

Preparation of Hydrogen from Glycerol via Steam Reforming Process

R. N. Reddy, S. S. Patel, Sai Kumar Nair and Y.V.N.S. Suvikram

Abstract-- The development of alternative sources of energy is becoming important in this era of diminishing petroleum reserves and increased environmental awareness. Hydrogen production from biomass has attracted great interest because of the potential application in fuel cells. 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. With increased production of biodiesel, a glut of glycerol ($C_3H_8O_3$) is expected in the world market, and therefore it is essential to find useful applications for glycerol. Finding alternative uses for glycerol is important.

Using glycerol as a source of producing hydrogen is a good possibility. Steam reforming is a promising way to utilize the diluted glycerol aqueous solution to produce hydrogen. Glycerin is a potential feed stock than ethanol for hydrogen production because one mole of glycerin can produce up to four moles of hydrogen.

An attempt is made to identify new catalyst with high selectivity towards hydrogen and sufficient reaction rate at mild conditions. The catalysts used in other processes are studied and their effects on temperature, contact time, and water to glycerol ratio, metal loading on hydrogen yield are investigated. Other considerations such as catalyst activity, catalyst lifetime and operating conditions are estimated for over all process economics. Thus, the paper covers the selection of process and catalyst, process parameters, catalyst properties and economics related to it.

Keywords: Hydrogen production, biomass, transesterification, steam reforming, catalyst activity, catalyst properties, economics

I. INTRODUCTION

THIS section deals with the introduction to glycerol, need of converting glycerol to hydrogen, steam reforming using catalyst.

1) Introduction to Glycerol:

Properties of Glycerol:

- Glycerol is a simple polyol compound.
- It is a colourless, odourless, viscous liquid that is widely used in pharmaceutical formulations.
- Glycerol is present in fats and oils in combination with fatty acids, both saturated and unsaturated.

Chemistry:

Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol backbone is central to all lipids known as *triglycerides*. Glycerol is sweet-tasting and of low toxicity. The term polyglycerol refers to many glycerol molecules together.

Glycerol can be produced by saponification of fats, e.g. a byproduct of soap-making. Saponification is also referred to as the hydrolysis of esters in basic solutions or environments. The mechanism of this reaction involves a very rapid equilibrium where the alkoxide functions as a base deprotonating the carboxylic acid.

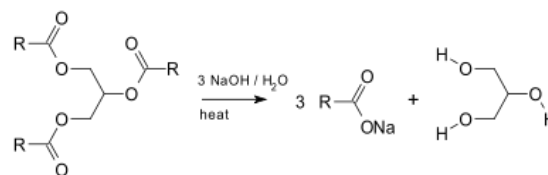


Fig. 1.1 Saponification reaction that produce Glycerol as byproduct

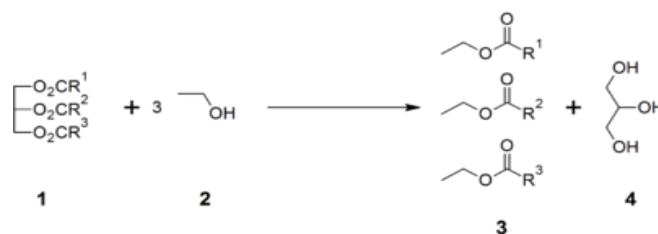


Fig. 1.2 Transesterification that produce Glycerol as byproduct

It also is a byproduct of the production of biodiesel via transesterification. Triglycerides (1) are reacted with an alcohol such as ethanol (2) with catalytic base to give ethyl esters of fatty acids (3) and glycerol (4).

Uses of Glycerol:

- Glycerin is used in food industry, Pharmaceutical and personal care applications, antifreeze.
- It is also used in production of various chemical intermediates like citric acid, lactic acid, 1,3-propane diol, acrolein, hydrogen, ethanol etc.

