Autonomous catalytic hydrogen generator based on bioethanol steam reforming

project № 6-21

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BIOMASS

BIOETHANOL
\( C_2H_5OH \)

\[ C_2H_5OH + H_2O \rightarrow \text{CATALYST} \rightarrow \text{Gas turbines} \]

\[ \text{CO}_2 + \text{H}_2 \]

Chemical, metallurgical, petrochemical, food industry

Engines

Fuel Cells
Ethanol steam reforming

\[ C_2H_5OH + 3 H_2O = 2 CO_2 + 6 H_2 \]

Advantages of the ethanol steam reforming

- Ethanol can be produced from biomass fermentation, which is renewable and sustainable.
- Ethanol displays a lower toxicity than methanol, and is easy to transport and store.
- In the absence of side products 50% of the hydrogen can be produced from the water, and the other 50% from the ethanol.
- The \( \text{CO}_2 \) produced can be converted back to biomass by plants, as part of the carbon cycle, and reduce the greenhouse gas emissions

Limitations of the ethanol steam reforming

- Significant number of by-products: oxygenates, carbon monoxide, which leads to poisoning of fuel cell electrodes
- formation of carbon deposits, which leads to deactivation of catalysts
- The process is endothermic, requiring additional thermal energy.
Goal:

- The purpose of this project was to develop the scientific basis for the creation of bioethanol conversion catalysts for promising autonomous energy supply systems based on hydrogen and fuel cell based on renewable raw materials.

Objectives:

- experimental study and evaluation of the possibility of obtaining hydrogen of the required purity for the operation of fuel cells by steam reforming of bioethanol on oxide catalysts;
- optimization of the chemical composition of the catalyst, the initial reaction mixtures and the conditions of the catalytic steam reforming to obtain hydrogen;
- development of bioethanol vapor conversion reactor design; calculation of energy and heat balance of the reactor;
- development of a model of a hydrogen generator based on heterogeneous catalytic conversion of bioethanol and testing it;
If bioethanol is used, the highest yield of hydrogen (95.3%) is achieved at 600 °C; if the stoichiometric mixture is used, the maximum yield of hydrogen (74.7%) is obtained at 800 °C,
Catalyst design: nanosized catalysts based on 3d-metal oxides for reforming biooxygenates

- Mono- and bicomponent metal catalysts on oxide and carbon supports: Cu/ZrO$_2$, Ni/ZrO$_2$, Co/ZrO$_2$, Fe/ZrO$_2$, NiCu/ZrO$_2$, CoCu/ZrO$_2$, FeCu/ZrO$_2$, Cu/SKT, Cu/CNT, Fe/CNT

- Mixed oxides – MFe$_2$O$_4$ (M = Ni, Co, Fe, Mn, Cu, Mg, Zn) ferrites with the spinel structure

Benefits:

- Noble and/or rare earth metals are not present in the catalyst
- CO-free hydrogen can be obtained, which is important for use in low-temperature fuel cells.
Relationship between hydrogen yield in ethanol steam reforming and selectivities for carbonaceous products

\[ Y_{H2} = (4S_{CO} + 6S_{CO2} - 2S_{CH4} + \frac{2}{3}S_{CH3COCH3} + S_{CH3CHO}) \cdot X \]

Comparison of the hydrogen selectivity reported in the literature and the hydrogen selectivity calculated according to equation

| Ethanol conversion % | Product distribution, mol. % | Yield of H₂ mol/mol EthOH, | Yield of H₂ calculated according to equation |
|----------------------|-----------------------------|---------------------------|---------------------------------------------|
|                      | H₂  | CO  | CO₂ | CH₄ | CH₃CHO |
| Catalyst 0,23NaCoZn (Llorca J. et al., J. Catal., 2004) |
| 73,7                 | 72,6 | 0   | 23,8 | 1   | 2,5    | 3,58 | 3,61 |
| 100                  | 73,9 | 0   | 25   | 1,1 | 0      | 5,66 | 5,66 |
| Catalyst 30% Ni/ZrO₂ (Biswa P. et al., Int. J. Hydrogen Energy, 2007) |
| 100                  | 72,2 | 6,8 | 17,8 | 3,2 | 0      | 5,2  | 4,6  |
| 100                  | 74,3 | 6,9 | 17,3 | 1,5 | 0      | 5,8  | 5,0  |
Single-step method for hydrogen production from bioethanol

\[ \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} = 2 \text{CO}_2 + 6 \text{H}_2 \]

Comparison of product distribution ESR at 550°C

| Catalyst                | X, % | H₂  | CO  | CO₂ | CH₄ | CH₃CHO |
|------------------------|------|-----|-----|-----|-----|--------|
| Rh/CeO₂-ZrO₂           | 100  | 70,3| 1,5 | 20,9| 7,3 | 0      |
| Ni/Ce₀.₇₄Zr₀.₂₆O₂       | 100  | 75,2| 6,1 | 13,9| 4,5 | 0,3    |
| 0,23NaCo/ZnO           | 100  | 70,9| 2,0 | 25,0| 1,1 | 0      |
| Fe/Co₃O₄               | 100  | 74,2| 0,9 | 24,3| 0,6 | 0      |
| MnFe₂O₄                | 100  | 73,7| 0   | 25,1| 1,2 | 0      |

Diagne et al. 2002
Bismas et al. 2007
Llorca et al. 2004
O’Shea et al. 2008
This study
Temperature dependence of the alcohol conversion (a) and hydrogen selectivity (b) during C$_3$ – C$_5$ alcohols steam reforming over MnFe$_2$O$_4$ catalyst.

