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Selective production of Hydrogen by steam reforming of glycerin over alumina- supported Nickle catalyst

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Abstract : The exhaust of fossil fuels with their ever increasing prices has paved ways for alternative fuels. Biodiesel is one of those alternative fuels which have picked up keen interest of the people due to its similar properties to diesel. However due to biodiesel being costlier than diesel in the present scenario, it has not been preferred to diesel. However if the cost of biodiesel is reduced then its effective usage can be made, either by blending with conventional diesel or by utilizing its by-product (glycerol) effectively. One way is to use glycerol to produce hydrogen. Hydrogen, being another source of renewable energy, is also seen as a clean fuel for transportation purpose. Hydrogen can be prepared through glycerol via various routes namely steam reforming, auto-thermal reforming, partial oxidation, etc. The paper focuses on the steam reforming process. This process is used widely used in the industries and it would not require much change in the system if the feedstock is changed to glycerol from naphtha or natural gas. However like every process this process also has some limitations which hinder the effective production of hydrogen. The paper discusses the experimental study of the reaction using Ni based catalysts and pure glycerol, the experimental work here focuses on the understanding of activity of Ni based catalysts, based on the different base metal loading under the one reaction condition.

Keywords : Glycerol, Steam reforming, Hydrogen production, Biodiesel.

1. Introduction

The ever increasing prices of crude oil, which leads to the increase in prices of fuels from it, and the limiting reserves of conventional fossil fuels along with ever growing population and pollution has led the people to come up with alternative fuels which would be cheaper, efficient and causing less pollution. As a result, new technologies requiring the use of renewable feedstock have been the focus of intense process development within the past decade[1].

In this respect, green catalytic processes which utilize renewable feedstock for the conversion into commodity chemicals and clean biofuels have attracted considerable attention. So, alternative bio-based fuels are emerging as the long-term solution. The Biofuels have become alternate to fossil-based fuels because they are renewable and theoretically, carbon dioxide (CO_2) neutral.

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Many researchers have been doing research on biofuels and Bio-diesel is one of them. Today, Biodiesel has become more competitive against petroleum diesel due to the higher prices of crude oil and increased demand for environmentally acceptable fuels[2]. However, the popularity of bio-diesel among the world has not picked up much due to its competitive nature with diesel in terms of price per liter. Figure 1 shows the graphs of comparison in prices of diesel and bio-diesel. Hence it is important, for effective usage of Bio-diesel; the price has to be lowered. With the production of Biodiesel, glycerol (1,2,3-propanetriol), a carbohydrate ($C_xH_yO_z$), is obtained as by-product during biodiesel production from vegetable oil and bioethanol[3]. By utilizing this by-product of bio-diesel efficiently the cost of biodiesel can be reduced (as shown in Fig 2)[4]. Glycerin is produced about 10% of the total quantity of the biodiesel produced, i.e. for 10 kg of total production 9kg would be biodiesel and 1 kg would be glycerol.