2) Need of Converting Glycerol to Hydrogen:

Alternative energy resources are becoming increasingly important because of dwindling petroleum reserves and mounting environmental concerns that are associated with fossil fuel utilization. Consequently, alternative bio-based fuels are emerging as the long-term solution. Over the last few years, the demand and production of biodiesel has increased tremendously. With the production of biodiesel, glycerol is being produced as a byproduct and several efforts are being made to utilize excess glycerol and produce valuable added products.

At present, almost 95% of the hydrogen is being produced from fossil fuel-based feed stocks and most is used as a chemical ingredient in petrochemical, metallurgical, goods and electronic processing industries. Demand for hydrogen, the simplest and most abundant element, is growing due to the technological advancements in fuel cell industry.

If the present scenario in the production of hydrogen exists, the more carbon will be converted in to carbon dioxide, leading to global climatic changes. Renewable resource-based technologies for hydrogen production are seen in viable options for the future due to the carbon neutral nature with lesser effects on global climate.

II. METHODS OF PRODUCTION OF HYDROGEN FROM GLYCEROL

Glycerin is a potential feed stock than ethanol for hydrogen production because one mole of glycerin can produce up to four moles of hydrogen. Various methods used for production of hydrogen from glycerin are

- Steam reforming by using catalyst
- Partial oxidation
- Aqueous phase reforming
- Supercritical water reforming

1) Steam Reforming Process using catalyst

Introduction

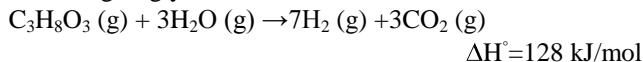
The steam reforming is the most commonly used method for producing hydrogen in the chemical industry. In this process, the substrate is reacted with steam in the presence of a catalyst to produce hydrogen, carbon dioxide, and carbon monoxide. The steam reforming of hydrocarbons has been the preferred method for many decades for industrial scale hydrogen production.

Properties of Steam Reforming:

Steam reforming is a high temperature endothermic process which uses a catalyst to react the glycerol with water to produce hydrogen.

Chemical Reaction

The overall reaction of hydrogen production by steam reforming of glycerol is as follows:



Catalysts

Many researchers investigated the effects of catalysts on the steam reforming of glycerol for hydrogen production. The various types of catalyst which are in use are Nickel-based catalysts with MgO, CeO₂, and TiO₂ supports. Besides nickel based catalysts, other type of catalyst like Ir, Co, Ru/Y₂O₃, Ir/CeO₂ are also used.

Adhikari et al. focused on the study of nickel-based catalyst with MgO, CeO₂, and TiO₂ supports. They found that maximum hydrogen yield that is, 4 mol of hydrogen out of 7 mol of stoichiometric maximum, could be obtained at 650 °C with MgO supported catalysts.

Irion do et al. modified alumina –supported nickel catalysts with Ce, Mg, Zr and La to produce hydrogen from glycerol. Among the ceria-supported metal catalysts examined, the Ir/CeO₂ catalyst showed promising catalytic performance with more than 85% hydrogen selectivity and 100% glycerol conversion at 400 °C.

Process Parameters

Optimal conditions for production of hydrogen from glycerin were found to be as follows:

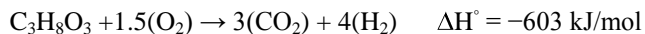
Temperature	= 925-975 K
Water/glycerin ratio	= 12
Pressure	= 1 atmosphere
Desired output	= The maximum number of 6.2 moles of hydrogen can be produced with one mole of glycerin.

2) Partial Oxidation

Introduction

Partial oxidation is the process in which a substrate is reacted with oxygen at sub-stoichiometric ratios.

Reaction



Dauenhauer *et al.* performed glycerol oxidation at different carbon-to-oxygen (C/O) ratios and temperatures using noble metal catalysts. Partial oxidation of glycerol at reactant steam-to-carbon ratio (S/C) = 0 achieved equilibrium H₂ selectivity for all C/O ratios <1.3 with a maximum of 56% at C/O = 1.2.

