Journal of Research
Available at https://edupediapublications.org/journals
e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 04 Issue 13
October 2017

Clean Energy hydrogen production by steam reforming of biodiesel By-product using Nickel-based catalysts with different supports

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Abstract:

Rising prices of petroleum fuel and environmental issues turns researcher's attraction towards production of new renewable fuel sources. Biodiesel can be most prominent solution. Production of biodiesel via transesterification of vegetable oil produces glycerol as major by-product. Glycerol can be utilized for clean energy carrier: hydrogen production via steam reforming. This study focuses production of hydrogen in fixed bed reactor utilizing nickel based catalyst supported by MgO, Al_2O_3, SiO_2 with 1:9 feed ratio of glycerol to water varying temperature range in between 550 °C to 800 °C. 15wt % Ni loaded on Al_2O_3 at 800 °C shows highest hydrogen yield and almost completes glycerol conversion. It was found that activity of supported nickel catalyst as follows: Al_2O_3> MgO> SiO_2. X-Ray powder Diffraction (XRD) and Thermal Gravimetric Analysis (TGA) was used for characterization of catalysts.

Keywords

Biodiesel, Glycerol, Hydrogen, Nickel, Steam Reforming

1. Introduction

In 21st century to overcome from addiction of fossil fuels is major issue. Biodiesel can be solution because it possess environmental favorable characteristic, which produced by transesterification of vegetable oil in which 10wt% of glycerol produced as major by-product. Due to hike demand of a biodiesel, glycerol stock increases which leads to environmental issues. Reducing glycerol into useful chemical compounds is favorable [1]. Many researcher pays their attention to solve this problem. Conversion of glycerol into hydrogen is most interesting way of reduction of glut stock [2-3]. Various water reforming processes [4] used for conversion of glycerol to hydrogen. Amongst all steam reforming process is more benign over supercritical and liquid water reforming processes [5] which provide 7 hydrogen moles using single glycerol mole, however in practice 5.7 to 6 moles of hydrogen can be produced.

2. Steam reforming of glycerol is largely endothermic and favors atmospheric pressure. The major reaction pictured as follows [6]:

3. $C_3H_8O_3+3H_2O \rightleftharpoons 3CO_2+7H_2$, ($\Delta H^0$=128KJ/mol)

Table 1. Method used in production of hydrogen from glycerol

Sr. No.	Various Method Used in Hydrogen Production from Glycerol	
	Method	***Energy Requirements***
1	Liquid phase reforming	High pressure, T< 400 °C [7]
2	Steam Reforming	Atmospheric pressure, T> 450 °C [8-9]
3	Partial oxidation gasification	Highly endothermic, T> 900°C [10]
4	Supercritical water reforming	P>Atmospheric pressure, T>384°C [11]
5	Auto thermal reforming	540^0C < T <1000°C [12]

Several studies have been done using nickel catalyst in alcohol steam reforming with magnesium, cerium, and lanthanum as promoter [13]. By analyzing the action of impetus metals loaded on oxides (ZrO_2, La_2O_3, CeO_2, Y_2O_3, SiO_2, Al_2O_3, MgO), the lineup of catalyst Ru > Ni > Co > Pd was best supported on La_2O_3. Amongst all 3wt. %Rh/Y_2O_3 was found more efficient in conversion of glycerol and hydrogen conversion [14]. Co impetus loaded on economic supports such as La_2O_3, YSZ and ZrO_2 were figured out for supercritical steam reforming. In which 10wt% cobalt loaded on YSZ showed highest glycerol conversion [15]. Considering above study selection of catalyst and support shows important change in glycerol conversion and yield of hydrogen.

In this research synergistic study of nickel catalyst loaded on MgO, Al_2O_3, and SiO2 have been prepared and analyzed for production of hydrogen from glycerol via steam reforming.

2. EXPERIMENTAL

2.1. Preparation of Catalyst

Different batches of nickel catalyst loaded on MgO, Al_2O_3, SiO_2 was prepared. Nickel nitrate hexahydrate [Ni $(NO_3)_2.6H_2O$] provided by CDH was used as metal precursor for nickel. Formulations of catalysts were done by wet impregnation method. After loading of catalyst on support overnight drying provided on 110 °C followed by calcinations at 570°C. Catalysts were sieved in 35-50 mesh screen used in experiments.

