



HYDROGEN PRODUCTION BY STEAM REFORMING OF RENEWABLE RAW MATERIALS

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ABSTRACT

The paper is based on study of steam reforming of renewable raw materials (bioethanol, biomethane) in stainless steel fixed bed reactor. The β -alumina catalysts with nickel has been synthesized and tested supported. The influence of operating conditions about steam reforming reaction and methanation reaction was studied.

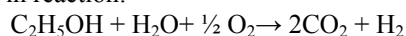
KEYWORDS: reforming, methanation, catalyst, fixed bed reactor, bioethanol, biomethane

1. Introduction

Knowing that hydrogen is the less pollutant fuel, having a lot of utilizations – internal combustion engines, combustion cells, heating fuels - many technologies for hydrogen production were developed. The one of most important technologies is steam reforming of hydrocarbons and alcohols, from which steam reforming of bioethanol and biomethane are realized on industrial range [1]. In steam reforming process for obtains syngas and hydrogen production can be analyzed a lot of raw materials such: methane, GPL, gasoline fractions, methanol and ethanol. For steam reforming process a wide variety of supported nickel catalysts, supported alumina and silica catalysts are used. The more frequent raw materials are hydrocarbons, methanol being used at smaller range and in special situations. Increases of bioethanol production and other compounds from biotechnologies (e.g. biomethane) increased interest for study of these processes as hydrogen source [2, 3].

The presence of an efficient steam reforming catalyst represents the key of this process for hydrogen production.

In literature are presented alternatives of hydrogen production from ethanol. Thus, recent studies [4] show that ethanol can be used with water in partial oxidation or total oxidation and steam reforming, processes that convert ethanol in hydrogen such in reaction:



This reaction occurs at high temperatures (800°C), to obtain as mainly product hydrogen

through partial oxidation and steam reforming of ethanol by exothermal process. The water obtained in excess by partial oxidation is used in steam reforming process.

This study aim is to promote vegetable sources as raw materials, by revaluation of renewable resources as biomass through pure technologies which can generate hydrogen production. Bioethanol is product of biocatalyst and enzymatic convert of some compounds by photosynthesis. Enzymatic conversion of polysaccharides in bioethanol is a process that demands less energy consumption related to petrochemical processes of ethanol conversion. Technology for bioethanol obtaining needs to extend farming cultures with high polysaccharides potential, preserving the equilibrium between photosynthesis and biological degradation and the natural cycle of oxygen and carbon dioxide.

The motivation of bioethanol use in hydrogen production presents a lot of advantages, such that bioethanol is available from renewable sources, bioethanol has low impact on greenhouse gases, that bioethanol is economic and has a high content of hydrogen and the fact that bioethanol is miscible with water.

Bioethanol can be considered, in present, a good raw material, because of its availability, non-toxicity and safe storage and control conditions and because UE promotes policies concerning acquirement of fuels from renewable sources, as an alternative of irreversible combustion of fossil-based materials. In the same time with cell combustion systems implementation and increases of fuels with low sulfur



content demand, hydrogen production will be remarkably developed [5].

Hydrogen production from renewable raw materials can be realized converting the conventional technology of methane steam reforming to reforming of biomethane derived from fermentation of some animal wastes [6], which is studied in present in current research project [7]. In these actual studies for this alternative, the catalysts are supported ruthenium catalysts [8] and nickel and lanthanum catalysts [7].

Biogas composition can be variable due to carbon dioxide content.

2. Experimental study

Research aim is to obtain hydrogen from renewable raw materials in advantageous conditions.

Objectives:

- bioethanol steam reforming to obtain syngas;
- study of selected catalyst efficiency for bioethanol steam reforming;

- influence of operation conditions (temperature and space velocity) on the steam reforming of bioethanol and biomethane. Raw material representing bioethanol was prepared as a solution by diluting 10% ethanol with 90% deionized water, which similar concentration obtained by renewable raw materials. For biomethane steam reforming was used raw material like that result from fermentation processes, having composition 60% vol. methane and 40% vol. CO₂. Experimental studies concerning steam reforming of bioethanol was carried out in a stainless steel fixed bed reactor having the thermocouple for measure of temperature in zone reaction. Biomethane flow was realized for mixture between methane and CO₂, which was controlled as a flow on each flux. In case of biomethane experiment, catalyst volume was 20 cm³, respectively for biomethane steam reforming, catalyst volume was 15 cm³. In this study, was used supported nickel ZSM5/ Zn catalyst for reforming of bioethanol, respectively supported β -alumina catalysts with Nickel and Lanthanum for biomethane reforming. The study was carried out by varying the operating conditions, such as reaction temperature, water to ethanol ratio, respectively methane to CO₂ ratio, space velocity and constant compositions of raw material. Values between 1.5 - 4 h⁻¹ has been chosen

for space velocity for bioethanol steam reforming, respectively constant gaseous space velocity for biomethane reforming. The used catalysts were prepared by impregnation with nickel. Nickel, as a precursor (from aqueous solution of nickel nitrate) was impregnated on zeolitic support modified by zinc, in many steps and than dried at 120°C. The impregnated catalyst is calcinated for six hours at 550°C with nitrogen oxide elimination.

