



Hydrogen generation by steam reforming process from glycerin over Ni, Li-Al₂O₃ catalyst

Md. Suruzzaman^{a*}, Li Lei^b, Guo Wali^c

^{a,b,c} Department of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang, Liaoning 110142, China

^aEmail: shohel.rana43@gmail.com

^bEmail: lilei1204@126.com

^cEmail: gw13730@yahoo.com.cn

Abstract

Ni catalyst had good catalytic activity for hydrogen generation from glycerin. The results showed that, 15 % Ni and 2 % Li loading was the best loading. The best impregnation sequence was dipping Li first and then Ni. 15 % Ni, 2 % Li-Al₂O₃ catalyst was suitable for hydrogen generation. The suitable operation conditions were temperature 600°C, glycerol liquid space velocity of 0.24h⁻¹ and water/alcohols ratio: 16. In these conditions, the hydrogen generation rate was up to 6.2. Ni was the active component and Li changed the carrier's pore structure by increasing catalysts resistance of carbon deposition.

Keywords: Glycerin; fuel cell; steam reforming; hydrogen; catalysts.

1. Introduction

Day to day huge consumption and limitation of natural resource, it has become essential to find an alternative way which can be sustainable and renewable energy source [1]. Biodiesel has been attracted and now commercially produced due to its environmental benefits and national energy security [2]. As the biofuel production significantly increasing by the transesterification of vegetables oil where almost 10 % (w/w) glycerin produced as a byproduct.

* Corresponding author.

E-mail address: shohel.rana43@gmail.com

Several applications of glycerin negotiable in different areas such as in food, cosmetics and pharmaceutical and other industries, although it is costly to refine crude glycerin for small and medium sized plants [3, 4]. Hydrogen generation can be the most acceptable way from byproduct glycerin. Hydrogen is the easiest and abundant element for the fuel industry[5]. Now, it has been essential to find a renewable and sustainable raw material source for hydrogen generation where approximately 95 % H₂ produced from fossil fuel-based feed stocks which are nonrenewable and also create environmental problems [6]. Several processes such as aqueous-phase reforming (APR) [7, 8], gasification[9], auto thermal reforming [10], supercritical water reforming [11] and steam reforming [12] processes use to produce hydrogen.

In this paper, steam reforming process studied where certain catalysts contributed to yield the hydrogen generation and carbon deposition. γ -Al₂O₃ as a carrier used because of cheaper, high availability and low reactivity characteristics although observed some disadvantages for example low reactivity and surface area affecting the metallic dispersion and the metal-support interaction [13]. Catalysts such as Pt, Ni, Ru, Pd and Ir mentioned good activity and selectivity for hydrogen generation for aqueous-phase reforming process [7, 8, 14, 15]. Even combination with Sn to Ni catalyst accelerated the selectivity for hydrogen production and decreased the selectivity toward the alkane formation which reported by Dumesic Research [16-18]. Here in this paper, Li was effectively increased the resistance for carbon deposition, and the best capacity was 2 %. It was observed Li should be dipped after dipping Ni, and 15 % Ni 2 % Li-Al₂O₃ catalyst had best stability, catalytic activity and resistance of carbon.

2. Experimental methods and procedures

2.1 Catalyst preparation

The catalyst was prepared by impregnation method. A certain amount of alumina put into muffle furnace and calcined for 5 hours while 600 °C temperature was used to obtain γ -Al₂O₃ as a carrier. Nickel nitrate was added with a certain amount of deionized water to make Ni dipping solution. Lithium Nitrate also was added with a certain amount of deionized water to make Li dipping solution. γ -Al₂O₃ carrier was weighed and impregnated into the impregnating solution for 12 hours at 120 °C in oven and dried to 7 hours at 600 °C then calcined was used a muffle furnace for 6 hours which showed in figure 1(a) .