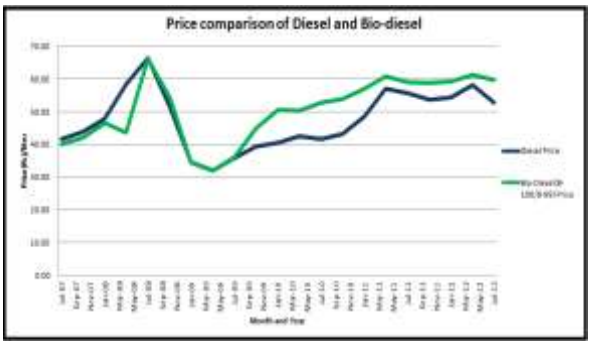

Fig. 1. Graphical presentation of prices of diesel and biodiesel

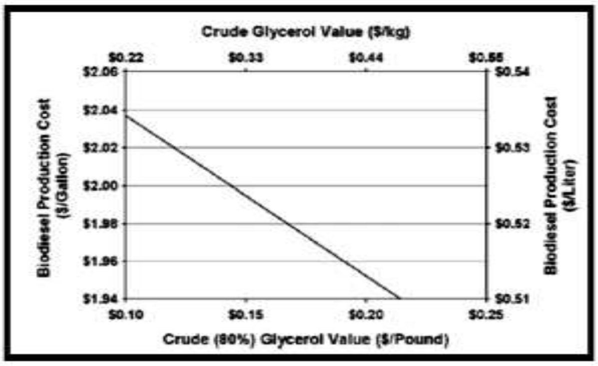

Fig.2. Change in the biodiesel cost with thecrude glycerol value

1.1 Biodiesel By-product: Glycerol

Currently, almost two third of the industrial uses of glycerol are in food and beverage (23%), personal care (13%), oral care (20%), tobacco (12%), etc[5]. The purification of crude glycerine from the biodiesel plants is a major issue. Also the disposal of glycerol by the emerging biodiesel industry is therefore a new engineering challenge in order to make it more competitive with the conventional fossil diesel[6]. With the ever-increasing production of biodiesel, a glut of glycerine ($C_3H_8O_3$) is expected in the world market[7]. Hence it is necessary to explore alternative uses of glycerine.

One promising way is to use glycerin to produce hydrogen or synthesis gas via steam reforming. Hydrogen is a clean energy source with uses including ammonia production, petroleum processing, and power generation in fuel cells[8]. Due to environmental concerns, the global demand for hydrogen is expected to greatly increase in the future.

Why Glycerol for hydrogen production?

Fossil fuels are the dominant source of industrial hydrogen. Hydrogen can be generated from natural gas with approximately 80% efficiency or from other hydrocarbons to a varying degree of efficiency. Specifically, bulk hydrogen is usually produced by the steam reforming of methane or natural gas. At high temperatures (700–1100 °C), steam (H_2O) reacts with methane (CH_4) to yield syngas.

$CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H = +191.7$ kJ/mol(1)

In a second stage, further hydrogen is generated through the lower temperature water shift gas reaction, performed at about 130 °C.

$CO + H_2O \rightarrow CO_2 + H_2 \Delta H = - 40.4$ kJ/mol(2)

Essentially, the oxygen (O) atom is stripped from the additional water (steam) to oxidize CO to CO_2. This oxidation also provides energy to maintain the reaction. Additional heat required to drive the process is generally supplied by burning some portion of the methane. As per stochiometry the moles obtained by steam reforming of natural gas is 4. While hydrogen obtained from steam reforming of glycerol is 7 as per equation (3). So as per study, glycerol provides most number of moles of hydrogen and hence can be preferred over the fossil fuels.

$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO_2(g)$

Hydrogen production from glycerol through different routes

Demand for hydrogen (H_2), the simplest and most abundant element, is growing due to the technological advancements in fuel cell industry. At present, almost 95% of the world’s hydrogen is being produced from fossil fuel based feed stocks. Renewable resources based technologies for hydrogen production are attractive options for the future due to carbon neutral nature of these technologies with lesser effects to the environment. A great interest in utilizing glycerol for hydrogen production is seen over the last few years. Most of the studies on hydrogen production are focused on thermo-chemical routes[6].

Hydrogen can be produced from glycerol by the following ways

- Steam reforming process
- Partial oxidation gasification process
- Auto-thermal reforming process
- Aqueous-phase reforming process
- Supercritical water reforming process

Challenges in the process of steam reforming of glycerol and their possible solution

A. Steam reforming process

The process for production of hydrogen from glycerol is a very good option for producing a renewable source of energy. However like every process, there are few loop-holes or challenges in the effective production of hydrogen through steam reforming of glycerol. The challenges need to be overcome for the effective commercializing of the process.

Following are the few problems which have been observed from the literature survey.

- Stochiometrically the glycerol steam reforming reaction states that for one mole of glycerol there should be 7 moles of hydrogen formed. However, when it comes to the practical operation, it has been observed that the production/yield of hydrogen limits to 5.8 to 6 moles while the minimum amount of hydrogen obtained is 4 moles.
- The steam reforming process is endothermic reaction and hence requires a high temperature. Also it is been observed that the yield of hydrogen increases with the increase in temperature but up to a critical temperature after which the yield decreases. The temperature range for the process is around 800 K – 1000 K. The control of this high temperature is a difficult task and it adds to the operational cost. Moreover high temperature would increase the capital cost of the reactor in terms cost of material of construction[15].
- Very few studies have been performed using crude glycerol. The crude glycerol consists of water, ash, methanol and few of the fatty materials, the effective usage of crude glycerol may lead to the decrease in the overall cost of the process, as the refining stage of glycerol would be eliminated[9-16].
- The steam reforming of glycerol apart from producing hydrogen, produces 3 moles of carbon dioxide stochiometrically. It is well known that release of carbon dioxide is an environmental concern, and hence effective utilization of carbon dioxide is required.

