

Conversion of Bio mass derived glycerol to hydrogen gas by steam reforming process over Ni/Al₂O₃ catalyst

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ABSTRACT: In this work, hydrogen is produced from bio mass derived glycerol by steam reforming process over Ni/Al₂O₃ catalyst with low methane and carbon monoxide formation. Experiments were conducted in a tubular fixed-bed flow reactor over a temperature range of 650°C- 700°C and 1atm pressure, feed concentrations up to 40 wt% glycerol and water to glycerol molar ratio(WGMR) of 9:1 are the best conditions for hydrogen production. Thermo dynamically under this conditions coke formation will be inhibited and methane production is minimized. Glycerol was completely gasified to hydrogen, carbon dioxide, and methane along with small amounts of carbon monoxide. At dilute feed concentrations, near-theoretical yield of 7 mol of hydrogen/mol of glycerol was obtained, which decreases with an increase in the feed concentration. Water gas shift reaction, further converts CO into CO₂ and H₂. X-ray diffraction and electron microscopy were used to study the crystal structure, and morphology of the catalysts. The catalysts studied Ni/Al₂O₃ gives the maximum yield in which nickel is in interacted form and the best operating conditions for Ni/Al₂O₃ are 700⁰ C and 120 ml/hr of feed rate.

Keywords: Steam reforming, Glycerol, Fixed bed reactor

1. INTRODUCTION:

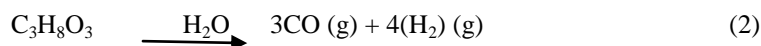
Owing to high energy content of hydrogen and the possibility of converting this energy fuel cell devices into electric power without any pollutant emissions, hydrogen has grown to be one of the most useful sources of energy, especially it is produced from renewable sources. The development of alternate sources of energy is becoming important in this era of diminishing petroleum reserves and increased environmental awareness. Hydrogen production from biomass derived Glycerol has attracted great interest because of the potential application in fuel cells [1] and essentially carbon dioxide neutral since CO₂ generated during the fuel use is subsequently fixed by growing plants during photosynthesis [2]. Significant amount of Glycerol is produced as a by-product during bio-diesel production by transesterification of vegetable oils, which are available at low cost in large supply from renewable raw materials [1]. With increased production of bio diesel, a glut of glycerol (C₃H₈O₃) is expected in the world market, and therefore it is essential to find useful applications of glycerol. In general, for every 100 pounds of biodiesel produced, approximately 10 pounds of crude glycerol are produced as a by-product. Currently, glycerol is used in many applications including personal care, food, oral care, tobacco, polymers, and pharmaceuticals. Another use is the production of 1, 2-propanediol and 1,3-propanediol by hydrogenation of glycerol.[3]. Another Use was glycerol as a source of producing hydrogen is a good possibility.

Steam reforming is the promising way to utilize the diluted glycerol aqueous solution to produce hydrogen. Glycerol is a potential feed stock than ethanol for production of hydrogen because one mole of glycerol can produce up to seven moles of hydrogen [1]. Hydrogen is the most abundant element in the universe and with an energy yield of 2.75 times by mass higher than that of an average hydrocarbon fuel, this hydrogen is the most beneficial source of energy. 1mol of glycerol can theoretically produce 7mol of hydrogen gas; glycerol utilization in hydrogen production would be a potentially economically and environmentally friendly option. One possible option for the efficient conversion of glycerol into hydrogen is the steam reforming process [2]. Steam reforming of hydrocarbons and biomass materials has been paid more attention recently by Adam J. Byrd [4]. Supercritical reforming found that addition of Ru/Al₂O₃ catalyst, glycerol produced a stream rich in H₂ and CO₂ with small amounts of CH₄ and CO.

Steam reforming is an endothermic reaction. Energy is needed for this process to break up C-C and C-H bonds in the hydrocarbon chain. The density of steam reforming is higher than that of super critical water reforming resulting in a higher space time yield, and higher thermal conductivity and specific heat, which are helpful in carrying out the endothermic reforming reactions [5]. Steam reforming has both low viscosity and high diffusivity. The formation of carbon and CO is also minimized because sufficient steam will lead to high process conversions. It can operate at low pressures and can produce higher concentrations of hydrogen with high fuel conversion. At very high temperature, reforming is highly favorable for decomposition of glycerol. Significant quantities of CO may be produced and hydrogen may be consumed through the reverse water gas shift reaction at high temperatures.

Reforming of glycerol for hydrogen production can be summarized by following reactions [2].