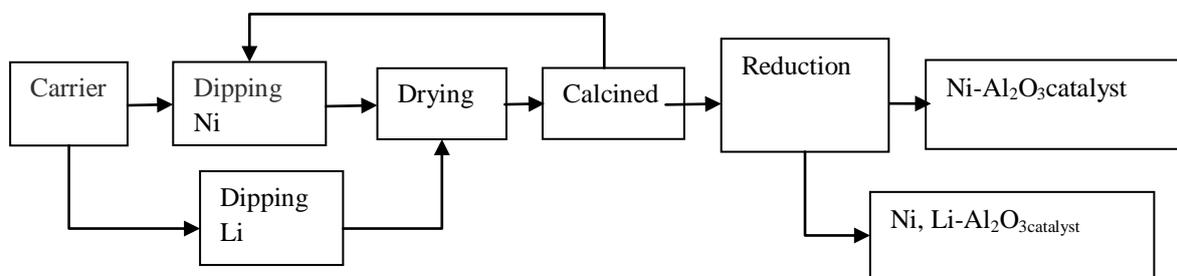


figure 1 (a) . Catalyst flow chart

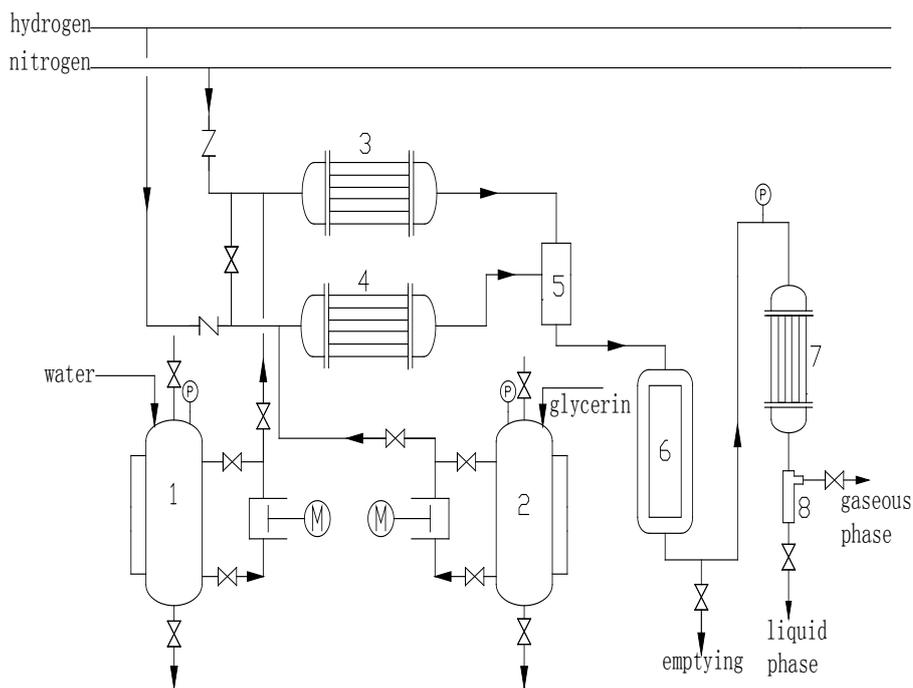
Before using catalyst should be reduced according to hydrogen reduction method by following way: catalyst kept into the tubular reactor with 700 °C temperature. N₂ was purged before heating piping. Temperature increasing led to high purity hydrogen. The reduction of catalyst was done at 700 °C for 4 hours.

2.2 Characterization catalyst

Surface area is the total surface area per unit mass of material; the total surface area per gram of substance, unit: m²/g. Catalyst surface area was characterized by SSA-4300-type surface area analyzer. The instrument principle was based on the analysis of multi-layer adsorption theory, by BET equation.

2.3 Steam reforming process

Glycerol and water were used for the superheated steam gasification which was mixed by a static mixer. Then imported into the tubular reactor for steam reforming. After the reaction it went through the condenser divided into two parts: liquid and gas. Condensate and gas products were collected from liquid phase and analyzed by gas chromatography. Flow chart of the reaction showed in Fig 1(b).