- The glycerol steam reforming process sometimes has to face certain side reactions which hinders the production as well as the purity of hydrogen. One such side reaction is the formation of methane. This methane is either formed through the reaction of carbon dioxide and hydrogen (eq (5)) or reaction between carbon monoxide and hydrogen (eq (6)) or through hydrogenolysis of glycerol (eq (7)). These reactions need to be subsidized inorder to have higher and purer yield of hydrogen.

$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$ (5)
$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$(6)
$C_2H_8O_3(g)+2H_2(g) \rightleftharpoons 2CH_4(g)+CO(g)+ 2H_2O(g)$ (7)

- The process also deals with the formation of coke/ carbon during the process. This carbon/coke acts as a poison and clogs the pores of the catalyst and hence deactivates the catalyst thus affecting the process as well as the yield and purity of hydrogen. It is observed that the coke formation increases with the increase in temperature. If the temperature could be lowered down the coke formation may decrease but this also may affect the yield of hydrogen[17-19].

B. Factors affecting the steam reforming process

The factors affecting the production of hydrogen from steam reforming process are

- Temperature
- Pressure
- Water to Glycerol Feed Ratio (WGFR)
- Feed reactants to inert gas ratio
- Feed gas rate

It has been observed that these factors hold a key role in order to have a high hydrogen yield and a good glycerol conversion. As per various researches[2, 20-23], it has been found that for optimum results the process of glycerol steam reforming requires a high temperature (800K-1000K), a atmospheric pressure (~ 1 atm), the feed reactants to inert gas ratio and feed gas rate should be low. It has also been suggested that the water to glycerol ratio (WGFR) should be around 9:1, i.e. Steam to carbon ration should be around 3:1. The glycerol conversion is a strong function of water to glycerol ratio, but a weak function of other parameters over the conditions of the process.

Catalystseparation and activity

A. Catalyst preparation

Four Nickel based catalyst were prepared by using wet impregnation method. Nickel nitrate was used as a precursor for the nickel metal while gamma alumina was used as a support. The precursor solution was impregnated to support followed by shaking for 4 hours, followed by drying for 12 hours at 120 ^{o}C, and calcinations for 6 hours at 500 ^{o}C. The catalysts prepared are shown in Fig 3.

Fig 3 Catalysts after calcinations (a) 5% Ni/Al_2O_3 (b) 10% Ni/Al_2O_3 (c) 15% Ni/Al_2O_3 (d) 20% Ni/Al_2O_3

1.1. Activity of catalysts

1.2. The catalysts were undergone reduction for 2 hours at 500 °C in presence of H_2 (H_2:N_2=15:85 vol %). The activity of the catalysts was tested in atmospheric gas solid reactor, Chemitolaboratory systems. The glycerol to water ratio was taken to 9:1 w/w, the temperature range was taken between 500 °C to 900 °C. The amount of catalyst was taken as 1g and the flow rate of the reaction mixture was kept at 2.8 ml/min. The reaction mixture through the pump passed through vaporizer followed by pre-heater and reactor. The products and the un-reacted reaction mixture were condensed through a condenser and were collected in acollection tank. The gaseous products were analyzed in GC-2010, Shimatdzu, usingTCD. While the liquid products obtained were collected and then were analyzed in the same GC using FID.

