

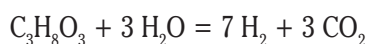
# Hydrogen from Glycerol by Steam Reforming

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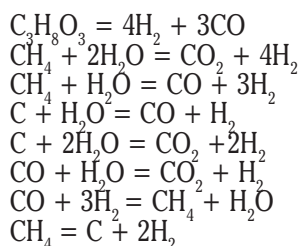
*The increasingly demand of more alternative fuels such as biodiesel has as the effect the increasing of the amount of glycerol - product of the transesterification process of vegetable oils. One of the recovery methods of this product is the steam reforming, to produce hydrogen. This paper studies some new mono and bimetallic catalytic systems and the influence of metal content deposited on the support over hydrogen yield obtained by glycerol aqueous solutions reforming. The prepared catalysts were characterized in terms of textural. The chromatographic analysis of liquid and gaseous phases and the results showed that the catalytic materials are able to be used in steam reforming of glycerol reaction.*

*Key words: bimetallic catalyst, conversion, alternativ fuel.*

Among the materials that can be used to obtain hydrogen glycerol is included and in recent years has been proposed several methods to obtain hydrogen starting from this raw material. These methods include catalytic steam reforming on different catalysts in vapor and aqueous-phase reforming [1-3], bioconversion based on GM enzyme [2], auto-thermal reforming on Rh catalyst [3]. Glycerol is particularly interesting as a by-product from biodiesel production and the increasing demand for biofuel involve large amounts of glycerol to be recovered. Glycerol resulting from transesterification processes has a low commercial value. In contrast, the relatively high water content recommends this mixture to be used as feedstock in steam reforming processes. Experimental studies presented in literature have shown that the process can occur in relatively mild conditions of temperature, with low energy consumption, oxygenates and water vaporization not prior required [6], or in more sever conditions, the so called steam reforming. The glycerol reforming takes place according to global reaction:



which takes into account most of the reactions that may occur during the process [7, 8]:



The reaction of CO or CO<sub>2</sub> with H<sub>2</sub> allows the formation of lower saturated hydrocarbons, which lead to reduced hydrogen efficiency for the entire process. However, these reactions can be controlled using a suitable catalytic material, both in terms of active metal and in terms of support acidity. Because methane formation is the favorite stage in glycerol reforming process, the catalyst used must also have the ability to reform the entire quantity of methane, with its subsequent conversion to hydrogen and carbon monoxide, and the complete transformation the last one into carbon dioxide [8, 9]. If the steam reforming of ethanol has been extensively studied, in terms of glycerol

conversion few studies have been published. The studied catalytic systems are especially monometallic, based on noble and transition metals, Pd [10], Ir, Co [11], Rh, Ru [10, 12], Ni [10, 11, 13, 14]. The noble metals have proved to be the most active and relatively stable in the steam reforming of glycerol. However, these metals are responsible for the formation of carbon, as coke deposited on catalyst. Furthermore, noble metals raise some problems for the use of these catalysts on industrial scale, because of high cost [15].

For this reason, we have been proposed some new catalysts based on Ni. In addition, it was found that the activity of monometallic catalysts can be improved by using a second metal, due to the emergence of the phenomenon of synergism [16, 17], for which reason catalysts were prepared with different proportions of Mn.

On the other hand, the nature of the substrate, i.e. its acidity or basicity, influences catalytic activity and products distribution resulting from the reaction. Among the supports mentioned in the literature there are: alumina, silicon dioxide, activated carbon, magnesium oxide or different zeolite materials [6]. For the formulation of our catalysts, we choose the active carbon as support.

## Experimental part

There were prepared three catalysts by wet impregnation method, monometallic one and two bimetallic, to be tested on the steam reforming of glycerol. The active metal used is nickel, deposited by impregnating on active carbon, the concentration of the active metal being 10% weight. The second metal used was Mn in proportions of 3 to 5% weight. The precursors used, metallic salts from Merck, were nickel nitrate hexahidrate, Ni(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O, 99,0% purity, and manganese nitrate tetrahydrate, Mn(NO<sub>3</sub>)<sub>2</sub> · 4 H<sub>2</sub>O, 98,5% purity. There were prepared aqueous solutions of these salts, to ensure the support loading with 10% Ni, 3% and 5% Mn respectively. Catalysts were noted as follows: Cat 1 - 10% Ni / active carbon, Cat 2 - 10% Ni + 3% Mn / active carbon, Cat 3 - 10% Ni + 5% Mn / active carbon.