First, the steam reforming of glycerol:



Followed by the water-gas shift reaction:



Followed by the Overall reaction:



Some hydrogen is also lost via the methanation of CO and CO₂:



As a result, the product stream is a mixture of above gases. Furthermore, the yield of hydrogen depends on several process variables, such as system pressure, temperature, and water to glycerol feed ratio, catalyst and pressure. [6,10] Most of the above studies were done in batch mode, in which the glycerol /water/catalyst is loaded in a small steel tube reactor which is placed in a furnace. After the reaction, the mixture is quenched and analyzed. Typical reaction time varied from minutes to hours. The aim of this study is to examine hydrogen production from glycerol by steam reforming in a fixed Bed reactor, production of high amount of hydrogen with less pollutants and Ni/Al₂O₃ is chosen as a catalyst. The effects of the process variables such as temperature, contact time, and water to glycerol ratio on hydrogen yield are investigated [7].

2. Catalysts Used in Steam Reforming of Glycerol

Many researchers invested number of catalysts for steam reforming of glycerol for hydrogen production. The various types of catalysts which are in use are Nickel based catalysts supported on silica, alumina, MgO, CeO₂, and TiO₂. Other type of catalysts like Ir, Co, La, Ru/Y₂O₃, Ir/CeO₂ are also used as supports. [8] Various types of catalyst used in this process are given in

Table1: CATALYST AND OPERATING CONDITIONS FOR STEAM REFORMING OF GLYCEROL [9]

Catalyst	Operating Conditions	Remarks
Ir/CeO ₂ , Ni/CeO ₂ , Co/CeO ₂	Temperature=400-550 ^o C Mass of catalyst: 200Mg Particle Diameter: 40-60 mesh C ₃ H ₈ O ₃ :H ₂ O:He = 2:18:80 Vol %	Ir/CeO ₂ gave the hydrogen selectivity and glycerol conversion of 85% and 100% respectively, at 400 ^o C.

Y ₂ O ₃ , ZrO ₂ , CeO ₂ , La ₂ O ₃ , SiO ₂ , MgO, and Al ₂ O ₃ , supported Group 8-10 metals.	Temperature=500-600 ⁰ C Steam/ carbon molar ratio(S/C)=3.3 Pressure = Atmospheric pressure	A complete conversion of glycerol was achieved over ruthenium on Y ₂ O ₃ (Ru/ Y ₂ O ₃) at 600 ⁰ C at similar conditions. hydrogen yield was 82.8% from the list of the tested catalysts, Ru/ Y ₂ O ₃ was found to be the best.
Ni/ Al ₂ O ₃	Temperature=850 ⁰ C Steam/ carbon molar ratio(S/C)=2.1&2.6	The yield of hydrogen was 23.6g/100 g of glycerol (77% of stoichiometric yield) at S/C of 2.6.
Pt/ Al ₂ O ₃ , Ni/ Al ₂ O ₃ , Pd/Al ₂ O ₃ , Ru/ Al ₂ O ₃ , Rh/ Al ₂ O ₃	Feed flow rate = 0.15-0.5ml/min Temperature=600-900 ⁰ C Steam/ carbon molar ratio(S/C)=1/3-3.0	About 80% hydrogen selectivity was obtained with Ni/ Al ₂ O ₃ , whereas the selectivity was 71% with Ru/ CeO ₂ / Al ₂ O ₃ at a S/C =3900 ⁰ C temperature, and feed flow rate of 0.15ml/min.
Ni/MgO, Ni/CeO ₂ , Ni/TiO ₂	Feed flow rate = 0.5-0.7ml/min Temperature=550-650 ⁰ C Steam/ carbon molar ratio(S/C)=2-4 Catalyst loading = 0.75-1.5g (Ni 9.6-12.7 wt%)	Ni/CeO ₂ , best performing catalyst than Ni/MgO and Ni/TiO ₂ under the experimental conditions Ni/CeO ₂ gave the maximum hydrogen selectivity of 74.7% at S/C ratio of 4, temperature of 600 ⁰ C, and a feed flow rate of 0.5 ml/min compared to Ni/MgO(38.6%) and Ni/TiO ₂ (28.3%) under the similar conditions.
Pt/ Al ₂ O ₃	Temperature=800 ⁰ C Glycerol flow per kg catalyst= 0.12 mol/min S/C = 2.5	Hydrogen selectivity of 70% and glycerol conversion to gas 100%
Pt supported on Al ₂ O ₃ , Zr O ₂ , CeO ₂ /ZrO ₂ , MgO/ZrO ₂ , and carbon	Temperature=350 ⁰ C Pressure= 1 bar Aqueous glycerol feed solution (30wt%) Over oxide supported Pt catalysts(1.0 g) or Pt/C catalyst (0.060g) And a feed flow rate of 0.32cm ³ min ⁻¹ . Pt/c catalyst was tested at various feed rates and temperatures. Other catalysts tested were Pt-Ru	Pt/C catalysts showed the superior performance at 400 ⁰ C and pressure = 1 bar ,100% glycerol conversion was achieved at feed rate of 0.32 cm ³ min ⁻¹
Pd/Ni/Cu/K supported on α-Al ₂ O ₃	Temperature=550-850 ⁰ C S/C = 3.0	Hydrogen yield was 42% at 850 ⁰ C
Ni/ α -Al ₂ O ₃ Modified with Mg, Ces, La, Zr.	Temperature=600 ⁰ C Concentration = 1 Wt%	100% conversion was achieved with all the catalysts. Catalyst promoted with Zr showed the highest H ₂ selectivity.