1--water tank; 2--glycerin storage tank; 3--water vapor chamber;
4--glycerol vaporization chamber; 5--static mixer; 6--reactor; 7--condenser; 8--cold trap

Figure 1(b): Glycerin steam reforming process

Reaction products were divided into gas and liquid. Gas products contained N₂, H₂, CH₄, CO, CO₂. SP-2100 gas chromatograph was used for testing compositions. Liquid was collected with a cold trap, and then GC112A gas chromatograph was used for the condensate unreacted glycerol analysis.

2.4. Analysis methods (liquid, gas)

2.4.1. Condensate analysis

GC112A gas chromatograph was used for analyzing glycerol condensate. Area normalization of quantitative methods was used by using FID detector to determine the composition and content of the condensate in order to calculate the unreacted amount of glycerol.

Preparations of sample solution: measured 2ml condensate 50ml in the jar, added 20ml ethanol, shook well. GC112A gas chromatograph analysis test conditions shown in Table 1.

Table 1. GC112A analysis of test conditions

| chromatography name | stationary phase | oven temperature (°C) | detector temperature (°C) | injector temperature (°C) |
|---------------------|------------------|-----------------------|---------------------------|---------------------------|
| GC112A | SE-54 | 220 | 300 | 300 |

N₂ carrier gas: 0.04MPa, and the volume: 0.02μL

2.4.1. Gas product analysis

GC112A gas chromatograph was used to analyze the glycerol hydrogen gas products by Dual-valve two-pillar system. Correct normalization of quantitative methods were used by using TCD detector to determine the gas composition and content of the product. SP-2100 gas chromatograph was analyzed the test conditions which showed in Table 2.

Table 2. SP-2100 analysis test conditions

| chromatography name | stationary phase | oven (°C) | detector temperature (°C) | injector temperature(°C) | Sample Injection |
|---------------------|-------------------------------|-----------|---------------------------|--------------------------|-------------------------|
| SP-2100 | GDX-502 5A molecular sieve | 60 | 100 | 60 | Six-way injection valve |

Ar carrier gas: 0.04MPa, Hot-wire temperature: 150°C

Correction factor was calculated by the standard gas chromatographic analysis. Laboratory standard gas content showed in Table 3; the correction factor and retention time statistics showed in Table 4.

Table 3. Content of the standard gas

| Name | CO | CO ₂ | H ₂ | CH ₄ | N ₂ |
|-------------|----|-----------------|----------------|-----------------|----------------|
| Content (%) | 3 | 16.11 | 49.97 | 4.99 | 25.93 |

Table 4. Correction factor and retention time tables

| Name | H ₂ | CO ₂ | N ₂ | CH ₄ | CO |
|-------------------|----------------|-----------------|----------------|-----------------|-----------|
| Correction factor | 0.0000682 | 0.001575 | 0.00065 | 0.000296 | 0.0008968 |
| Retention time | 20771 | 40465 | 60460 | 80772 | 14.456 |

3. Experiments

3.1. Single-factor experiment

The life of the catalyst were investigated to ensure that the catalyst had sufficient stability to support experiments for a longer period of time. For the active component of Ni as a catalyst, the experiment on the Ni loadings were studied. In order to increase the resistance against coke formation the loadings of Li also studied.

N₂ was used as the entrained air to keep better flow rate in the pipeline. Temperature also an important factor in the reaction. Indeed, temperature and molar ratio was studied as well.

3.2. Orthogonal experimental Design

Single factor experiment identified 15%Ni2%Li-Al₂O₃ catalyst and the influence of various factors had studied. In order to find the optimum conditions for 15%Ni2%Li-Al₂O₃ catalyst four factors and three-level orthogonal test were studied which showed in Table 5 and 6, respectively.

