

Hydrogen Generation from Ethanol by Allothermal Reforming

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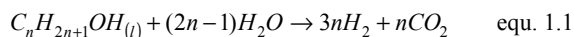
Abstract:

The use of biomass for energy generation is an effective solution for the reduction of CO₂ emissions and preserves the fossil energy resources. Taking these aspects into consideration ethanol, a CO₂ neutral fuel, is suited to substitute the conventional fossil fuels based on petroleum or natural gas. Funded by the European Commission, a research project for the use of bioethanol as fuel for generation of hydrogen by a reforming process was started in 1998. The motivation of this project is to use the fallow land in the European countries to supply bio fuels for energy generation. The feedstock of the fermentation process are starch containing crops such as corn, maize, sugar beet and sugar cane. Beside the opportunity to use the ethanol as raw material for the chemical industry to produce products like acetaldehyde or ETBE which is used as an octane enhancer it is possible to insert ethanol directly as a fuel as a gasoline replacement or as a blending additive. Ethanol as a liquid fuel has the advantages that it is on one hand easy to handle with respect to the storage and transportation and on the other hand it has a relative high mass specific energy content. Another application field is to use the ethanol as a feedstock for a steam reforming process to generate a hydrogen rich gas stream. The hydrogen is used as a fuel for a polymer electrolyte fuel cell (PEFC). Possible applications of the fuel cell technology are either stationary systems such as small CHP-units and or mobile applications for vehicles. The electrochemical energy conversion process of H₂ in a fuel cell causes no emissions of CO or NO_x. But hydrogen has some disadvantages: it is not available all over Europe, it is difficult to store and difficult to handle. These were the reasons why the reforming technology for generation of hydrogen became interesting even for small scale applications: decentralised stationary systems or even on board of a vehicle. The PEFC reaches high electric efficiencies of about 50 % and thus is an interesting power generator, especially in the small power range in comparison to conventional systems. The main target of the project is to develop and investigate a fuel cell system in the kW range. The work carried out at FHG ISE includes the reforming process and the shift process for gas purification. For the reformer process, a catalyst screening is carried out. The influence of different parameters on the reforming reaction is evaluated. The operation pressure is varied in a range of 2–9 bar. The temperature range is 600 to 800 °C, the steam-to-carbon ratio is varied between 2-4 (mole C to mole H₂O). Based on these investigations a combined burner/reformer unit is developed to supply a hydrogen flow with an energy content of about 3 kW.

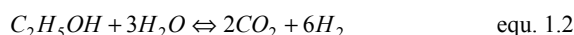
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1. Introduction

During an EU-project the hydrogen generation from ethanol by an allothermal reforming process has been investigated. The product gas of this process will be used for the stationary power generation in a fuel cell system. In a catalytic steam reforming process the ethanol is converted in combination with water into a hydrogen rich gas which consists of H₂, CO, CO₂, CH₄ and H₂O. The allothermal reforming process of alcohol is generally characterised by the equation (1.1):

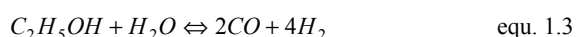


For the case of ethanol as fuel for the steam reforming process the stoichiometric reaction is defined as follows (1.2):



The reforming process is an endothermic reaction, which consists of two reaction steps. The first reaction step (1.3) represents the endothermic cracking process in which the ethanol and water react to carbon monoxide and hydrogen. The following reaction step (1.4) characterises the

exothermal heterogeneous water gas reaction where additional hydrogen is formed.



The CO in the reforming product gas will deactivate the anode catalyst of the PEM fuel cell. Therefore a gas cleaning process is necessary. A catalytic high and low temperature shift reaction reduces the CO content of the reforming product gas to about 0,2 Vol. %. Then, a pressure swing adsorption process reduces the CO value further to about 20 ppm before the hydrogen streams into the PEM fuel cell. The pressure of the main process will be determined through the adsorption pressure level of the pressure swing adsorption process (PSA). The necessary pressure level for the adsorption process is about 7 bar. The regeneration of the adsorbents is carried out by pressure reduction and also by cleaning the adsorbents with part of the hydrogen from the product gas. The waste gas of the regeneration process of the PSA is a low calorific gas, which can be used as fuel for the burner in the allothermal reformer. The figure 1.1 represents the flow sheet diagram of a PEM fuel cell system (1) with the reformer part, the two shift reactors, the fine gas cleaning process and the PEM fuel cell. Moreover, the ethanol/water inlet stream of the reforming process, the gas composition of the several

process steps, the heat flow of the endothermic and exothermic processes and the heat losses are presented.