2) Autothermal Reforming

Introduction

Autothermal reforming process combines the effect of partial oxidation and steam reforming by feeding fuel, air, and water together into the reactor.

Reaction

$C_3H_8O_3 + O_2 + H_2O \rightarrow 3(CO_2) + 5(H_2)$ $\Delta H^\circ = -269$ kJ/mol
Dauenhauer *et al.* found that the addition of steam at S/C = 4.5 increased the equilibrium H₂ selectivity by 30 – 40%. However, the observed H₂ selectivity from glycerol departed from equilibrium for C/O > 1.0, producing a maximum of 79% selectivity to H₂. High selectivities to H₂ were achieved by adjusting the fuel/air and fuel/steam feed ratios.

Swami *et al.* conducted autothermal reforming at a steam-to-carbon ratio of 3 and an oxygen-to-carbon ratio of 0.3 in the range of 550-850 °C using the Pd/Ni/Cu/K catalysts. Their results showed that the hydrogen yield during autothermal reforming was greater than that of steam reforming, though the hydrogen yield for both reactions increased with temperature.

Douette *et al.* performed a series of tests using a factorial experimental design to determine the effects of the operating parameters, including C/O and S/C ratio, and temperature. A 4.5 mol quantity of hydrogen was produced per mole of reagent-grade glycerin at oxygen to carbon ratio of 0, S/C ratio of 2.2, and temperature of 804 °C. Initially, similar hydrogen yield was obtained when using crude glycerin, the by-product of biodiesel production. However, due to the catalyst deactivation and coke and deposit formation in the reformer, the hydrogen yield decreased quickly. This may be correlated with the possible contaminants, chloride and sodium cations, present in crude glycerin.

3) Aqueous-Phase Reforming

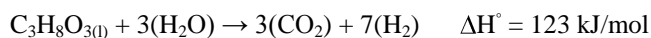
Introduction:

The aqueous-phase reforming (APR) process was established by Cortright *et al.* using platinum based catalysts and mild reaction conditions (200-250 °C, 20-25 bar) for the production of hydrogen and light alkalines from oxygenated hydrocarbons.

Lehnert *et al.* used several platinum based catalysts for catalytic conversion of glycerol to hydrogen by APR. Their study indicated that the catalytic reaction selectivity to hydrogen increased with increasing particle size from 78% to 95% while the conversion of glycerol remained almost constant at 20%.

Furthermore, it was found that the mixture of γ -, δ -, and θ -phase can increase the hydrogen production to $7.6 * 10^{-3}$ mol min⁻¹/g_{cat}, compared with pure γ -alumina ($1.2 * 10^{-3}$ mol min⁻¹/g_{cat}). Crude glycerol can also be used as starting material. However, the rate of hydrogen production was lower than for pure glycerol due to the impurities, such as NaCl.

Reaction



4) Supercritical Water Reforming

Introduction

Supercritical water, defined as water that is heated and compressed at its critical temperature (374 °C) and pressure (22.1 MPa), is a promising medium for reforming of glycerol to produce hydrogen.

Byrd *et al.* selected Ru/Al₂O₃ as the catalyst to generate hydrogen from glycerol by supercritical water reforming. Their experiments revealed that hydrogen yields increased directly with temperature and near-theoretical yield of **7 mol of hydrogen/mol of glycerol** could be obtained at dilute feed concentrations at 800 °C. Also, it was found that up to 40 wt% glycerol in the starting material could be completely gasified.

III. FACTORS AFFECTING FORMATION OF HYDROGEN FROM GLYCEROL

- Glycerol concentration (steam to carbon molar ratio)
- Temperature of reaction
- Pressure
- Flow rates of glycerol feed
- Catalyst loading
- Water to glycerol ratio
- Space Time and Space Velocity

IV. CATALYST USED IN THE PROCESS

1) Preparation of Catalyst

Following methods are used to prepare catalysts

1.1) Deposition-precipitation method

This method comprises application of active component onto an existing support via chemical reaction. The reaction forms an insoluble compound which involves the active element.