Catalysts for steam reforming of hydrocarbons are mainly based on nickel as active component supported on oxides with high thermal stability. Although noble metals (Ru, Rh, Pt) are more effective for the steam reforming of hydrocarbons than Ni but less susceptible to carbon formation.[10] Such catalysts are not common in industrial applications because of their high cost. Effective catalyst for production of hydrogen by aqueous phase reforming of oxygenated hydrocarbons must break C-C, O-H and C-H bonds in the oxygenated hydrocarbon reactant and facilitate the water gas shift reaction to remove adsorbed Carbon from the surface. Ni is active & selective for production of hydrogen and also showing a particular interest to develop this catalyst is due to its low cost. The structural characteristic and performance of supported nickel catalysts are strongly by the nature of support where the metallic crystallites are deposited. The uses of support with high thermal stability that stabilizes nickel particles against sintering and that promote the carbon gasification are necessary to develop catalysts with high activity and stability in the steam reforming of glycerol.[12] Ni/Al₂O₃ enhances both steam adsorption and stability of nickel against sintering [14]. Among non-noble metal catalyst

Cu, Ni, Ir and Co were reported as most active metals[13]. The nature of metal and support contributes the selection of path for hydrogen generation. Highly acidic nature of support facilitate dehydration [15] of glycerol whereas basic nature ($\text{La}_2\text{O}_3, \text{MgO}, \text{SiO}_2$) or addition of promoters (alkali and alkaline earth metals) which reduce acidity [16], hinders dehydration and deactivation of catalysts by carbonaceous deposition. The higher capability of nickel to break C-C and O-H bond and hydrogenation, leading to molecular hydrogen formation makes it a best option for GSR (Glycerol Steam Reforming). Furthermore addition of alkali and alkaline earth metals effects the interaction between metal and adsorbed species[17] However $\gamma\text{-Al}_2\text{O}_3$ support was reported as highly active in terms of selectivity for different noble metals catalyst but optimum loading of metals is not same. Among non noble metal catalysts Ni is reported as highly active. Few non noble metals also show 100% glycerol conversion over other supports at low temperature but selectivity of hydrogen is relatively low. Nickel dispersion and nickel-support interaction with the type of the modifier added to Al_2O_3 . Al_2O_3 was explained in terms of the lower acidity and better dispersion achieved in the former, the most stable system resulted to be $\text{Ni/CeO}_2/\alpha\text{-Al}_2\text{O}_3$.

3.1 CATALYST PREPARATION

Glycerol (99.5% purity) was obtained from Fisher Scientific and 5 weight % of $\text{Ni/Al}_2\text{O}_3$ was used for this process. Now a day's many of the industries are using wet impregnation method for the preparation of catalyst. Impregnation is a means of supported catalyst preparation is achieved by filling the pores of a support with a solution of the metal salt from which the solvent is subsequently evaporated. The required amount of nickel is taken as Nickel nitrate hexa hydrate $\text{Ni}(\text{NO}_3)_6\text{H}_2\text{O}$ and diluted with 20ml of distilled water until the clear solution is formed. Then add 90gms of Al_2O_3 Support following by little amount of water, until the support gets immersed in the clear solution. Then the support is left a side till overnight. After that the excess amount of water is removed by using Rota vapor and the catalyst is separated and kept in oven for 4hrs at 100°C . Then the catalyst is calcined at 450°C for 5hrs. After calcinations are completed the catalyst is available as NiO. During Reduction NiO will convert into Ni in specified time. Normally the reduction will be done for 10-12 hrs. Among the catalysts studies were done for 10% $\text{Ni/Al}_2\text{O}_3$ which gives the maximum yield in which nickel is in interacted form.