Table 5. Factors level table

| Factors level | temperature | Water /alcohol | liquid space velocity of glycerol | blank |
|---------------|-------------|----------------|-----------------------------------|-------|
| Level 1 | 600°C | 16 | 0.36 h ⁻¹ | e |
| Level 2 | 700°C | 8 | 0.24 h ⁻¹ | e |
| Level 3 | 500°C | 24 | 0.12 h ⁻¹ | e |

Table 6. Orthogonal design table

| Factors level | Reaction temperature / °C | Water/alcohol | Liquid space velocity / h ⁻¹ |
|---------------|---------------------------|---------------|---|
| Level 1 | 600 | 16 | 0.36 |
| Level 2 | 600 | 8 | 0.24 |
| Level 3 | 600 | 24 | 0.12 |
| Level 4 | 700 | 16 | 0.24 |
| Level 5 | 700 | 8 | 0.12 |
| Level 6 | 700 | 24 | 0.36 |
| Level 7 | 500 | 16 | 0.12 |
| Level 8 | 500 | 8 | 0.36 |
| Level 9 | 500 | 24 | 0.24 |

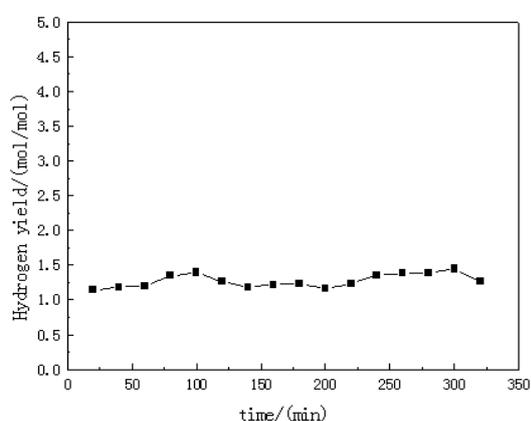
4. Results and discussion

4.1. Catalyst behavior and factors affecting

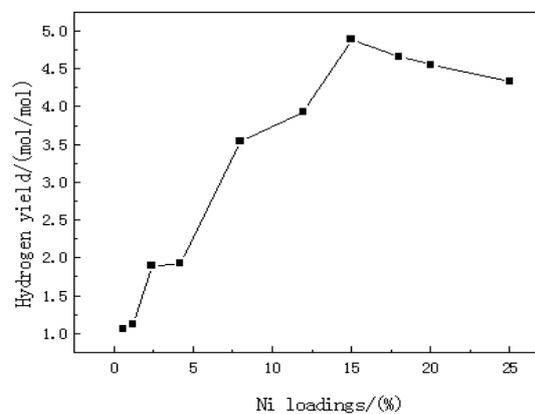
4.1.1. Catalyst life and the impact of Ni / Li loadings

According to Fig 2 (a), the hydrogen production rate is very stable and that represents catalyst deactivation after the reaction of hydrogen within six hours. Hydrogen production rate increases with the increasing of Ni loading but the hydrogen production rate decreases significantly with the excessive Ni loadings according to Fig 2 (b). The optimal Ni loading is 15 % which obtain by following conditions: glycerol flow rate 0.04ml/min, water flow rate 0.80ml/min, entrained gas flow rate 10ml/min, catalyst bed temperature 600 °C, Ni-Al₂O₃ (Ni loading of 0.6 %) and the catalytic activity versus time.

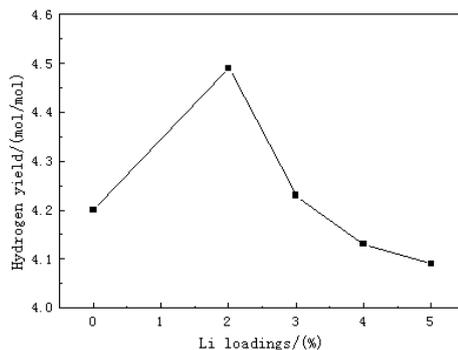
According to fig 2 (c), the hydrogen yield goes higher with increasing of Li loading at first and then decreases. Because Li can effectively reduce the catalyst activity and increases the resistance for carbon deposition. The best Li loading determine is 2 %.