The insoluble compound can be formed by an increase of the pH of the solution, a valence change of the element in question and the like. Under certain conditions, such as a suitable interaction between the compound and the carrier, the preparation has a number of unique features, e.g. a uniform distribution of the active component over the carrier surface even at high loadings

1.2) Wet impregnation method

Impregnation as 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 catalyst is prepared either by spraying the support with a solution of the metal compound or by adding the support material to a solution of a suitable metal salt, such that the required weight of the active component is

incorporated into the support without the use of excess of solution.

TABLE 1.1.
CATALYSTS AND OPERATING CONDITIONS FOR STEAM REFORMING OF GLYCEROL

Catalysts and Operating Conditions used for STEAM REFORMING of Glycerol		
Catalyst	Operating Conditions	Remarks
Ir/CeO ₂ , Ni/CeO ₂ , Co/CeO ₂	Temperature = 400–550 °C Mass of catalyst : 200 mg 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 °C. ^[24]
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 C Steam-to-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 °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 °C Steam-to-carbon ratio (S/C) = 2.1 and 2.6	The yield of hydrogen was 23.6 g/100 g of glycerol (77% of stoichiometric yield) at S/C of 2.6. ^[26]
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 = 0.15–0.5 mL/min Temperature = 600–900 °C Steam/carbon molar ratio (S/C) = 1/3–3.0	About 80% of hydrogen selectivity was obtained with Ni/Al ₂ O ₃ , whereas the selectivity was 71% with Rh/CeO ₂ /Al ₂ O ₃ at a S/C = 3, 900 °C temperature, and feed flow rate of 0.15 mL/min. ^[27]
Ni/MgO, Ni/CeO ₂ , Ni/TiO ₂	Feed flow rate = 0.5–0.7 mL/min Temperatures = 550–650 °C Steam/carbon molar ratio (S/C) = 2–4 Catalyst loading = 0.75–1.5 g (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 a S/C ratio of 4, temperature of 600 C, and a feed flow rate of 0.5 mL/min compared to Ni/MgO (38.6%) and Ni/TiO ₂ (28.3%) under similar conditions. ^[29]
Pt/Al ₂ O ₃	Temperature = 880 °C Glycerol flow per kg catalyst = 0.12 mol/min S/C = 2.5	Hydrogen selectivity of 70% and glycerol conversion to gas 100%. ^[30]
Pt supported on Al ₂ O ₃ , ZrO ₂ , CeO ₂ /ZrO ₂ , MgO/ZrO ₂ , and Carbon	Temperature = 350 °C Pressure = 1 bar Aqueous glycerol feed solution (30 wt.%) over oxide supported Pt catalysts (1.0 g) or Pt/C catalyst (0.060 g) and a feed flow rate of 0.32 cm 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 C and pressure = 1 bar, 100% glycerol conversion was achieved at feed rate of 0.32 cm ³ min ⁻¹ ^[31]
Pd/Ni/Cu/K supported on c-Al ₂ O ₃	Temperature = 550–850 °C S/C = 3.0	Hydrogen yield was 42% at 850 °C. ^[32]
Ni/c-Al ₂ O ₃ modified with Mg, Ce, La, Zr.	Temperature = 600 °C Concentration = 1 wt.%	100% conversion was achieved with all the catalysts. Catalyst promoted with Zr showed the highest H ₂ selectivity. ^[28]

1.3) Co-precipitation

An example of this technique is the coprecipitation of metal ions with aluminium ions to produce a precipitated alumina gel containing the metal hydroxide. This precipitate when

calcined produces a refractory support with active component dispersed throughout the bulk as well as at the surface.

However, in the preparation of multicomponent catalysts, it is possible under improper conditions to obtain a heterogeneous product because of the different solubility products of the constituents.