3. Experimental section

All experiments were conducted over the $\text{Ni/Al}_2\text{O}_3$ catalyst to investigate the optimal operating conditions for hydrogen production by the steam reforming of glycerol in a fixed-bed stainless steel reactor. In these experiments, glycerol and water mixed at specific molar ratios were fed to the core of the reactor. Required amount of the catalyst ($\text{Ni/Al}_2\text{O}_3$) is weighed and that nickel catalyst was placed over a glass wool support is called catalyst bed. After loading of the catalyst Reduction of catalyst is a must procedure as it reduces the oxygen present over the catalyst as it gets passivated when it is kept for open air before loading. Thus oxygen gets passivated over Nickel forming Nickel oxide. The gas that is using for reducing is mixture of Hydrogen and Nitrogen gases. A catalyst will have its reducing temperature and it is known by performing TPR (Temperature programmed reduction). A catalyst will have its reducing temperature and it is known by performing TPR. HPLC (High performer liquid chromatography) pump was used to inject the feed solution into the reactor. Feed rate is to be calibrated by which the feed is pumped (HPLC pump). Feed contains mixture of Glycerol and water i.e. in 1: 9 molar ratios. The temperature should increase slowly from the ambient temperature by passing carrier gas (mixture of Hydrogen and Nitrogen gas). Temperatures are maintained by using PID controller. Thermo couples are provided inside and outside of the reactor to vary the skin and bed temperatures. Reactor is divided in to 4 zones. The feed was vaporized using a pre-heater placed before the reactor. Feed passes through the inert ceramic beds and through the catalyst. Catalyst is placed in 3rd zone, which is called as catalyst bed. In the catalyst bed one mole glycerol reacts with three moles water and excess un reacted water is obtained at the bottom as 'CONDENSATE.' The reactor is connected with condenser at the bottom. In the condenser un reacted gases are condensed and collected in the gas liquid separator. The outlet of the gases is connected with wet gas flow meter by which is gases are measured. After measuring the gases are sent out through outlet. Gas is collected in the gas collector. For optimization purposes,

the gas sample of all experiments was analyzed at the first hour of the reaction. The separated gases were sent to an online gas chromatography GC instrument for gas analysis. The responses that were investigated in this work were measured in terms of hydrogen yield and the conversion of glycerol into gaseous products. The response parameters were calculated according to the following equations:

Hydrogen Yield, % = [Hydrogen moles produced/Maximum moles of hydrogen (=7 × moles of glycerol fed)]*100

Glycerol conversion to gases, % = [C atoms in the gas product stream/Total C atoms in the feedstock]*100

4. Results and discussion

4.1 TEMPERATURE PROGRAMMED REDUCTION (TPR)

TPR analyses were performed to investigate the reducibility of Ni species present in the fresh catalysts and values of the catalyst are measured and the values are displayed in the table below. TPR profile of Treat well shows sharp intense peaks at 460⁰ C due to reduction of Ni⁺² species that are in no interaction with the support and TPR of 10 % Ni/Al₂O₃ shows that it is a three step reduction process but the more intense peaks are observed at 710⁰C which confirms that Ni⁺² species are strongly interacted with the Al₂O₃

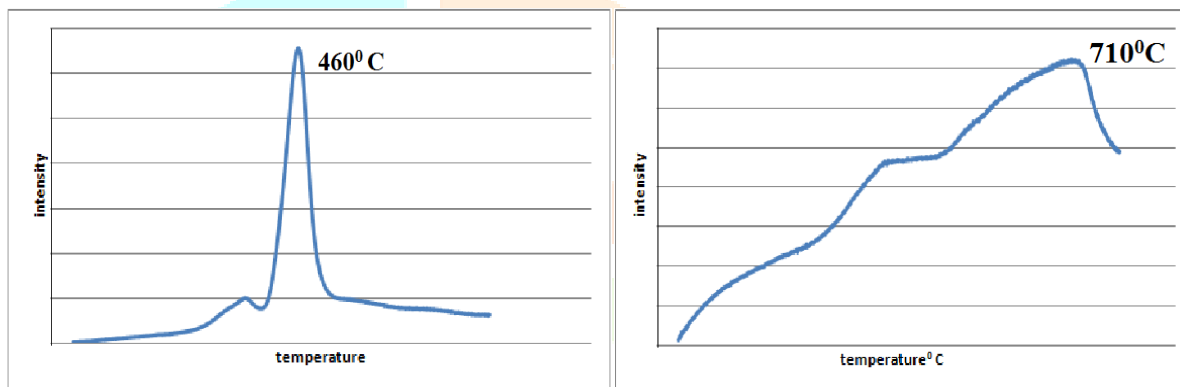


Fig.4.1 Treat well, 10% Ni/Al₂O₃

4.2 Scanning electron microscope (SEM)

Catalysts were characterized using SEM before the reaction. The images obtained for different catalysts before and after the reaction are shown in Figure 4.2 and 4.2.1. The fresh catalyst shows the homogeneous distribution whereas the heterogeneous morphology is observed in the used catalyst. It was observed that there was coke deposition after the reaction.