## Catalysts characterization

For all catalysts the textural measurements were performed with a Quantachrome Autosorb-1 gas sorption analyzer. The specific surface area was calculated from the linear part of the adsorption branch of isotherms by the Brunauer-Emmett-Teller (BET) method and the

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	Specific surface area (m <sup>2</sup> /g)		Pore volume (cc/g)		Average pore diameter (nm)
	BET	micropore	total	micropore	
10%Ni/C	916.9	451.6	1.864	0.165	8.132
10%Ni3%Mn/C	585.6	0	1.985	0	18.68
10%Ni5%Mn/C	289.9	0	2.734	0	27.39

**Table 1**  
THE SPECIFIC AREA FOR THE TESTED CATALYSTS

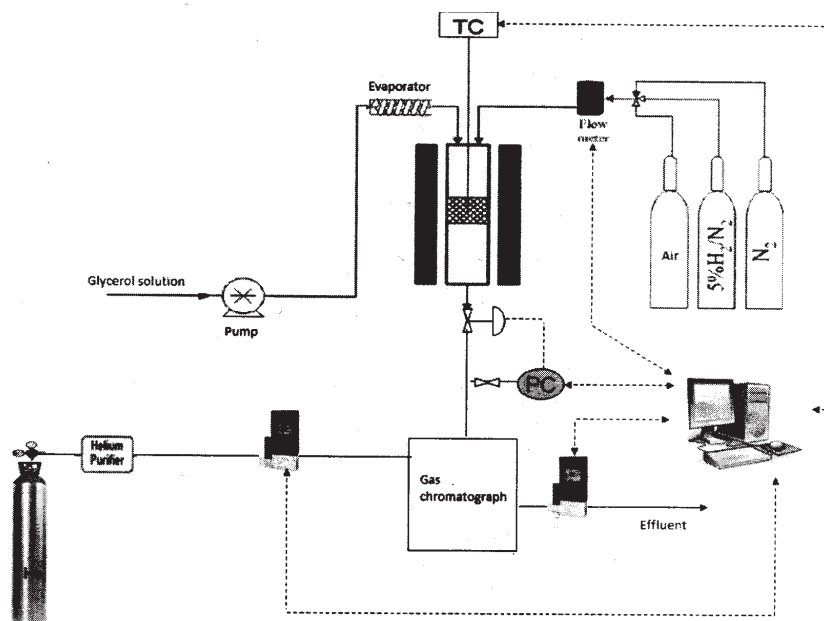


Fig. 1 The glycerol reforming plant

corresponding pore size distributions were determined from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda method (BJH). The t-plot method was used to evaluate the presence of micropores in prepared samples. The results of these tests are presented in table 1. Before each test the catalyst was activated at 3-5 atm pressure and temperature of 400°C, the hydrogen flow at 30 l/min rate. Catalyst activation time was 6 h.

The reforming process was performed in continuously system, in a reactor coupled to a Varian CP-3800 gas chromatograph (fig. 1), at 370°C and 2 atm.

The volume of catalyst used in catalytic tests was 45 cm<sup>3</sup>. The feedstock was an aqueous solution of glycerol 25% (volume), pumped into the reactor with a HPLC type pump at constant flow rate of 1 mL/min. All experiments were conducted at flow rate of glycerol 0.1 h<sup>-1</sup>. The reaction products mixture was passed through a condenser and a gas-liquid separator to separate gas and liquid products for analysis. The gas phase was analyzed by direct sampling from the plant exhaust stream, through a process gas chromatograph VARIAN CP 3800 type, equipped with a valve system that allows parallel analysis on a TCD type detector and hydrogen oxides of carbon and a TCD type detector for methane and other organic compounds present. The components separation on each circuit was made on the PoraPlot 25 m x 0.53 + Molsieve 5A 25 m x 0.53 and CPWAX 57 CB 30m x 0.32 capillary columns.

The characterization of the liquid phase from the separator vessel was achieved by gas chromatographic method, using a 5890 Network GC unit of Agilent Technologies company, equipped with flame ionization detector (FID), using a polar capillary column DB - WAX 30m length and 0.32 mm inner diameter, operated at temperatures between 20 and 220°C. Two experiments were performed for each reforming catalyst, causing gas sampling at 1 or 2 h.

## Results and discussions

According to data obtained from the characterization of the catalytic materials presented in this paper, for the bimetallic catalysts, the total area decreases significantly as the amount of secondary metal (manganese) added increases. This can be attributed to reducing of the number of micropores, as a result of the micropores blocking with Mn particles.

Preliminary tests aimed to establish the performance of the prepared catalysts in glycerol steam reforming reaction. This evaluation was performed by determining the glycerol conversion and the yield and selectivity in hydrogen. The glycerol conversion was determined on the basis of untransformed glycerol content of the liquid phase taken from the phase separator (as determined by chromatography) and the concentration of hydrogen was determined by gas chromatographic analysis of gas phase going out from the separator vessel, through the process chromatograph. The results of massic balance and catalytic tests are summarized in tables 2 and 3. Table 2 summarizes the glycerol conversion and hydrogen yield in relation to glycerol. Conversion of glycerol,  $x$ , was calculated with the equation:

$$x = \frac{m_{\text{glycerol\_initial}} - m_{\text{unused\_glycerol}}}{m_{\text{glycerol\_initial}}} 100 = \frac{m_{\text{glycerol\_initial}} - L \times \text{conc}_{\text{unused\_glycerol}}}{m_{\text{glycerol\_initial}}} 100$$