1.4) Combustion

Combustion Synthesis, the exothermicity of the redox (reduction–oxidation or electron transfer) chemical reaction is used to produce useful materials. Depending upon the nature of reactants: elements or compounds (solid, liquid or gas); and the exothermicity (adiabatic temperature, T), Combustion Synthesis is described as:

- Self-propagating high temperature synthesis (SHS)
- Low-temperature combustion synthesis (LCS),
- Solution combustion synthesis (SCS),
- Gel-combustion, Sol–gel combustion
- Emulsion combustion, volume combustion (thermal explosion), etc.

2) Properties of the catalyst to be characterized

- Density
- Pore volume
- Pore size and size distribution
- Surface area
- Crushing strength
- Homogeneity
- Chemical structure
- Surface reactivity

3) Characterization of selected catalyst:

The following instruments are used to characterize various properties of catalys

3.1) Powder X ray diffraction (XRD):

X-ray diffraction (XRD), X-ray scattering techniques and computed tomography (CT) are versatile, non-destructive methods that reveal detailed information about the chemical composition, crystallographic and micro structure of all types of natural and manufactured materials.

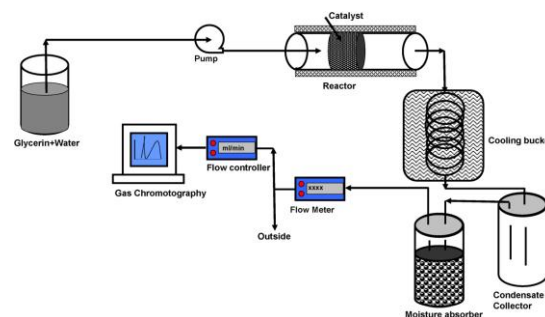
3.2) Micrometrics micro pore surface area analyser:

Surface area analysers rapidly and reliably produce accurate and repeatable surface area and porosity results. Their low cost, high speeds, simplicity of use, reliability, and ruggedness have earned them best option for surface area analyser.

3.3) Catalyst scanning Electron micrograph:

A micrograph or photomicrograph is a photograph or similar image taken through a microscope or similar device to show a magnified image of an item. A microphotograph is a very small picture, e.g. a microdot. Microphotography is the production of such very small photographs. Two important applications of microphotography were the creation of computer chips and the creation of microdots to hide information. An electron micrograph is a micrograph prepared using an electron microscope.

V. EXPERIMENTAL SET-UP^[23]



The experiments are carried out in a tubular furnace at a constant flow rate of 0.5 ml/min unless otherwise mentioned and at four furnace temperatures from 600 to 900 °C.. The furnace temperatures could reach up to 1100 °C. Glycerin and water were mixed in a separate container and the mixture is supplied into the reactor using a HPLC pump. As depicted in fig. of experimental set up, the coated monoliths were placed in the middle of the tubular reactor. Monoliths were held at the center of the reactor with the help of alumina cloths. Molar concentration of glycerin and water is 1:6, which is kept constant throughout the process.

Gas stream from the reactor was cooled using crushed ice and water. The un-reacted water and other liquids formed during the reaction were collected. The outlet gas was sent through a moisture trap before purging to the gas chromatograph. H₂ content in the outlet was analyzed by a thermal conductivity detector with Molecular Sieve column. The concentrations of carbon monoxide (CO), methane (CH₄), and CO₂ were analyzed by a flame ionization detector with HP-Plot Q column. Only four gases including H₂ were analyzed in this study.

The performance of the catalyst is presented in terms of H₂, CO, CH₄, and CO₂ selectivity, and glycerin conversion.