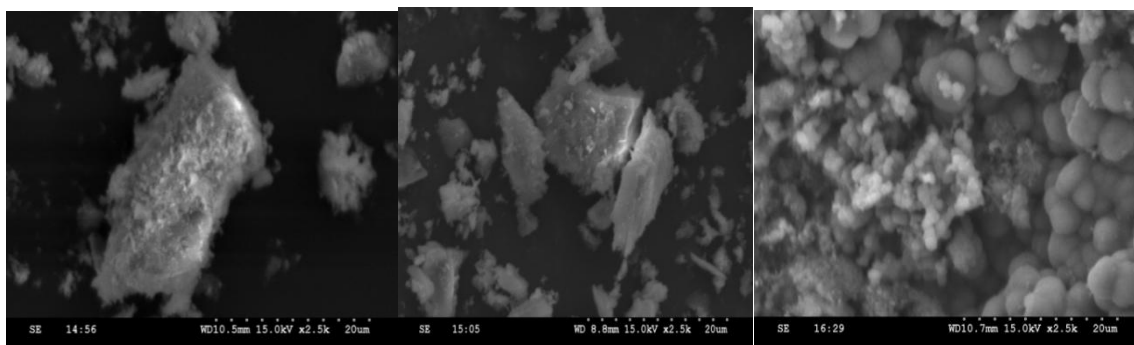


Fig.4.2 SEM images of 10% NA fresh, used, dust.

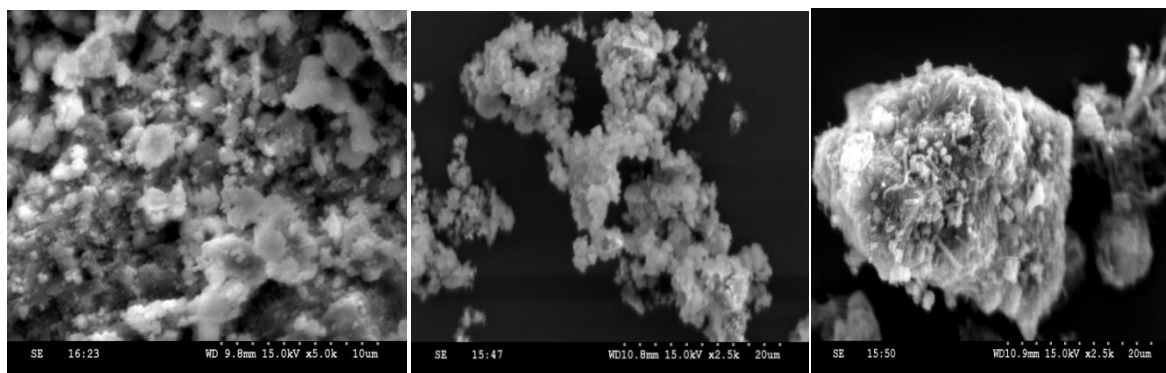


Fig.4.2.1SEM images of Treat well fresh, used and dust

4.3 X-Ray Diffraction (XRD)

X-ray diffraction was carried out to identify the phases present in different catalysts. X-ray diffractions patterns of fresh and used catalysts are shown in the Fig. 4.3. The diffraction pattern of X% Ni/Al₂O₃ fresh is in amorphous state and no crystalline peaks are observed. In the used catalyst the characteristic peaks of nickel are found at $2\theta = 44.38^\circ$ and at 51.72° . The sharp characteristic peaks of Ni confirm the formation of the crystals during the course of reaction. The diffraction patterns of Treat well fresh indicates that the sharp Ni crystal peaks are observed initially at $2\theta = 44.38^\circ$. In the XRD of the used catalysts Ni is observed at $2\theta = 44.38^\circ$ which confirms after post reaction NiO is reduced to Ni and the carbon peak at $2\theta = 25^\circ$ confirms coke is formed during the course of reaction. In treat well we can observe that the nickel peaks are large in comparison with the fresh sample.