2.2. Catalyst Characterization

The powder X-ray diffraction (XRD) by using a Philips X'pert MPD system instrument was carried out. For which diffraction angle 2Θ from 20° to 80° was kept employing Copper Kα radiation filtered by graphite, generator setting current of 30 mA and voltage of 40kV. Continuous mode with very minute step interval applied. Thermo Gravimetry Analysis (TGA) for estimation of coke deposition done by using Mettler Toledo (Model No: TGA-180) instrument. 20 mg of catalyst were weighed in alumina crucible with 10°C/min of heating rate and 20 ml/min of nitrogen as carrier gas up to the 900°C.

2.3. Experimental procedure

The weighted amount of catalyst loaded in center of reactor supported by ceramic wool reduced by ramping the temperature of reactor by 10°C up to 450°C by flow rate 50 ml/min of hydrogen and 280 ml/min nitrogen as carrier gas. Glycerol and water in 1:9 mol ratio respectively fed by peristaltic pump at constant flow rate 3 ml/min, followed by vaporizer at 250°C, which again followed by preheater at 400°C causing conversion of liquid into fully vaporized form. Different temperature was set of a reactor for steam reforming ranging from 450°C to 850°C. After completion of reaction product sent to condenser followed by gas liquid separator from which product sent to analysis. The actual experimental flow path shown in fig.1

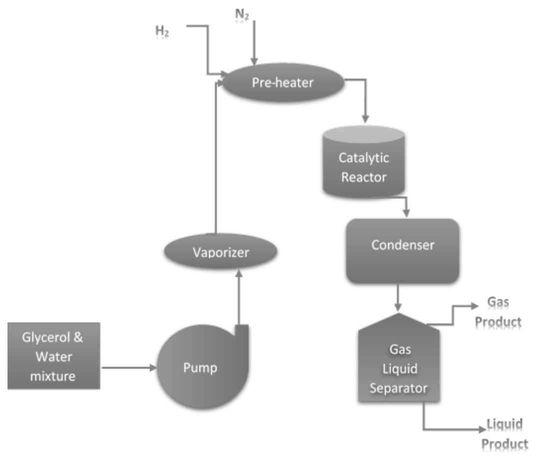

Fig. 1. Experimental flow sheet

2.4. Product analysis

The gaseous product separated at gas liquid separator was analyzed in Gas Chromatograph (Shimadzu GC-10) equipped with thermal conductivity detector (TCD) using Chin carbon CT100/120 micro packed column having dimension 3m length and 1.2mm inner diameter. For detection of CO_2, CO, H_2, CH_4 gas chromatograph calibrated before doing all the experiments by using pure samples of said gases. Activity of catalyst measured in terms of glycerol conversion, hydrogen yield and selectivity using following equations [16-19]:

$$\text{Glycerol conversion\%} = \frac{(\text{CO} + \text{CO}_2 + \text{CH}_4)\text{generated}}{\text{glycerol in feed} \times 3}$$

$$\%\ \text{H}_2\ \text{yield} = \frac{\text{moles of H}_2\ \text{generated}}{7 \times \text{ moles of glycerol fed}} \times 100$$

$$\%\ \text{H}_2\ \text{selectivity} = \frac{\text{moles of H}_2\ \text{generated}}{\text{C atoms in gas product}} \times \frac{3}{7} \times 100$$

$$\%\ \text{selectivity of i} = \frac{i_{out}}{(CO + CO2 + CH4)_{out}} \times 100$$

3. Results

3.1. Effect of temperature on glycerol conversion

As the temperature increases glycerol conversion also increases and highest seen in 15% Nickel loaded on lanthanum oxide. Also the activity of catalyst for

e-ISSN: 2348-6848
p-ISSN: 2348-795X
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glycerol conversion in order of 15%Ni/Al_2O_3> 10%Ni/Al_2O_3> 15%Ni/MgO> 10%Ni/MgO> 15%Ni/SiO_2 was seen from all experiments according to temperature effect.