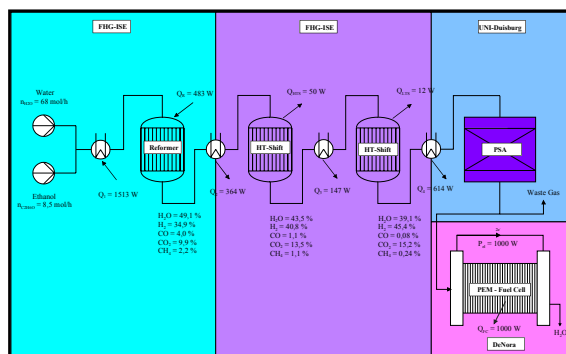


Figure 1.1: Flow sheet diagram of a PEM fuel cell system

2. Catalyst Screening

2.1 Structure of the experimental reactor

The catalyst screening is carried out in a tube reactor with an inner diameter of 47 mm. The catalyst material is arranged as bulk material in an ideal tube reactor. To guarantee isothermal conditions, the catalyst material is mixed with inert material in a proportion of 1 to 10. Quarz sand with a particle size of 200 - 300 μm serves as inert material. The sand acts as a thermal buffer that provides a constant temperature of the bulk material during the endothermic steam reforming reaction.

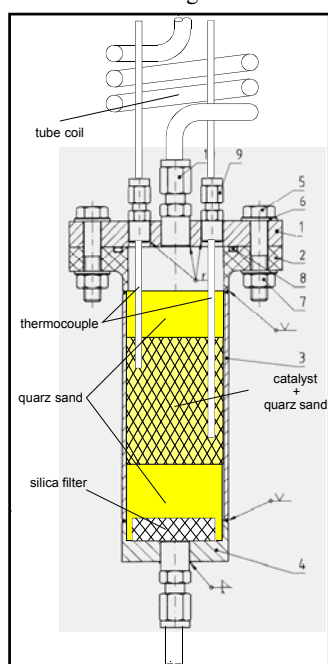


Figure 2.1.1: kinetic reactor for the steam-reforming

The illustration 2.1.1 represents the schematic design of the tube reactor. After the ethanol/water flow has passed the vaporiser the mixture streams through the tube coil into the kinetic reactor. In the tube reactor the gas first flows through a 20 mm thick layer of sand that is supposed to avoid discharge of catalyst materials. This layer is followed by 110 cm^3 catalyst/sand mixture in which the reaction takes place. Two thermocouples are placed in the upper and lower third of the mixture layer in order to control the

temperature gradient over the height of the catalyst bed. A silica filter at the bottom of the reactor avoids the discharge of sand or catalyst material. Isothermal flow reactors can be classified by the following characteristics:

- plug flow
- dispersion negligible
- secondary flow negligible

The reformer product gas usually is composed of hydrogen, carbon dioxide, carbon monoxide and methane. All carbon containing gases are analysed quantitatively with an NDIR spectrometer. The volume of the generated gas is measured by a gas meter and the difference is attributed to the hydrogen content of the gas. For some examples, the gas composition was additionally controlled by measurements with the FTIR-spectrometer, and ethylene (C_2H_4) and acetaldehyde (CH_3CHO) as side products could be detected principally at reforming temperatures as low as 600 $^\circ\text{C}$ with palladium and platinum as catalyst material.

2.2 Parameter of the catalyst screening

The following table 2.2.1 shows the different catalysts, which have been investigated.