The hydrogen yield with the formula:

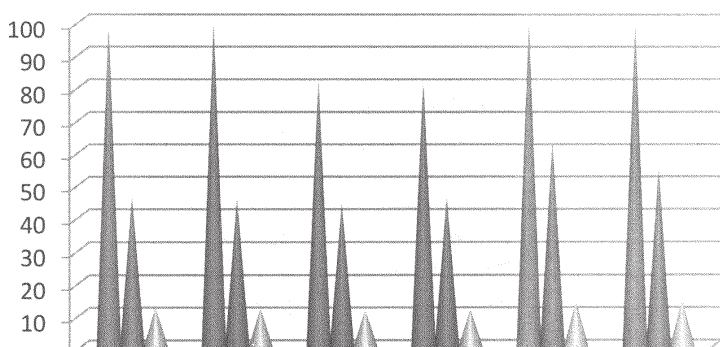
$$\eta_{\text{H}_2 \text{ versus\_glycerol}} = \frac{m_{\text{H}_2}}{m_{\text{glycerol\_initial}}} 100 = \frac{G \times \text{conc}_{\text{H}_2}}{m_{\text{glycerol\_initial}}} 100$$

where G is the weight of reaction products, in gas phases, in grams.

The selectivity in hydrogen in the gas phase,  $S_{\text{H}_2}$  represents hydrogen concentration in the gas phase resulted from reaction.

Catalyst	Reaction duration	Inlet, glycerol aqueous solution 25%		Output		
		ml	g	Liquid phase quantity, L, g	Liquid phase, G	
					ml	g
Cat 1	1 h	60	63,90	58,16	13,60	5,04
	2 h	120	127,80	117,30	26,63	10,10
Cat 2	1 h	60	63,90	58,21	13,44	4,98
	2 h	120	127,80	117,78	25,31	9,60
Cat 3	1 h	60	63,90	58,97	11,47	4,25
	2 h	120	127,80	116,22	26,78	10,16

No.	Catalyst	Reaction duration	Glycerol conversion %	S <sub>H<sub>2</sub></sub> , %	η <sub>H<sub>2</sub></sub>
1	Cat 1	1 h	100	46,53	12,40
2		2 h	100	45,81	12,24
3	Cat 2	1 h	82,44	44,22	11,65
4		2 h	82,47	46,33	11,76
5	Cat 3	1 h	100	63,43	14,26
6		2 h	100	55,14	14,82



Analyzing the data presented in the table 3 it is found that all synthesized catalysts can be used successfully in steam reforming of glycerol, ensuring a very high conversion of raw materials and good hydrogen selectivity (fig. 2). Also, we can say that as the reaction time increases, the catalyst is easily deactivated, as shown by the decrease of hydrogen content in exhaust gases.

### Conclusions

There were prepared two catalysts type, mono and bimetallic, Ni and Mn-based, supported on active carbon; it was found that by using the addition of Mn, the surface area of catalysts decreases, even more as the proportion of Mn is higher. This can be explained by the micropores blocking, mainly in number in the basic catalyst.

The catalytic tests were performed in a continuous system, in a micropilot reactor in fixed catalytic layer, with downward movement of the reactants, at glycerol flow rate 0.1h<sup>-1</sup>, 2 atm pressure and 370°C temperature.

The raw material used is cheap and available in large quantities, because the proposed method capitalizes the glycerol resulted as a byproduct from the vegetable oils transesterification.

By using this material the separation operations and glycerol purification are avoided - costly operations, necessary in other methods of glycerol recovery.

The conversion of glycerol on the Ni-based catalysts tested in standard chosen conditions had high values (approx. 100%). The content of hydrogen in the reaction products is relatively high, in accordance with existing results in the literature. As the process duration increases, the catalysts are slightly deactivated, as shown by the decrease of hydrogen content in exhaust gases.

The main byproducts of glycerol reforming process are carbon dioxide, carbon monoxide and methane.

It has been demonstrated that all examined catalysts make possible to achieve high conversions in the glycerol steam reforming, with high selectivity in hydrogen in

**Table 2**  
MATERIAL BALANCE FOR  
THE EXPERIMENTAL TESTS  
(PRESURE 2 ATM,  
TEMPERATURE 370 °C)

**Table 3**  
REFORMING AQUEOUS  
SOLUTION OF GLYCEROL ON  
THE PREPARED CATALYSTS  
(PRESURE 2 ATM,  
TEMPERATURE 370 °C)

Fig. 2. Glycerol conversion, the hydrogen yield and selectivity for the glycerol steam reforming over different catalysts

particular for the catalyst with 5%Mn. The addition of manganese increased the amount of hydrogen result, more pronounced at higher content of Mn - synergy effect.

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