Selectivity and the glycerin conversion were calculated based on the following equations:

$$\% \text{ H}_2 \text{ selectivity} = \frac{\text{H}_2 \text{ moles produced}}{\text{C atoms produced in gas phase}} \times \frac{1}{\text{RR}} \times 100$$

where RR is H₂/CO₂ reforming ratio and it is 7/3 in the case of glycerin steam reforming process.

$$\% \text{ Selectivity of } i = \frac{\text{C atoms in species } i}{\text{C atoms produced in gas phase}} \times 100$$

where species i = CO, CO₂, and CH₄.

$$\% \text{ Conversion} = \frac{\text{C atoms in gas products}}{\text{Total C atoms in the feedstock}} \times 100$$

VI. REFERENCES

- [1] Sushil Adhikari, Sandun D.Fernando, Agus Haryanto. Hydrogen production from glycerin by steam reforming over nickel catalysts. *Renewable Energy* 33(2008), 1097-1100.
- [2] Adam J.Byrd, K.K.Pant, Ram B.Gupta. Hydrogen production from glycerol by reforming in supercritical water over Ru/Al₂O₃. *Fuel* 87(2008), 2956-2960.
- [3] Xiaohu Fan, Rachel Burton and Yongchang Zhou. Glycerol (Byproduct of Biodiesel production) as a source of fuels and chemicals-Mini Review. *The open fuels and Energy Science Journal*, 2010, 3, 17-22.
- [4] Sushil Adhikari, Sandun D.Fernando, Agus Haryanto. Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts. *Catalysis Today* 129(2007), 355-364.
- [5] Nianjun.Luo,Xianwen Fu,Fahi Cao, Tiancum Xiao, Peter P.Edwards. Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst- Effect of catalyst composition and reaction conditions. *Fuel* 87(2008), 3483-3489.
- [6] Robinson L. Manfro, Aline F.da Costa, Nielson F.P.Ribeiro, Mariana M.V.M.Souza Hydrogen production by aqueous-phase reforming of glycerol over nickel catalysts supported on CeO₂. *Fuel Processing Technology* 92(2011), 330-335.
- [7] Derya Oncel Ozgur, Bekir Zuhtu Uysal. Hydrogen production by aqueous phase catalytic reforming of glycerine. *Biomass and BioEnergy* 35(2011), 822-826.
- [8] Sushil Adhikari, Sandun D.Fernando, Agus Haryanto. Energy Conversion and Management. *Energy Conversion and Management* 50(2009), 2600-2604.
- [9] Antonio Carlos Caetano de Souza, Jose Luz Silveira. Hydrogen production utilizing glycerol from renewable feedstocks – The case of Brazil. *Renewable and Sustainable Energy Reviews* 15(2011), 1835-1850.
- [10] V.Chiodo, S.Freni, A.Galvagno, N.Mondello, F.Frusteria. Catalytic features of Rh and Ni supported catalysts in Steam Reforming of glycerol to produce Hydrogen. *Applied Catalysis A:General* 381(2010),1-7.
- [11] K.K.Pant, Ruchin Jain, Sapna Jain. Steam reforming of glycerol to produce Hydrogen over Ni/CeO₂ Catalyst.
- [12] Adhikari S.Fernando, A.Haryanto. A thermodynamic analysis of Hydrogen by steam reforming of glycerol. *International Journal of Hydrogen Energy* 32(2007), 2875-2880.
- [13] Marek Stelmachowski. Utilization of glycerol, A byproduct of the Tranesterification process of vegetable oils: A Review. *Ecological chemistry and Engineering*, Vol.18 No.1 (2011).
- [14] Binlin Dou, Valerie Dupont, Gavin Rickett, Neil Blackeman. Hydrogen production by sorption-enhanced steam reforming of glycerol. *Bio resource Technology* 100(2009), 3540-3547.
- [15] Guangxing Yand Yu, Feng peng, Hongjuan Wang, Jian Yang, Donglaixie. Thermodynamics analysis of Hydrogen generation via oxidative steam reforming of glycerol. *Renewable Energy* 36(2011), 2120-2127.