2. Results and discussion

2.1. Activity of 5% Ni/Al_2O_3

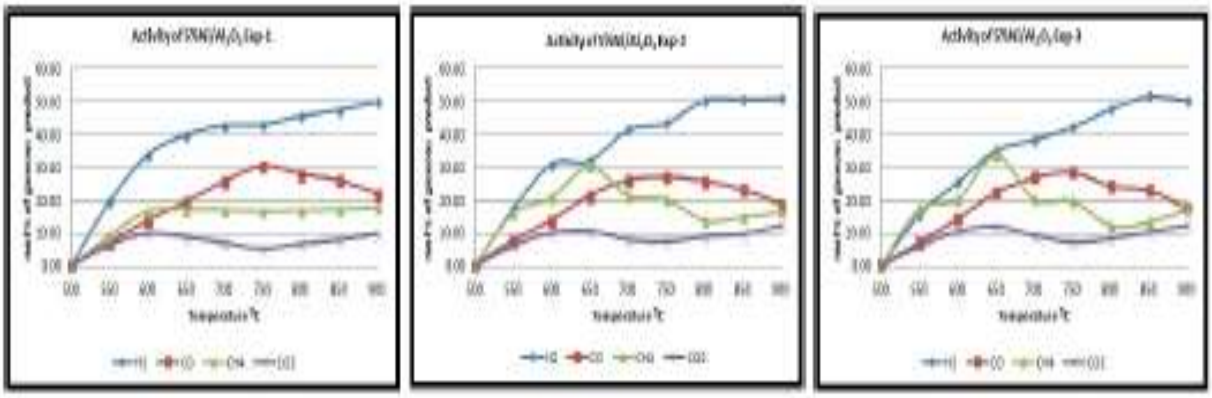

Fig. 4Mol% of gaseous products formed with respect to temperature for 5%Ni/Al_2O_3

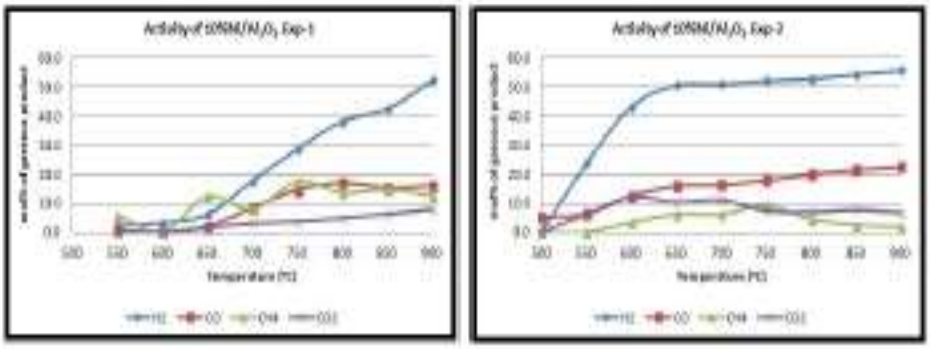

Fig 5. Mol% of gaseous products formed with respect to temperature for 10%*Ni/Al_2O_3*

The experiments were carried out under the reaction condition mentioned in the previous chapter. The samples here were taken in the interval of 30 minutes and rise of 50°C for every sample. It was observed that the amount of hydrogen produced was around 50 mol% of the gaseous product while CO_2 was about 7-8 mol% near a temperature range of 800-900 °*C*. Also the amount of CO follows a parabolic trend, indicating a higher rate of formation at mid temperature range and a lower rate of formation at higher temperature range simillarly the formation of CH_4 is higher at mid temperature range where as lower at higher temperature. Here the formation of white smoke was observed during the initial phase (i.e. lower temperatures) of the experiment. The relevant trends of the products with respect to temperature are shown in Fig 5.

2.2. Activity of 10% Ni/Al_2O_3

The gaseous products were analyzed using gas chromatograph. It was observed that the amount of hydrogen produced was around 50-58 mol% of the gaseous product while CO_2 was about 7-8 mol% near a temperature range of 800-900 °*C*. Also the amount of CO had higher rate of formation at higher temperatures, however the formation of *CH_4* was minimal at higher temperature. The relevant trends of the products with respect to temperature are shown in Fig 5.

2.3. Activity of 15% Ni/Al_2O_3

The gaseous products were analysed using gas chromatograph. It was observed that the amount of hydrogen produced was around 59-64 mol% of the gaseous product while CO_2 was about 10-12 mol% near a temperature range of 800-900 ^{o}C. Also the amount of CO had higher rate of formation at higher temperatures nut lower as compared to the previous catalysts. The formation of CH_4 was minimal at higher temperature. The relevant trends of the products with respect to temperature are shown in Fig 7.

2.4. Activity of 20% Ni/Al_2O_3

The gaseous products were analyzed using gas chromatograph. The samples here were taken in the interval of 30 minutes and rise of 50^{0}C for every sample. It was observed that the amount of hydrogen produced was around 40- 45 mol% of the gaseous product while *CO_2* was about 10-12 mol% near a temperature range of 800-$900^{o}C$. The formation of CO was very minimal for this particular catalyst while there was almost no formation of *CH*4 at higher temperature. This catalyst showed a better result in terms of lower formation of CO and *CH_4*, but lacked in the formation of hydrogen as compared to other catalysts. the relevant trends of the products with respect to temperature is shown in Fig 6.