(a)



(b)

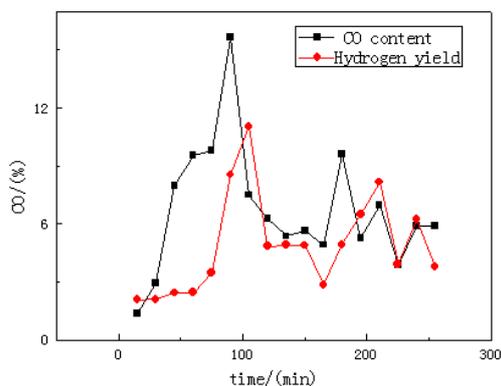


(c)

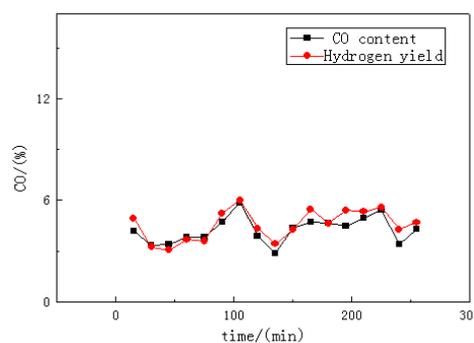
Fig. 2. (a) Catalyst life curve and (b) Hydrogen yield with Ni loadings of the curve (c) Hydrogen yields with Li loadings of the curve

4.1.5. The function of catalyst anti-carbon deposition

According to Fig 3(a) and 3(b), can be described the catalyst loading of Li effectively increases the resistance to carbon deposition. It can be mentioned from Fig 3(a), the hydrogen yield curve trends in CO content of the curve is consistent and hydrogen production rate appeared higher than the theoretical value of 7. The fluctuations of hydrogen production rate is large, but the average hydrogen production rate is still relatively higher. This is because of the hydrogen reaction process. The catalyst continues to deposit carbon but carbon accumulation on the catalyst to a certain extent, the reaction will occur as follows: $C + H_2O \rightarrow CO + H_2$. And it be seen from Fig 3(b),the hydrogen production rate is relatively stable, and the average hydrogen yield is not less than 3-5 average yield of hydrogen. Therefore, the Li loadings available in 2 % which effectively anti-carbon deposition.



(a)



(b)

Fig 3. (a) Ni15%-Al₂O₃ catalyst’s hydrogen yield and CO content curve (b) Ni15%Li2%-Al₂O₃ catalyst’s hydrogen yield and CO

4.2. Process conditions and the effect of hydrogen generation

4.2.1. The influence of temperature, water alcohol ratio, liquid space velocity & entrained gas flow

According to same conditions which mentioned in 4.1.1, the hydrogen yield and temperature curves shown in Fig 4(a) where firstly, the production of hydrogen increases. If the temperature exceeds 600 °C, the hydrogen production rate declines. Same conditions followed with Ni-Al₂O₃ (Ni loading of 0.6 %) catalyst which adjust the water flow so that water-alcohol ratio range is 8 to 24. Hydrogen yield and water-alcohol ratio curves shown in Fig 4(b) where the hydrogen yield increases with the water/ alcohol ratio and then decreases and point 16 is the best.

In Fig 4(c) shows, hydrogen yield decreases with the increasing liquid space velocity. Liquid space velocity of a reaction represent processing capacity, so the liquid space velocity is bigger than the processing capacity is better. When the liquid space velocity is 0.24 and 0.36, the hydrogen yield is still relatively high. But the liquid space velocity higher than 0.36, the hydrogen yield decrease significantly which indicating that the catalyst has limited handling capacity. So the best solution for the catalyst Liquid space velocity is 0.24h⁻¹. Again, in Figure 4(d) shows, the hydrogen yield increases in order to increase the entrained gas flow rate first increases and then decreases. The optimal flow of entrained gas is 10 ml /min. If the entrained gas flow too much, the residence time will be too short so the reaction will be incomplete.