- [16] Chinkuicheng,Say Yai Foo, Adesoji A Adesina. Hydrogen rich synthesis gas production over Co/Al₂O₃ Catalyst via glycerol steam reforming. *Catalysis Communication* 12(2010), 292-298.
- [17] Patel S., Pant. K.K. Kinetic modeling of oxidative steam reforming of Methanol over Cu/ZnO/CeO₂ /Al₂O₃ Catalyst. *Applied catalysis A: General* vol.356, Issue.2 pp.189-200(2009).
- [18] David B. Levin, Richard Chahine. Challenges for renewable hydrogen production from biomass. *International Journal of Hydrogen Energy* 35 (2010), 4962-4969.
- [19] Evandro Brum Peveiva, Pilar Ramirez dela piscine, Navies Homs. Efficient hydrogen production from Ethanol and glycerol by vapour-phase reforming processes with new cobalt-based catalysts. *Bioresource Technology* 102(2011), 3419-3423.
- [20] Haisen chen, YulongDing, Ngoc T.Cong, Binlin Dou, Valerie Dupont, Mojlab Ghadire, Paul T. Williams. A comparative study of Hydrogen production from Steam-glycerol reforming, thermodynamics and experimental. *Renewable Energy* 36(2011), 779-788.
- [21] Nianjun Luo, Xun Zhao, Fahai Cao, Tiancun Xiao and Dingye Fang. Thermodynamic Study on Hydrogen Generation from Different Glycerol Reforming Processes. *Energy & Fuels* 2007, 21, 3505-3512
- [22] R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angew. Chem. Int. Ed.* 45 (2006) 3982.
- [23] Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int J Hydrogen Energy* 2007;32(13):2367-73.
- [24] Hirai T, Ikenaga N-o, Mayake T, Suzuki T. Production of hydrogen by steam reforming of glycerin on Ruthenium catalyst. *Energy Fuel* 2005;19:1761-2.
- [25] Czernik S, French R, Feik C, Chornet E. Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion process. *Ind Eng Chem Res* 2002;41:4209
- [26] Adhikari S, Fernando S, Haryanto A. Production of hydrogen by steam reforming of glycerin over alumina supported metal catalysts. *Catal Today* 2007;129(3-4):355-64.
- [27] Iriando A, Barrio VL, Cambra JF, Arias PL, Guemez MB, Navarro RM, et al. Hydrogen production from glycerol over nickel catalysts supported on Al₂O₃ modified by Mg, Zr, Ce or La. *Top Catal* 2008;49:46-58.
- [28] Adhikari S, Fernando S, Haryanto A. A comparative thermodynamic and experimental analysis on hydrogen production by steam reforming of glycerin. *Energy Fuel* 2007;21(4):2306-10.
- [29] Slinn M, Kendall K, Mallon C, Andrews J. Steam reforming of biodiesel byproduct to make renewable hydrogen. *Bioresour Technol* 008;99:5851-8.
- [30] Soares RR, Simonetti DA, Dumesic JA. Glycerol as a source for fuels and chemicals by low-temperature catalytic processing. *Angew Chem Int Edit* 2006;45:3982-5.
- [31] Swami SM, Abraham MA. Integrated catalytic process for conversion of biomass to hydrogen. *Energy Fuel* 2006;20:2616-22.
- [32] Douette AMD, Turn SQ, Wang W, Keffer VI. Experimental investigation of hydrogen production from glycerin reforming. *Energy Fuel* 2007;21:3499-504.
- [33] Lehnert K, Claus P. Influence of Pt particle size and support type on the aqueous-phase reforming of glycerol. *Catal Commun* 2008;9:2543-6.
- [34] Luo N, Fu X, Cao F, Xiao T, Edwards PP. Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst—effect of catalyst composition and reaction conditions. *Fuel* 2008;87:3483-9.
- [35] Dauenhauer PJ, Salge JR, Schmidt LD. Renewable hydrogen by autothermal steam reforming of volatile carbohydrates. *J Catal* 2006;244:238-47.
- [36] Cortright RD, Davda RR, Dumesic JA. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 2002;418:964-6.