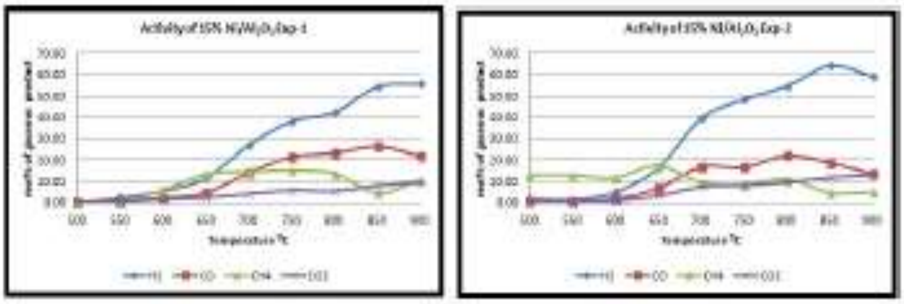

Fig 6. Mol% of gaseous products formed with respect to temperature for 15%Ni/Al_2O_3

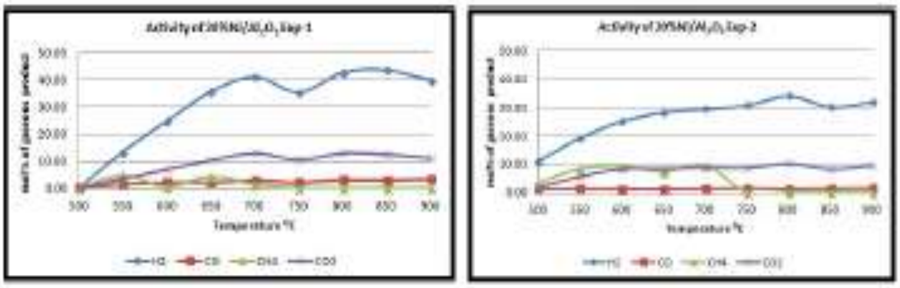

Fig 7. Mol% of gaseous products formed with respect to temperature for 20 %Ni/Al_2O_3

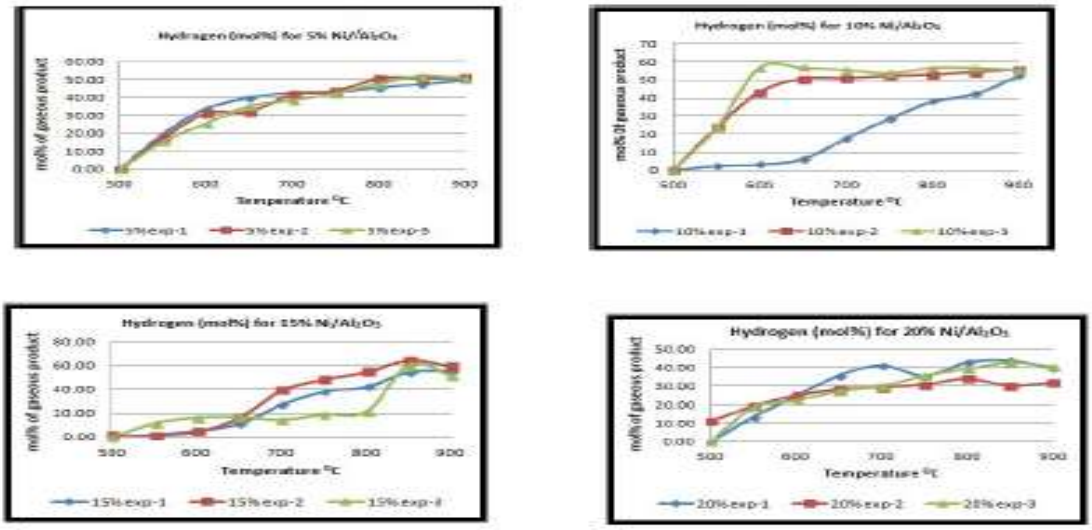

Fig 8. Mol% of gaseous products formed with respect to temperature for all catalysts

2.5. Comparison of the catalysts in terms of hydrogen production

On comparing all the catalyst with respect to the hydrogen production, it can be observed that 15% Ni/Al_2O_3 gave the best result. Though the formation of CO and CH_4 were minimal in case of 20% Ni/Al_2O_3 as compared to 15% Ni/Al_2O_3, however there was much difference observed in terms of hydrogen formation between the two catalysts. This can be depicted by the following figure.