Name	Sign.	Composition
Nickel	Ni	nickel on Al_2O_3
Ruthenium	Ru	ruthenium on Al_2O_3
Platinum	Pt	platinum on Al_2O_3
Palladium	Pd	palladium on Al_2O_3
Perovskite	Pe	lanthanum, manganese, cobalt, strontium
Nickel-Platinum	PN	nickel; platinum on Al_2O_3
Nickel-Palladium	NP	nickel; palladium on Al_2O_3

Table 2.2.1: catalyst materials chosen for the experiments

To evaluate the reforming behaviour of the several catalyst materials, it is necessary to find the optimal temperature range for the catalyst screening. As first example, the ruthenium catalyst was investigated at a fixed pressure $p = 9$ bar and a steam to carbon ratio $s/c = 4$ in a temperature range from 500 - 700 $^\circ\text{C}$, by heating up the reactor in 50 K steps. The H_2 content in the product gas stream was recorded and is given in table 2.2.2.

Reaction temperature	H_2 content [mole %]
500	36,8
550	44,9
600	59,6
650	67,7
700	69,0

Table 2.2.2: H_2 content; s/c -ratio = 4; $p = 9$ bar

The amount of hydrogen continuously increases with temperature, therefore the decision was made to investigate all other catalysts at the two temperatures 600 and 700 $^\circ\text{C}$ as basis information. By these two measurements it can be seen, if a lower temperature is applicable or not. The s/c ratio, which is selected for the catalyst investigations is determined by the limits for carbon formation. Thermodynamic calculations are made with the program EquiTherm. These calculations show the possibility of carbon formation at low steam concentrations, at $s/c \leq 1,5$. For this reason the lower s/c limit for the catalyst screening is 2,0. The influence of pressure on the thermodynamic

equilibrium of the reforming reaction is known, a low pressure favours complete ethanol conversion and a high hydrogen yield. In the following table 2.2.3 the parameters of the catalyst screening are listed:

s/c-ratio:	2, 3, 4
Pressure:	p = 2, 5, 9 bar
Temperature:	600; 700; 800 (Ni-catalyst) °C

Table 2.2.3: Parameters for the catalyst screening

2.3 Results of the catalyst investigations

The figures 2.3.1 and 2.3.2 show the hydrogen mole stream of the ethanol steam reforming reaction in dependence on the s/c-ratio at a temperature of $t = 700^\circ\text{C}$ and a pressure of $p = 2$ bar (2.3.1) or 9 bar (2.3.2). The legend sign of the catalyst corresponds to the table 2.2.1.

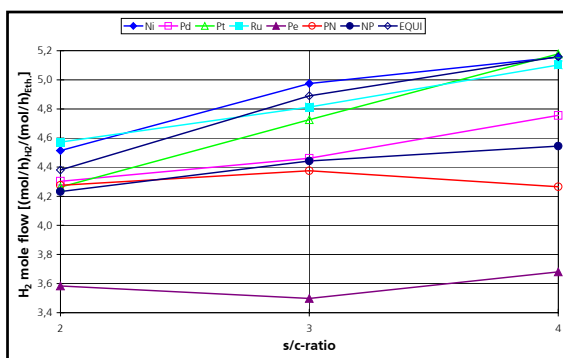


Figure 2.3.1: Normalised hydrogen stream in dependence on the s/c ratio; $p = 2$ bar, $t = 700^\circ\text{C}$

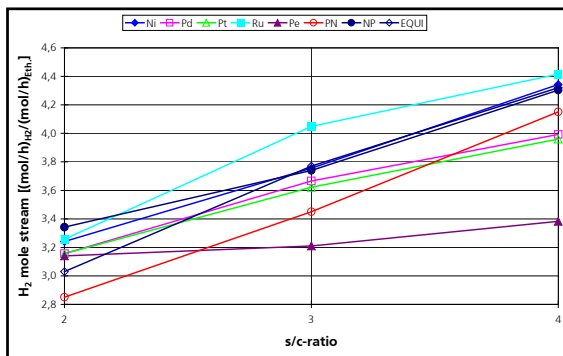


Figure 2.3.2: Normalised hydrogen stream in dependence on the s/c ratio; $p = 9$ bar, $t = 700^\circ\text{C}$

All catalysts show in principle the same behaviour, a higher pressure leads to a decrease of the hydrogen yield and a rise in S/C-value leads to a better ethanol conversion and a higher hydrogen output. The perovskite is the worst one among the investigated catalysts. Additionally the diagrams show the thermodynamic calculation with the program EquiTherm. The hydrogen yield with the nickel catalyst is better than the equilibrium. This is a sign, that the heterogeneous water gas reaction takes place at the end of the reforming reaction.