For reforming of biomethane catalyst was obtained by impregnation with nickel (from aqueous solution of nitrate nickel) and lanthanum as lanthanum nitrate. The support was β alumina. After drying, it was calcinated at 600°C for six hours.

The reactor can be both liquid and gaseous charged by the charging system in the reactor superior zone. The experimental system also includes cooling, condensation and separation systems, as well as electrical heating system.

The reaction products and raw material were analyzed by Gas Chromatography with a Carlo Erba HRGC 5300 Mega Series. Chromatographic column is stainless steel, with 12 m length, 4 mm interior diameter and 6 mm exterior diameter. The stationary phase is PORAPAQ O+R adsorbent. The detector is catarometer. Carrier gas is helium. Sampling and processing soft of analytical results was Crom Card for Windows. The experiments for bioethanol steam reforming carried out at three temperatures: 520°C, 560°C, 600°C and two liquid space velocities: LHSV = 2,5 h⁻¹, respectively 4 h⁻¹. For biomethane reforming the experimental program includes four experiments at reaction temperatures: 660°C, 705°C, 760°C, 800°C and constant gaseous space velocity: GHSV = 960 h⁻¹.

3. Results and discussions

Experimental data using the above mentioned experimental program, confirm the hypothesis that hydrogen could be obtained from renewable sources, such are bioethanol and biomethane.

Experimental conditions in laboratory micro pilot are presented in table 1 (reaction temperature, space velocity, feed-stock flow in cm³/min– ethanol and water – for 20 cm³ catalyst reaction zone).

Table 1. Work conditions for bioethanol steam reformings

Experiment	Temperature, °C	LHSV*, h ⁻¹	Flow, cm ³ /min
BE 1**	520	2,5	0,833
		4	1,333
BE 2**	560	2,5	0,833
		4	1,333
BE 3**	600	2,5	0,833
		4	1,333



*LHSV – hourly space velocity for liquid raw material (flow of liquid raw material divide to catalyst volume).

**BE1, BE2, BE3-indicator for bioethanol experiments.

Because water in the effluent is condensed and separated in reaction medium, in gaseous reaction product are only H₂, CO, CO₂, CH₄.

Experimental results to bioethanol reforming are presented in table 2 and they prove the possibility to

obtain hydrogen and carbon oxides from bioethanol as well as the limits of methanation following reforming.

We can see the significant conversion of ethanol in hydrogen and carbon oxides. It is important to emphasize that the main reaction (reforming) is always accompanied by methanation reaction. During this reaction the mixture of CO, CO₂ and H₂ are transformed in methane. This reaction increases with reaction temperature increasing. The key of this reaction is the catalyst.

Table 2. Composition of final products (H₂, CO, CH₄, CO₂,) for bioethanol steam reformings, % vol.

Experiment	Temperature, °C	LHSV, h ⁻¹	H ₂	CO	CH ₄	CO ₂
BE 1	520	2,5	1,7065	50,5119	16,3823	31,3993
		4	4,9689	36,0249	37,8882	21,1180
BE 2	560	2,5	4,0816	42,8571	32,1429	20,9184
		4	6,8627	40,1961	38,2353	14,7059
BE 3	600	2,5	4,9080	13,4969	40,4908	41,1043
		4	5,8824	21,5686	43,1373	29,4118

Concerning the effect of operation conditions over bioethanol reforming reaction, especially concerning hydrogen formation, from table 2 data and figure 1 we can easily observe that higher

temperatures favor bioethanol reforming, hydrogen content increasing continuously. (from 1,5 % vol. to 5 % vol.).