2.6. Activity of the better catalyst (15% Ni/Al_2O_3)

15% Ni/Al_2O_3 showed a better result in terms of hydrogen production. It was also observed that each catalyst gave a better result in the range of 800 – 900 ^oC. Hence the activity of the 15% Ni/Al_2O_3 was again tested in the range of 800 - 900^oC and over other same reaction conditions. The samples here were taken in the interval of 30 minutes and rise of 20^oC for every sample. The gas samples were collected and analysed in GC using TCD. Fig 8 shows the gas analysis of the two experiments carried out.

It can be observed from the figure that the amount of hydrogen is maximum at 860^oC (i.e around 76 mol%) , also the amount of CO and CH_4 were almost zero. It was also observed that as the catalyst achieved a temperature of 870-880 ^oC, the amount of hydrogen decreased, while there was an increase in the formation of CO the same trend is observable uptill 900 ^oC. This indicated that the catalyst deactivated around this temperature range. This suggested that for the particular condition the best result was obtained at 860*o*C, and the catalyst had to be tested at this particular temperature.

It can be seen that the production of hydrogen from glycerol is a very good option, keeping into mind that hydrogen as well as biodiesel are said to be the future fuels of the world. However the glycerol steam reforming possesses some challenges which need to be irradiated or avoided in order to have higher productivity as well as purity of hydrogen. Also From the above experimental study it can be observed and concluded that for the reaction conditions mentioned here 15% Ni/Al_2O_3 would give the best possible result. Also it was observed that as the amount of base metal increased the amount of CO and CH_4 decreased, i.e. higher in 5% Ni and least in 20% Ni. The 20%Ni based catalyst gave a desired result in terms of eliminating the side reactions, however the amount of hydrogen produced using this catalyst was much less to that produced by using 15% Ni based catalyst. The study of the better catalyst out of the four had led to a temperature (860 ^oC), from a wide range (500 – 900 ^oC), at which maximum amount of hydrogen can be generated. It was observed during the study that the catalyst deactivates at temperature greater than 870 ^oC, the amount of hydrogen decreases after 2 hours, indicated by the declining trends in the graph.

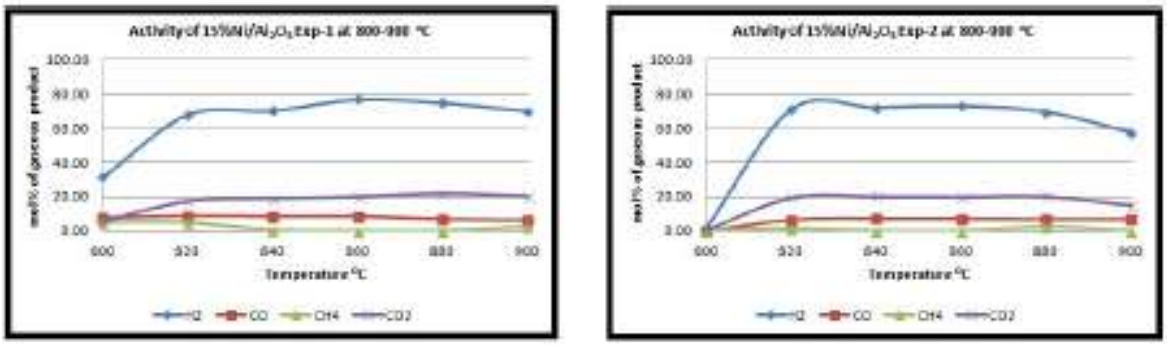

Fig 9. Activity of 15% Ni/Al_2O_3at 800-900°C

3. Conclusion

Glycerol steam reforming of has been studied using different temperature conditions and different composition of Nickel supported on alumina. The conclusion from experiment is as compositions of nickel increased in catalyst, yield of hydrogen is increased. Maximum yield of hydrogen and 100% conversion of glycerol was obtained at between 800℃ to 850 ° C. The best catalyst for getting maximum hydrogen yield is 15% Ni/Al_2O_3.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.

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