The following figure 2.3.3 represents for example the composition of the reforming product gas of the nickel catalyst (Ni). The hydrogen content is even decreasing for higher s/c values, though the absolute quantity of hydrogen is rising with higher s/c. The comparison of the three

graphs for the three pressure levels 2, 5 and 9 bars with identical s/c-ratio show the strong influence on the gas composition. The main result is the increasing amount of residual, unconverted methane for higher pressure levels.

The variation of product gas composition in dependence on s/c-ratio and pressure corresponds with the thermodynamic calculation of equilibrium. The values of the H_2 mole fraction are nearly identical with the measured equilibrium data. So for example $s/c = 3$ and for the pressure 1, 4, 8 bar the H_2 values are calculated to 44,9; 41,2 and 37,1 mole %, while the measured test result are 44,5; 41,4 and 37,3 mole %.

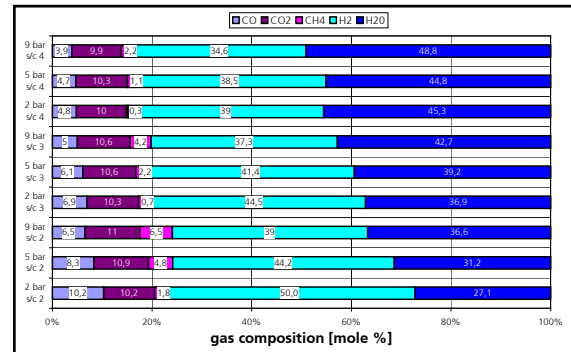


Figure 2.3.3: Gas composition of the nickel catalyst in dependence on s/c-ratio and pressure; $t = 700^\circ\text{C}$

3. Reformer investigation

3.1 Design of the ethanol reformer

Based on the results of the catalyst screening an allothermal compact reformer was developed. Figure 3.1.1 illustrates schematically the design of the reforming reactor for an 1 kW fuel cell system. A burner arranged in the centre of the reactor casing supplies the necessary heat for the endothermic reforming reaction and the evaporation heat for the liquid reactants (water and ethanol). Moreover the heat for the starting phase to heat up the casings of the reforming reactor and the both CO-Shift reactors is supplied by the burner. The radiation burner consists of a cylindrical porous volume. The material of this ceramic body is silicon carbide. The reaction zone of the combustion should be located in the pore volume, so that the ceramic body begins to radiate and the heat is transferred to the inner surfaces of the reactor tube.

The fuel for the radiation burner (waste gas and ethanol) and the air flow separately over the top of the burner into the porous body. The combustion reaction takes place in the porous volume. The exhaust gas leaves the combustion chamber at the bottom of the burner case. This waste heat can be used for the preheating of the air flow which is necessary for the combustion process. The liquid ethanol/water mixture flows at the bottom of the reformer into an internal heat exchanger. This heat exchanger has a function of a preheater and a vaporiser. After the evaporation of the reactants the gaseous ethanol/water mixture streams over the bottom of the reactor into the catalyst fixed bed. The catalyst material is arranged in an annulus between the inner and the outer reactor tube concentric to the cylindrical radiation source. The particle size of the bulk material has a diameter of about 4 mm. The volume of the catalyst fixed bed is about $300 [\text{cm}^3]$. The material is a commercial nickel catalyst.