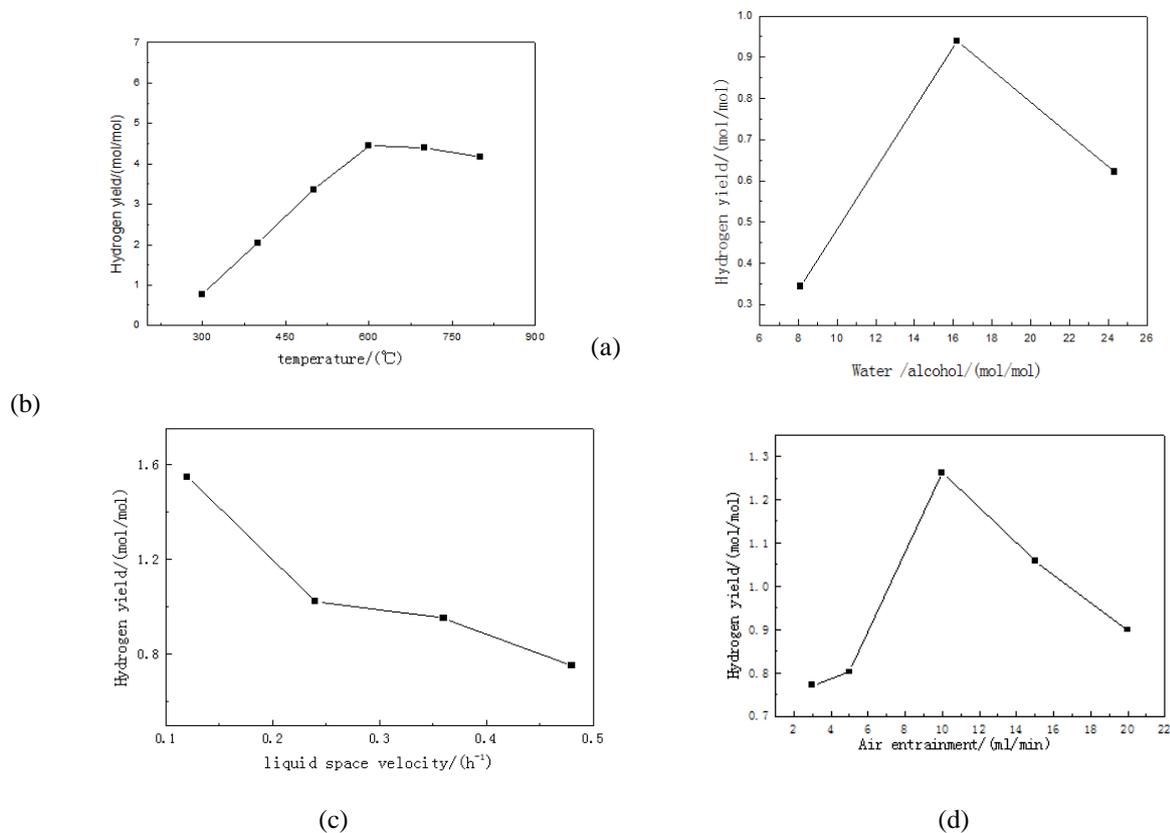


Fig 4. (a) Hydrogen yield and temperature curves (b) Hydrogen yield and water-alcohol ratio curve(c) Glycerol liquid space velocity on the impact of hydrogen yield (d)Hydrogen yield curve for entrained gas flow

5. Conclusion

Glycerin studied as raw material for hydrogen generation in steam reforming technology with the precious metals and non-precious metals catalyst system. The research results showed that the experiment device design was reasonable, met glycerin steam reforming hydrogen generation requirements. Single factor and orthogonal experiments result showed that with γ -Al₂O₃ carrier and Ni had good catalytic activity for glycerin steam reforming of hydrogen reaction. Among them the best capacity was Ni 15 %. And in the catalyst system, Li effectively increased the resistance for carbon deposition, and the best capacity was 2 %. Experiments also found that Li should be dipped after dipping Ni and 15 %Ni₂ % Li-Al₂O₃ catalyst had good stability, catalytic activity and resistance of carbon. The optimum process conditions for glycerin water vapor catalytic reforming reaction were: temperature 600°C, liquid space velocity 0.24h⁻¹, a molar ratio of water to alcohol 16. In the optimum process conditions, the hydrogen generation rate was 6.2; glycerol conversion rate was 94.16%, and the selectivity of hydrogen was 94.45%.