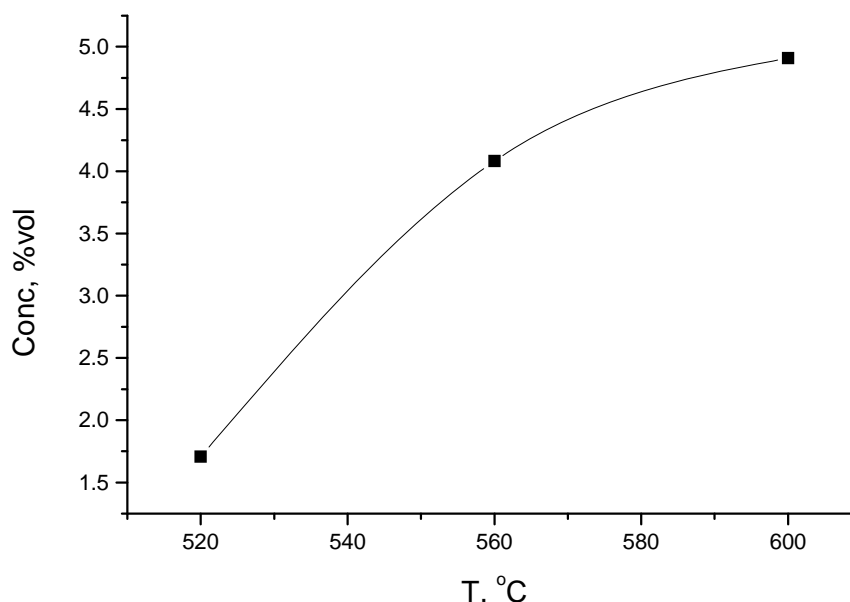


Figure 1. Variation of hydrogen concentration from gaseous reaction product from bioethanol reforming at liquid space velocity LHSV = 2,5 h⁻¹.

For experiments carry out to LHSV=4 h⁻¹ (figure 2), hydrogen concentration in gaseous products as a function of temperature vary to a maximum, followed by a slightly decrease due, the

most probably, to methanation reaction (CO + H₂ ↔ CH₄ + H₂O), related to the important concentration of methane - 43 % vol.

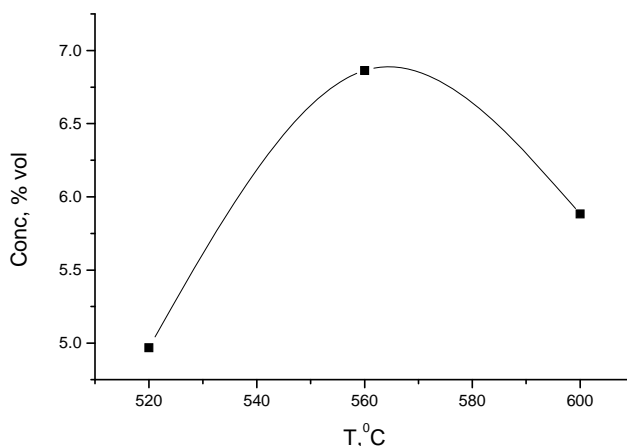


Figure 2. Variation of hydrogen concentration from gaseous reaction product from bioethanol reforming at liquid space velocity $LHSV = 4 h^{-1}$.

Table 3. Composition (% vol.) of final products for biomethane reforming

Experiment	Temperature, °C	LHSV, h ⁻¹	H ₂	CO	CH ₄	CO ₂
BM 1 ^{***}	660	960	1,04	18,09	75,66	5,19
BM 2 ^{***}	705	960	1,05	19,31	72,58	7,06
BM 3 ^{***}	760	960	1,19	16,39	78,25	4,16
BM 4 ^{***}	800	960	0,44	9,05	89,56	0,94

^{***}BM1, BM2, BM3, BM4 - indicator for biomethane experiments.

Concerning biomethane steam reforming, the mixture used in these experiments as feed stock have an initial composition of 40% vol CO₂ and 60% vol methane. Experimental conditions and gaseous effluent at the exit from reaction system, (after water condensation and separation) are presented in table 3.

From experimental data in table 3 it can be observed that CO₂ from feedstock was converted in methane due to methanation reaction, following reforming reaction. This explains the higher methane content in reaction products and the small hydrogen amount used for methanation.

To reduce undesirable effect of CO₂ methanation at biomethane steam reforming, the catalyst composition and preparation could be modified. Another way to block methanation process is a lower CO₂ content in the feed-stock.

4. Conclusions

- ZSM5 catalyst modified with Zn impregnated with 10% Ni is suitable for bioethanol steam reforming
- Higher hydrogen concentrations were obtained at 560 and 600°C for $LHSV = 2,5 h^{-1}$.
- Space velocities low values influence the bioethanol steam reforming process in the sense of a

higher hydrogen concentration and lower values for CO₂ and CO.

- The presence of CO₂ in biogas influences methane conversion.
- The catalyst significantly influences the methanation reaction of CO₂.

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