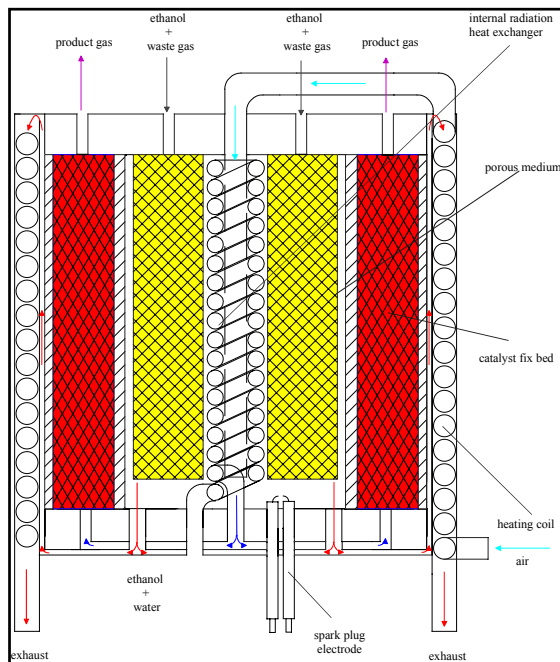


Figure 3.1.1: Schematic design of the compact reformer

3.2 Results of the reformer investigation

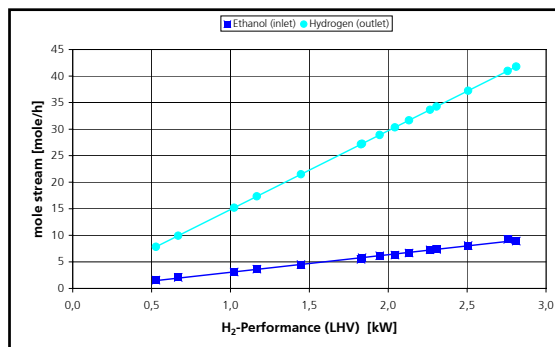


Figure 3.2.1: Performance range of the reformer

Figure 3.2.1 illustrates the investigated power range of the compact reformer. The generated hydrogen performance is in a range from 0,5 up to 3 kW (LHV_{H_2}). Moreover the ethanol inlet and the hydrogen outlet mole stream are shown. The diagram 3.2.2 presents the mole stream of the dry product gas in dependence on the generated hydrogen performance (LHV_{H_2}) at the reformer outlet.

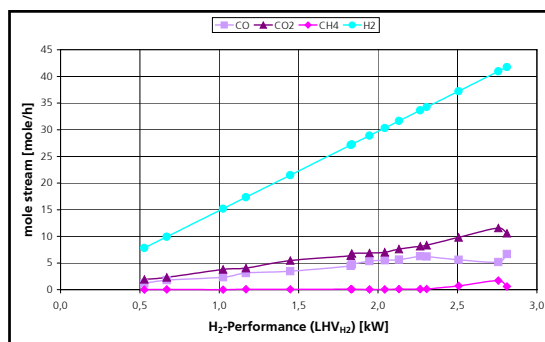


Figure 3.2.2: Mole stream of the reformer product gas

4. Burner Development

The heat supply for the endothermic reforming reaction and for the evaporation of the reactants is realised with a porous burner. The advantages of this kind of combustion type is on the one hand the 3-dimensional reaction zone with a large reaction volume, being the reason of the effective burnout of the fuel and consequently of low CO-emission. On the other hand the high effective thermal conduction (about 100 times higher than in a free flame) is an immense advantage. It guarantees a homogeneous temperature profile in the reaction zone, so that no temperature peaks occur. This means low mechanical stress of the reformer material and moreover no thermal NO_x -emission building.



Figure 4.1: Ceramic body of the porous burner

High power density and a stable burner operation is realised as well as a modulation range up to a ratio of 20:1 (2). This is important for the use of a low calorific gas as burner fuel like the waste gas from the regeneration process of the PSA device. The picture 4.1 shows the ceramic body which is used for the radiation burner of the allothermal ethanol reformer. The material of the body is Silicon/Carbid. The hollow ligaments of the ceramic body are filled with silicon. This porous body is manufactured by the Fraunhofer Institute IKTS in Dresden. The porosity of the used porous body is about 30 ppi.

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