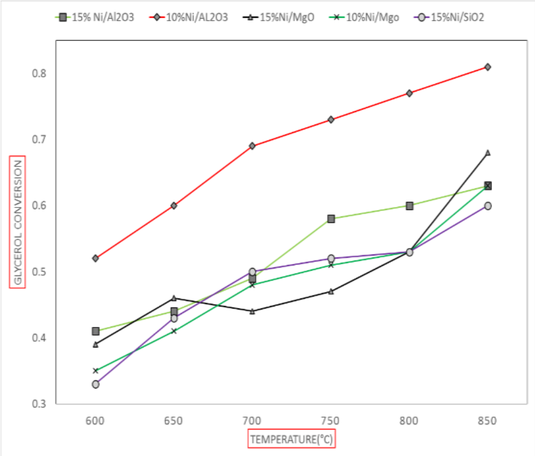

Fig. 2. Effect of temperature on glycerol conversion

3.2.Effect of temperature on hydrogen yield:

As the temperature increases hydrogen yield also increases and highest seen in 10% Nickel loaded on lanthanum oxide. Also the activity of catalyst for hydrogen yield in order of 15%Ni/Al_2O_3>> 10%Ni/Al_2O_3> 15%Ni/MgO> 10%Ni/MgO> 15%Ni/SiO_2 was seen from all experiments according to temperature effect.

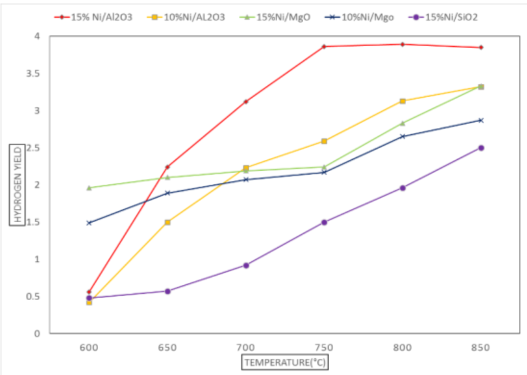

Fig. 3. Effect of temperature on hydrogen yield

3.3.Characterization result:

For all the runs of experiments it was seen that glycerol conversion and hydrogen yield is highest in 15%Ni/Al_2O_3. So X-ray diffraction(XRD) ang thermogravitometric investigation was done. From XRD it was concluded that pure phases of nickel oxide and aluminum oxide formed in catalyst and from TGA we can say that after heating catalyst at 900°C it can be reused. Figure 4 shows the XRD and TGA analysis respectively.

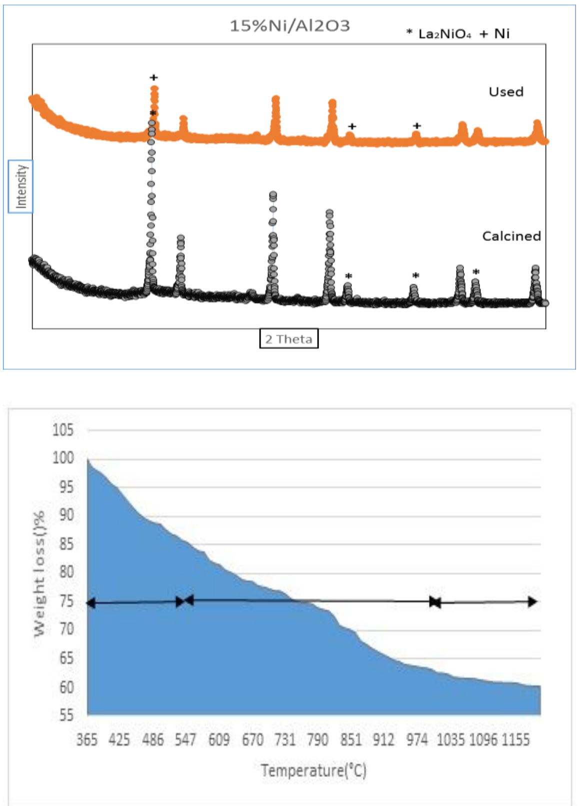

Fig. 4. XRD and TGA graph for 15%Ni loaded on aluminum oxide

4. Conclusion:

Steam reforming of glycerol yielding in hydrogen is one of the most attractive ways of hydrogen production. Hydrogen produced from steam reforming yields 4 to 5 moles comparing to 7 moles as stoichiometric conversion. Also from all the support used aluminum oxide with nickel was best combination which provides 4 moles of hydrogen at 850°C with 3ml/min of feed in proportion of 1:9 of glycerol to hydrogen. Hence it is proved that glycerol can be converted in clean energy hydrogen by steam reforming effectively.

5. Acknowledgements

The authors are grateful to Institute of Technology, Nirma University for its invaluable support provided in the form of research facilities.

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