TARGET COMPLEX PROGRAMME FOR RESEARCH OF NAS UKRAINE

«Development of scientific bases for hydrogen production, storage and use in autonomous energy supply systems»

Autonomous catalytic hydrogen generator based on bioethanol steam reforming

project № 6-21

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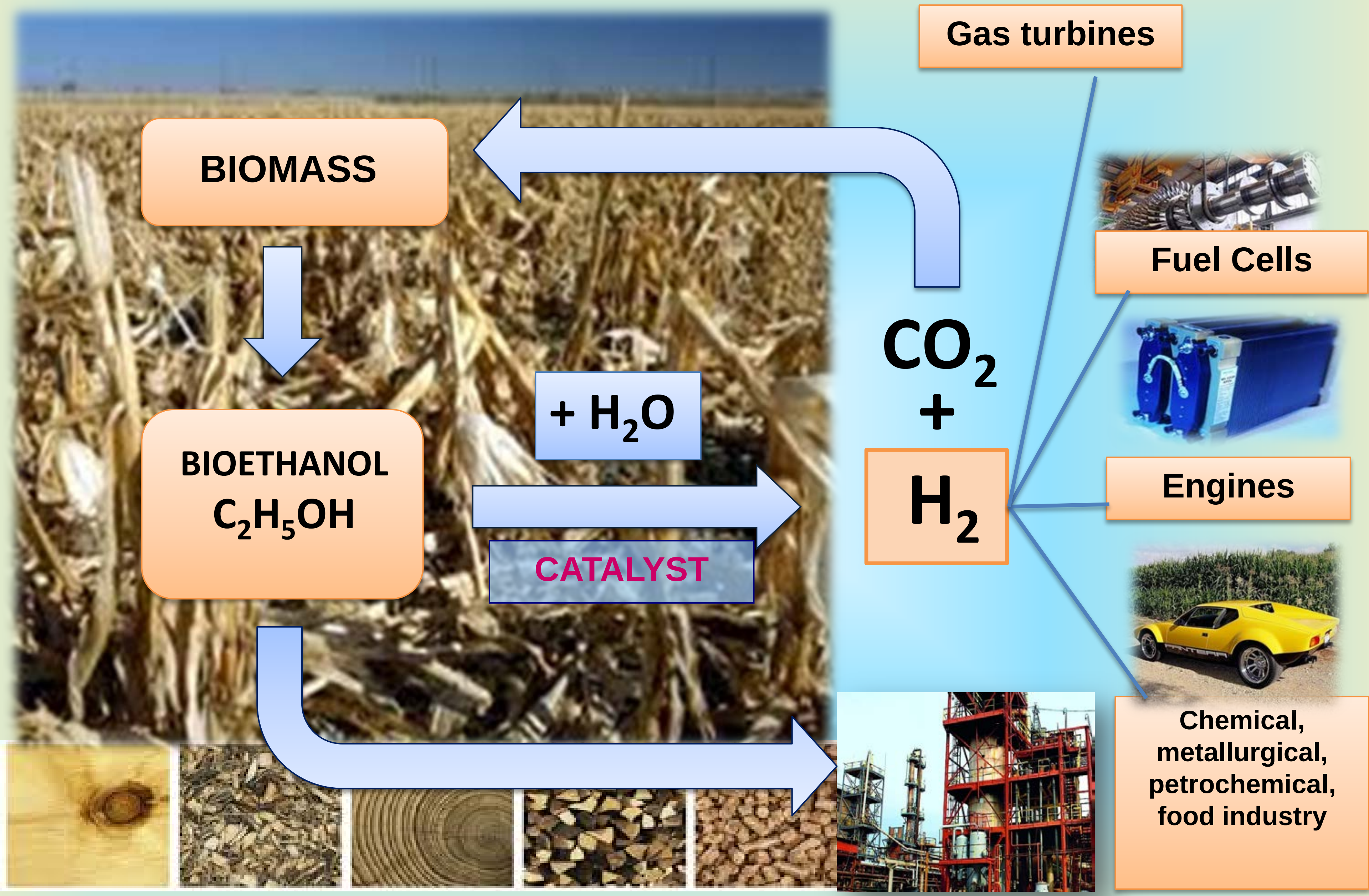


Gas turbines
BIOMASS
Fuel Cells
CO_2
+
$+ H_2O$
H_2
BIOETHANOL
C_2H_5OH
Engines
CATALYST
Chemical, metallurgical, petrochemical, food industry

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 CO_2 produced can be converted back to biomass by plants, as part of the carbon cycle, and reduce the green-house 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.