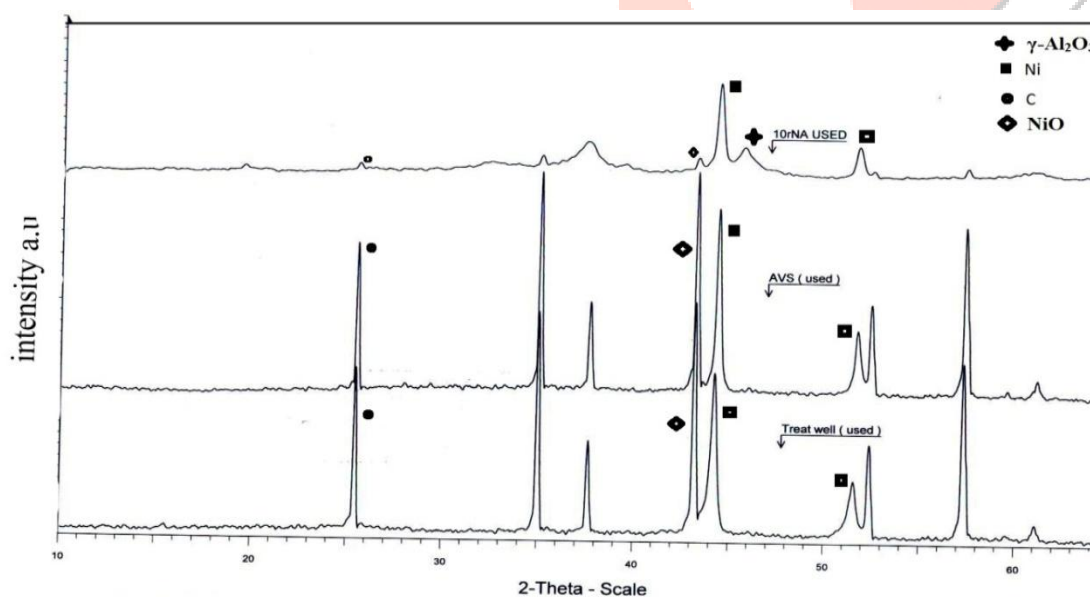


Fig.4.3 XRD graphs for 10% NA and Treat well dust

5.0 Reaction product analysis

The distribution of gases are analyzed through the gas chromatography and the results are discussed below

5.1 Time on stream

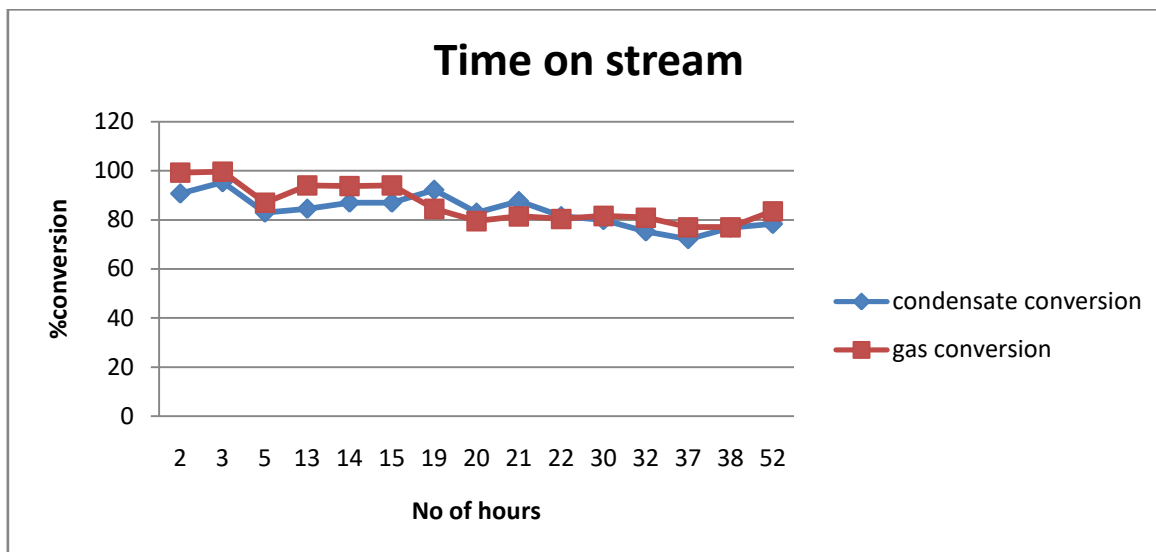


Fig.5.0 Time on stream with respect to %conversion

At the initial hours of the reaction gas based & liquid based conversions are high but as the reaction proceeds through there is gradual decrease in the conversions because of coke formation during the course of the reaction.