For the steam reforming of the ethanol and C$_3$ – C$_4$ alcohols mixture, the ethanol conversion reaches 97% at 500°C. For other alcohols in the mixture, conversion varies between 83% and 90% depending on the alcohol nature and the hydrogen selectivity is approximately 80%.

At 500 °C, productivity toward hydrogen of the steam reforming process is higher for alcohol mixture in contrast to the water-ethanol mixture without higher alcohols. This difference in productivity is governed by an effective steam reforming of higher alcohols with the utilization of the water vapor on the developed catalyst.
## Catalyst for hydrogen production from bioethanol

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Output Продуктивність, ml/h * gₖₘ.    | 450                                        |
| Selectivity, %                        | 80-94                                      |
| Mechanical strength, g/cm²            | 2,2 (≥ 6 kg/Granule)                       |
| Specific surface, m²/g                | 15                                         |
| Porosity, ε                           | 0,54                                       |
| Ignition temperature, °C              | 500                                        |
| Thermal stability, °C                 | 800                                        |
| Operating temperature, °C             | 600 ÷ 700                                  |
| Granule size, mm                      | 6x6                                        |
| Density, g/cm³                        | 4,500                                      |
| Particle density, g/cm³               | 2,07                                       |
| Working volumetric speed, h⁻¹         | 4000                                       |
| The ratio of reactor and catalyst diameters | ≥ 3                                         |
| Stream No | 1       | 2       | 3       | 4       | 5       |
|-----------|---------|---------|---------|---------|---------|
| Temp C    | 25.000  | 1.0000  | 1.0000  | 1.0000  | 60.0000 |
| Press bar | 1.0000  | 1.0000  | 1.0000  | 1.0000  | 92.6266 |
| Enth kJ/h | 7323.2  | 5359.6  | 4171.8  | 1000.00 | 6212.3  |
| Vapor mass frac. | 0.00000 | 1.0000  | 1.0000  | 1.0000  | 0.95651 |
| Total gmol/h | 25.8000 | 25.8000 | 49.0000 | 49.0000 | 25.8000 |
| Total g/h | 627.5002 | 627.5002 | 627.5049 | 627.5049 | 627.5002 |
| Total std L m3/h | 0.0007 | 0.0007 | 0.0017 | 0.0017 | 0.0007 |
| Total std V m3/h | 0.58 | 0.58 | 1.10 | 1.10 | 0.58 |
| Flow rates in g/h | | | | | |
| Ethanol   | 267.2002 | 267.2002 | 0.0000 | 0.0000 | 267.2002 |
| Water     | 360.3000 | 360.3000 | 46.8390 | 46.8390 | 360.3000 |
| Hydrogen  | 0.0000  | 0.0000  | 70.1498 | 70.1498 | 0.0000  |
| Carbonic anhydri | 0.0000 | 0.0000 | 510.5160 | 510.5160 | 0.0000  |
Basic parameters of hydrogen generator

\[ C_2H_5OH + 3 H_2O = 2 CO_2 + 6 H_2 \]

Mean water/alcohol ratio = 3,5(≈ 50%Vol.)

Water/alcohol mixture feed rate – 0,63 kg/h

Amount of hydrogen received – 780 l/h (13 l/min)

The amount of heat that is necessary for conversion reaction – 1,8MJ/h

- 0,2 kg/h a water/alcohol mixture.
- 0,05 kg/h Natural Gas
- Electroplates

Efficiency by alcohol = 44%
Conclusion

A portable autonomous catalytic hydrogen generator is developed. The generator is capable to produce 1 kW/h electricity with 0.63 kg/h water/alcohol mixture (50% ethanol) consumption. The energy conversion efficiency of the developed generator is 44%. The proposed hydrogen generator is suitable for various applications related to in-field hydrogen production.
Catalysts for hydrogen storage and transportation technologies

N\textsubscript{2} + 3H\textsubscript{2} \rightleftharpoons 2NH\textsubscript{3}

Liquid Hydrogen Carrier (LHC) technology for storage and transportation of hydrogen

| Storage density, MWh/Nm\textsuperscript{3} | H\textsubscript{2} Capacity, wt\% | H\textsubscript{2} Capacity, kg/m\textsuperscript{3} |
|-------------------------------------------|------------------|------------------|
| 1,58                                      | 6.1              | 47               |

| Dibenzyltoluene | Methylcyclohexane | Perhydrodibenzyltoluene |
|-----------------|-------------------|-------------------------|
| -9H\textsubscript{2} | +9H\textsubscript{2} | \textsuperscript{CATALYST} |
| +3H\textsubscript{2} | -3H\textsubscript{2} | \textsuperscript{CATALYST} |

Ammonia

| Storage density MWh/Nm\textsuperscript{3} | H\textsubscript{2} Capacity, wt\% | H\textsubscript{2} Capacity, g/L |
|-------------------------------------------|------------------|------------------|
| 3,5                                       | 17,6             | 118              |
Thank you