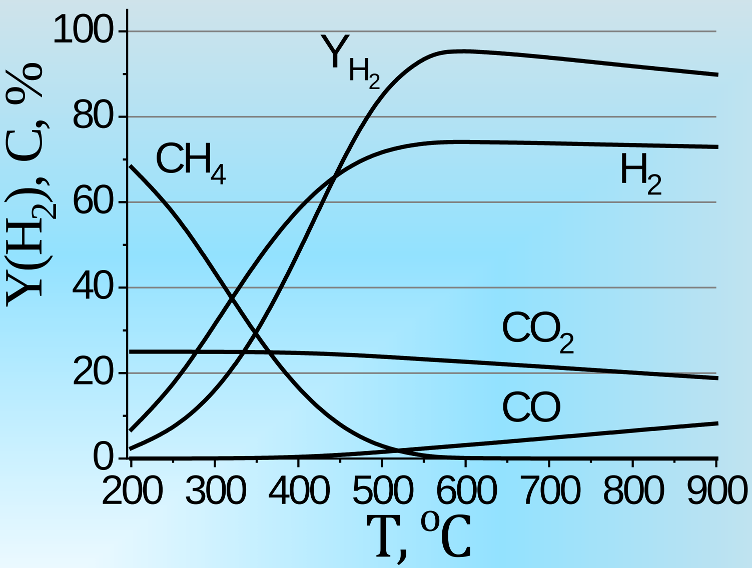
Goal :

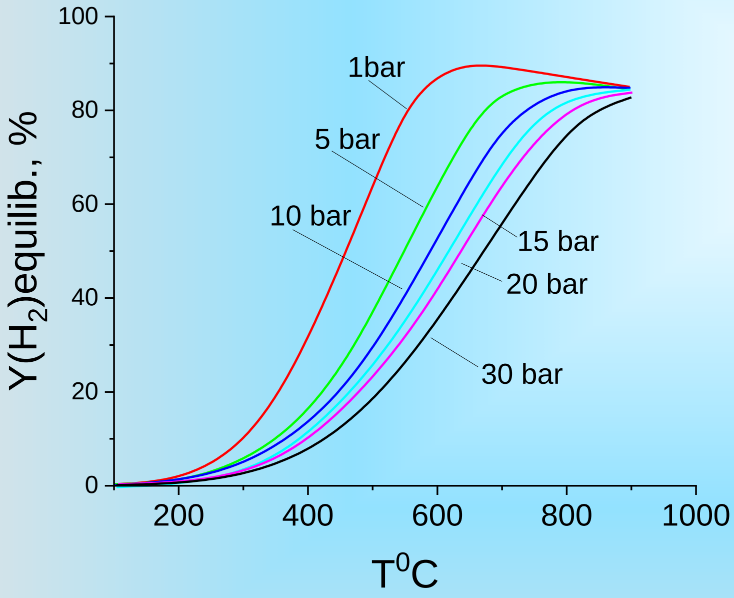
- The purpose of this project was to develop the scientific basis for the creation of bioethanol conversion catalysts for promising autonomous energy supply systems based on hydrogen and fuel cell based on renewable raw materials.

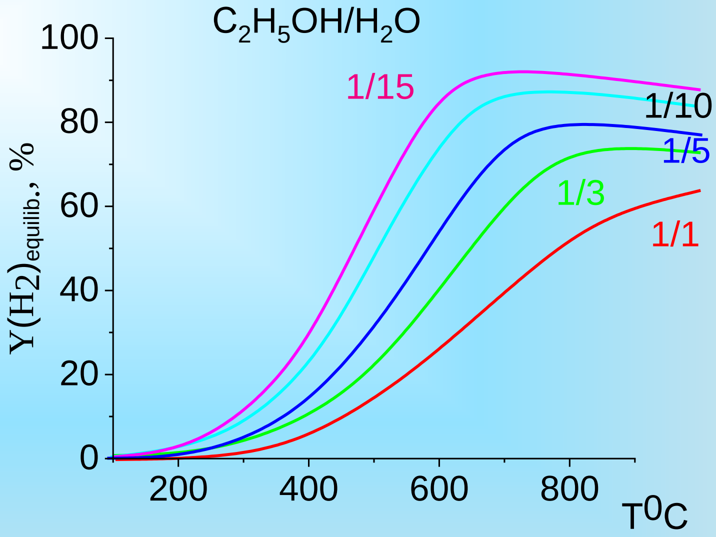
Objectives :

- 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;

Influence of pressure, temperature and alcohol concentration on the yield of hydrogen







If bioethanol is used, the highest yield of hydrogen (95.3%) is achieved at 600 ^{o}C; if the stoichiometric mixture is used, the maximum yield of hydrogen (74.7%) is obtained at 800 ^{o}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_2O_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 H_2 mol/mol EthOH,	Yield of H_2 calculated according to equation
	H_2	CO	CO_2	CH_4	CH_3CHO		
	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/ZrO_2 (Biswas 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**