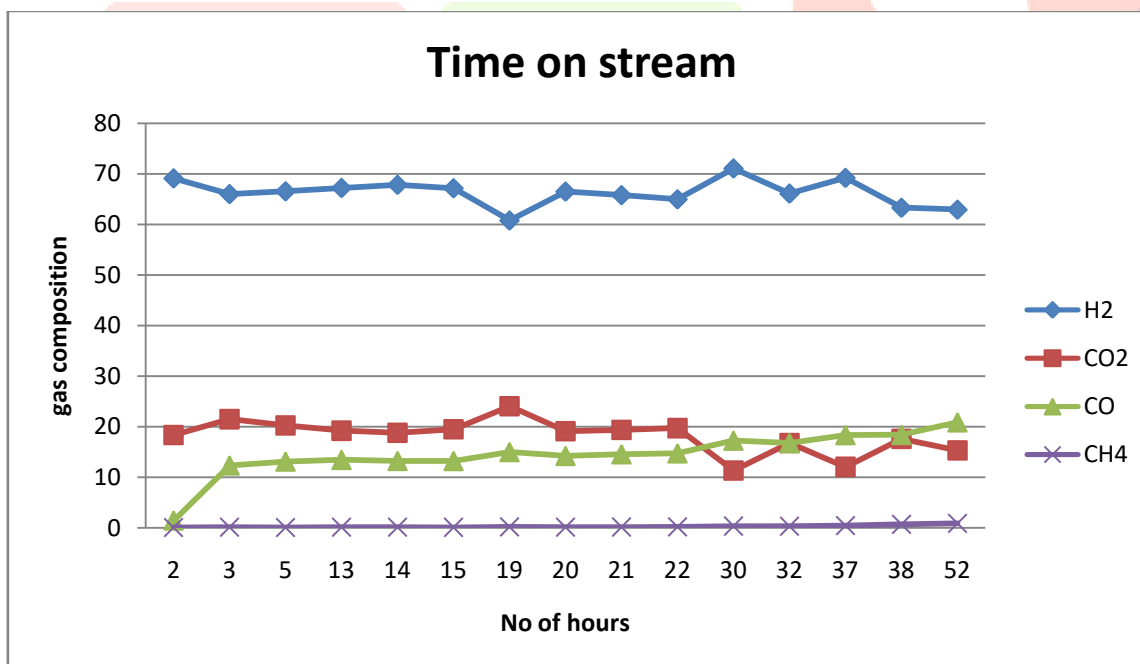


Fig.5.1 Time on stream with respect to gas composition

In the course of reaction the hydrogen composition is more or less the same but it decreases in the long runs because of unnecessary side reactions taking place which has same kinetics. But the CO₂ concentration is decreasing which simultaneously allows the gradual increase in the CO concentration is probably due to the occurrence of Reverse water gas shift reaction. If we create pressure inside the

reactor which increases its residence time, then we can definitely decrease the CO content in the product stream. Also CH_4 is almost constant during long runs of the reaction.

5.2 Effect of pressure

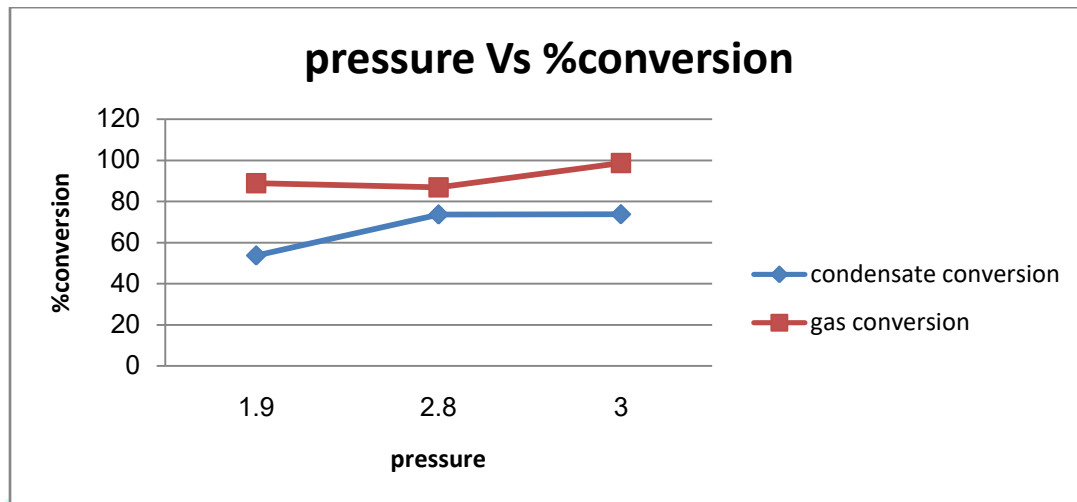


Fig.5.2 Effect of pressure with respect to %conversion

By increasing the pressure the gas based and condensate based conversions are increasing because of the more residence time. The reactants have more time to stay in contact with the surface of the catalyst which can definitely increase the conversions significantly.