References

- [1] A.E. Farrell, R.J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, D.M. Kammen, Ethanol Can Contribute to Energy and Environmental Goals, *Science*, 311 (2006) 506-508.
- [2] J.C. Thompson, B.B. He, Characterization of crude glycerol from biodiesel production from multiple feedstocks, *Applied Engineering in Agriculture*, 22 (2006) 261-265.
- [3] S. Adhikari, S.D. Fernando, A. Haryanto, Hydrogen production from glycerin by steam reforming over nickel catalysts, *Renewable Energy*, 33 (2008) 1097-1100.
- [4] N. Luo, X. Fu, F. Cao, T. Xiao, P.P. Edwards, Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst - Effect of catalyst composition and reaction conditions, *Fuel*, 87 (2008) 3483-3489.
- [5] S. Dunn, Hydrogen futures: toward a sustainable energy system, *International Journal of Hydrogen Energy*, 27 (2002) 235-264.
- [6] B.C.R. Ewan, R.W.K. Allen, A figure of merit assessment of the routes to hydrogen, *International Journal of Hydrogen Energy*, 30 (2005) 809-819.
- [7] R.D. Cortright, R.R. Davda, J.A. Dumesic, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water, *Nature*, 418 (2002) 964-967.
- [8] R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic, A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts, *Applied Catalysis B-Environmental*, 56 (2005) 171-186.

- [9] R. Hashaikheh, I.S. Butler, J.A. Kozinski, Selective promotion of catalytic reactions during biomass gasification to hydrogen, *Energy & Fuels*, 20 (2006) 2743-2747.
- [10] P.J. Dauenhauer, J.R. Salge, L.D. Schmidt, Renewable hydrogen by autothermal steam reforming of volatile carbohydrates, *Journal of Catalysis*, 244 (2006) 238-247.
- [11] A.J. Byrd, K.K. Pant, R.B. Gupta, Hydrogen production from glycerol by reforming in supercritical water over Ru/Al₂O₃ catalyst, *Fuel*, 87 (2008) 2956-2960.
- [12] G.A. Deluga, J.R. Salge, L.D. Schmidt, X.E. Verykios, Renewable hydrogen from ethanol by autothermal reforming, *Science*, 303 (2004) 993-997.
- [13] I.N. Buffoni, F. Pompeo, G.F. Santori, N.N. Nichio, Nickel catalysts applied in steam reforming of glycerol for hydrogen production, *Catalysis Communications*, 10 (2009) 1656-1660.
- [14] J.W. Shabaker, R.R. Davda, G.W. Huber, R.D. Cortright, J.A. Dumesic, Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts, *Journal of Catalysis*, 215 (2003) 344-352.
- [15] J.W. Shabaker, G.W. Huber, R.R. Davda, R.D. Cortright, J.A. Dumesic, Aqueous-phase reforming of ethylene glycol over supported platinum catalysts, *Catalysis Letters*, 88 (2003) 1-8.
- [16] G.W. Huber, J.W. Shabaker, J.A. Dumesic, Raney Ni-Sn catalyst for H₂ production from biomass-derived hydrocarbons, *Science*, 300 (2003) 2075-2077.
- [17] G.W. Huber, R.D. Cortright, J.A. Dumesic, Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates, *Angewandte Chemie-International Edition*, 43 (2004) 1549-1551.
- [18] J.W. Shabaker, G.W. Huber, J.A. Dumesic, Aqueous-phase reforming of oxygenated hydrocarbons over Sn-modified Ni catalysts, *Journal of Catalysis*, 222 (2004) 180-191.