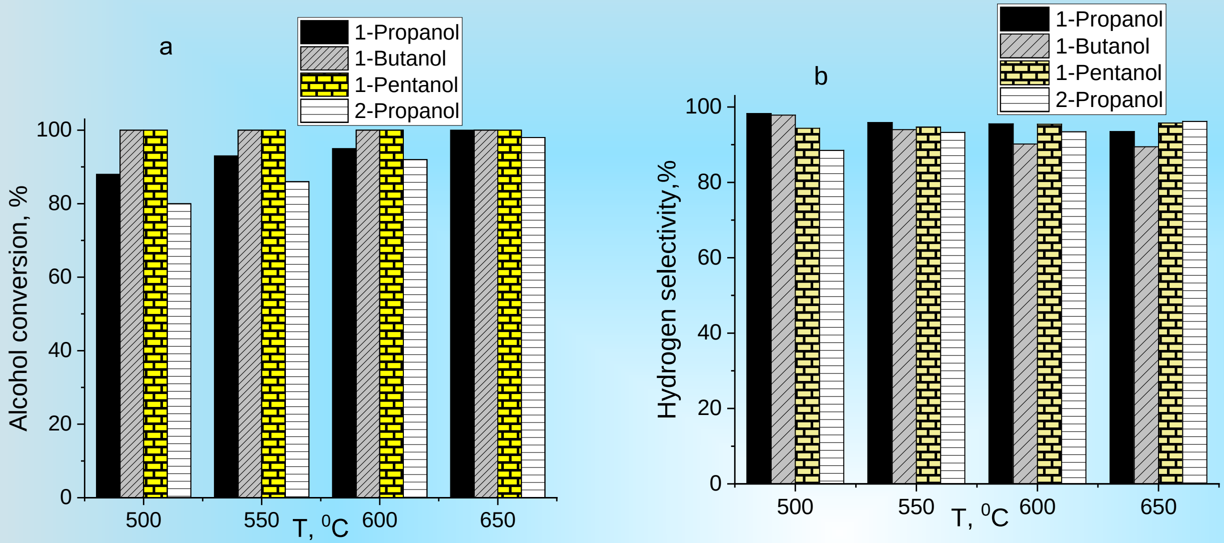
Single-step method for hydrogen production from bioethanol

$$C_2H_5OH + 3\ H_2O = 2\ CO_2 + 6\ H_2$$

Comparison of product distribution ESR at 550^{0}C

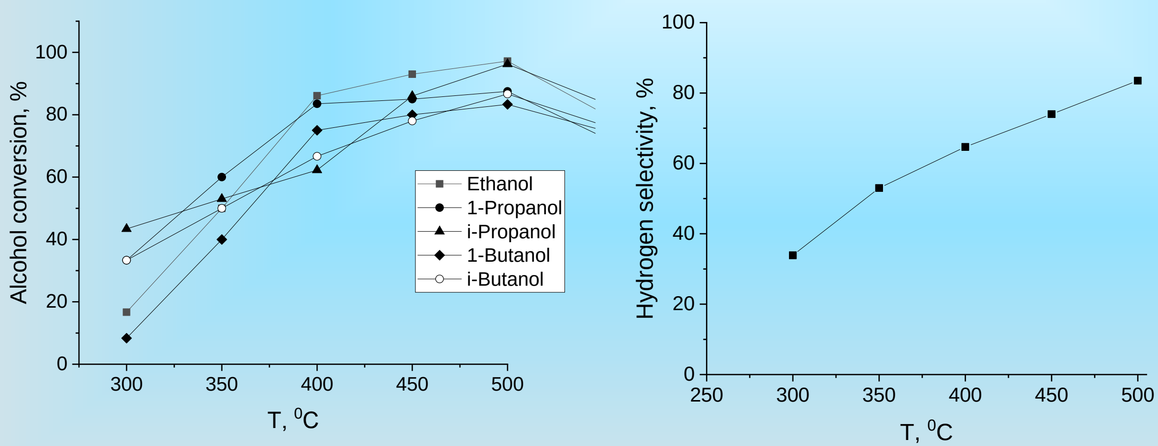
Catalyst	X, %	Product distribution, mol. %					
		H_2	CO	CO_2	CH_4	CH_3CHO	
Rh/CeO_2-ZrO_2	100	70,3	1,5	20,9	7,3	0	Diagne et al. 2002
$Ni/Ce_{0.74}Zr_{0.26}O_2$	100	75,2	6,1	13,9	4,5	0,3	Bismas et al. 2007
0,23NaCo/ZnO	100	70,9	2,0	25,0	1,1	0	Llorca et al. 2004
Fe/Co_3O_4	100	74,2	0,9	24,3	0,6	0	O'Shea et al. 2008
$MnFe_2O_4$	100	73,7	0	25,1	1,2	0	This study