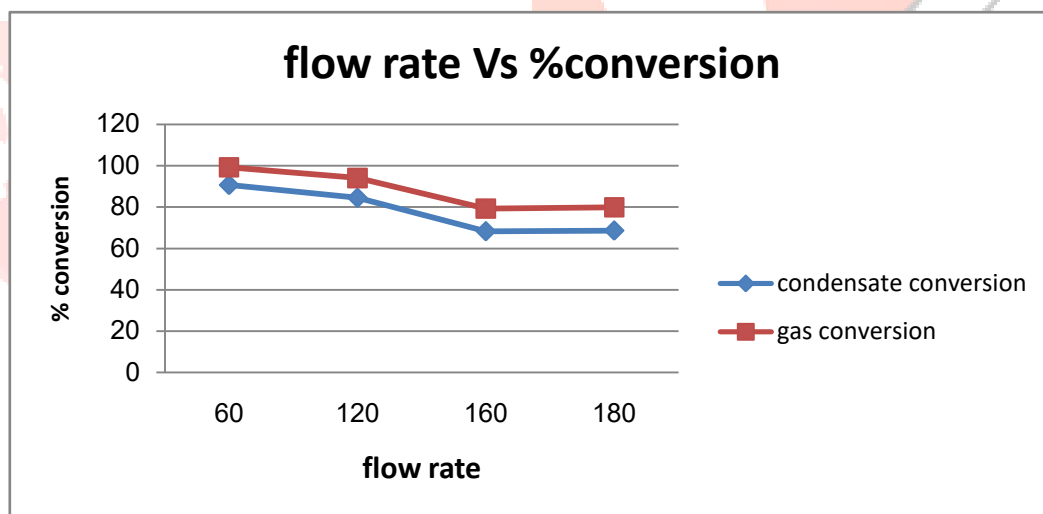


Fig.5.3 Effect of flow rate with respect to %conversion

5.3 Effect of flow rate

As the flow rate increases there is a gradual decrease in the conversions because of increase in space velocity for the particles, the reactants doesn't have much time to make contact with the catalyst which is a surface driven reaction.

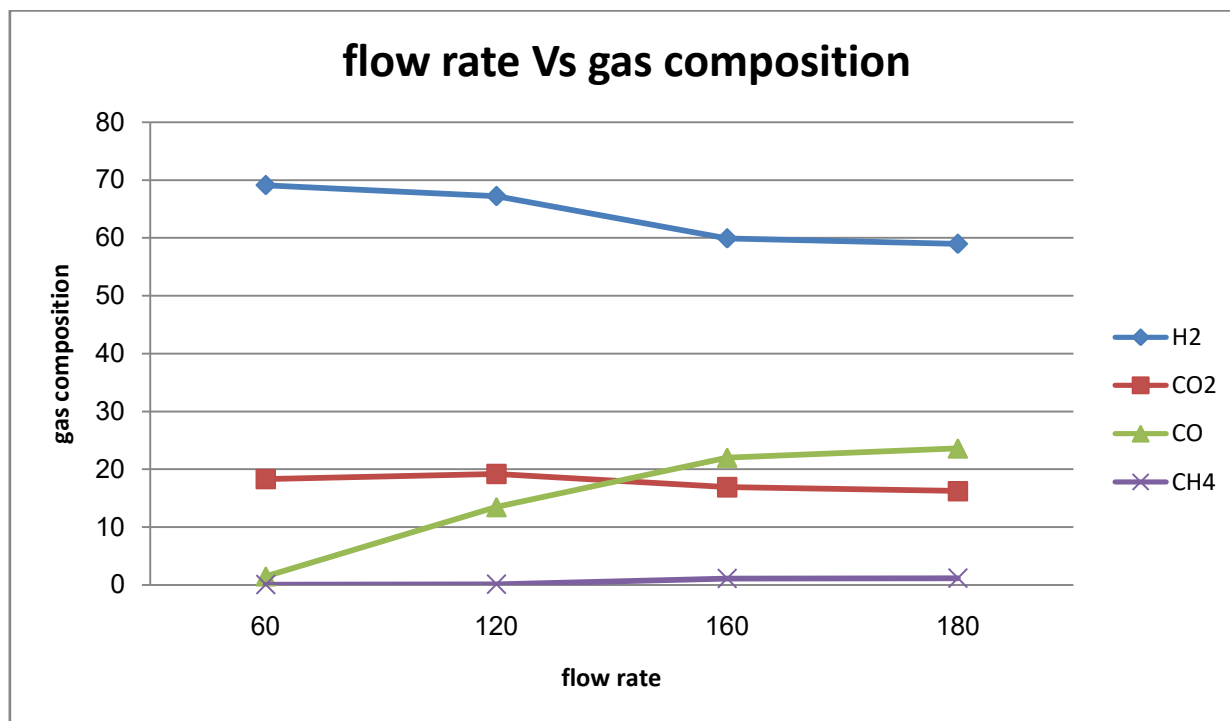


Fig.5.4 Effect of flow rate with respect to gas composition

As the flow rates increase there is a decrease in hydrogen selectivity which is followed by the shift in concentrations between CO and CO₂ because Water gas shift reaction is not occurring and due to increase in the flow rates there is a possibility to the formation coke which further hinders the product distribution.

6. Conclusions

Reforming of glycerol in steam over Ni/Al₂O₃ catalyst is an effective means of low pressure hydrogen production from a biomass-derived source. As pressure increases the methane concentration in the product gas is observed, thereby methanation reaction occurs, and it decreases the yield of hydrogen. Although near-theoretical hydrogen yields were obtained for dilute glycerol concentrations at 700°C, it was also found to be possible to completely gasify feed containing up to 40 wt% glycerol, but with increased methane formation. Hydrogen yields were found to increase directly with temperature and contact time. Methane formation can be reduced by increasing the water gas feed ratio so that we can reduce the formation of other byproducts also. It has been found effective catalyst for steam reforming of glycerol for hydrogen production. The catalysts studied Ni/Al₂O₃ gives the maximum yield in which nickel is in interacted form. The best operating conditions for Ni/Al₂O₃ are 700^o C and 120 ml/hr of feed rate.

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