Features of catalytic steam reforming of individual C_2-C_5 alcohols and mixtures thereof



Temperature dependence of the alcohol conversion (a) and hydrogen selectivity (b) during $C_3 - C_5$ alcohols steam reforming over $MnFe_2O_4$ catalyst

For the steam reforming of the ethanol and $C_3 - C_4$ alcohols mixture, the ethanol conversion reaches 97% at 500ºC. For other alcohols in the mixture, conversion varies between 83% and 90% depending on the alcohol nature and the hydrogen selectivity is approximately 80%



Alcohol conversion and hydrogen selectivity for ethanol-higher alcohols mixture during steam reforming over $MnFe_2O_4$ catalyst

At 500 ºC, 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

outputПродуктивність, ml/h*$g_{kat.}$	450
Selectivity, %	80-94
Mechanical strength, g/cm^2	2,2 (≥ 6 kg/Granule)
Specific surface, m2/g	15
Porosity, ε	0,54
Ignition temperature, ^0C	500
Thermal stability, ^0C	800
Operating temperature, ^0C	600 ÷ 700
Granule size, mm	6x6
Density, g/cm^3	4,500
Particle density, g/cm^3	2,07
Working volumetric speed, h^{-1}	4000
The ratio of reactor and catalyst diameters	≥ 3

An experimental batch of catalyst was prepared . It suitable for use in a pilot plant

FLOW SUMMARIES:

Stream No	1	2	3	4	5
Temp C	25.0000	650.0000	650.0000	60.0000	92.6266
Pres bar	1.0000	1.0000	1.0000	1.0000	1.0000
Enth kJ/h	-7323.2	-5359.6	-4171.8	-5282.7	-6212.3
Vapor mass frac.	0.00000	1.0000	1.0000	0.95651	0.94008
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

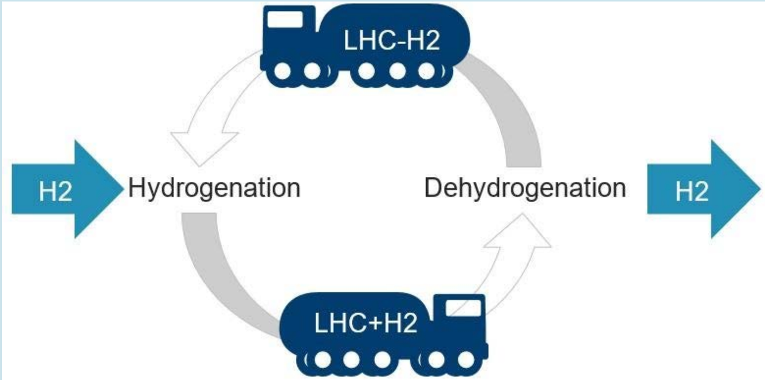
- 0,2 kg/h a water/alcohol mixture.
- 0,05 kg/h Natural Gas
- Electroplates

efficiency by alcohol = 44% $\left(\frac{}{} \right)$

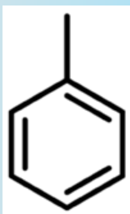
Conclusion

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



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



Toluene

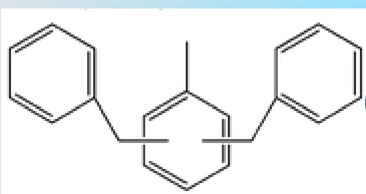
+3H2

CATALYST

-3H2

Methylcyclohexane

Storage density, MWh/Nm3	H2 Capacity, wt%	H2 Capacity, kg/m3
1,58	6.1	47

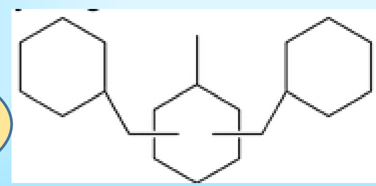


Dibenzyltoluene

+9H2

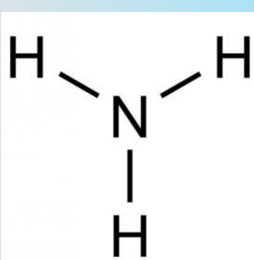
CATALYST

-9H2



Perhydrodibenzyltoluene

Storage density MWh/Nm3	H2 Capacity, wt%	H2 Capacity, kg/m3
2,05	6.2	57



Ammonia

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

CATALYST

Storage density MWh/Nm3	H2 Capacity, wt%	H2 Capacity, g/L
3,5	17,6	118

Thank you