

**A new reactor concept for the steam reforming of bio-ethanol  
 to produce a hydrogen rich gas for a CHP-Unit based on a PEM-fuel cell technology**

Thomas Rampe, Angelika Heinzel  
 ZBT GmbH-Duisburg  
 Carl-Benz Straße 201; 47058 Duisburg; Germany  
 phone +49-(0)203-7598-0 - fax +49-(0)203-7598-3946; e-mail: t.rampe@zbt-duisburg.de

Main advantages of ethanol for the daily use are the high volumetric energy capacity, the easy storage and transporting characteristics of a liquid fuel and the non toxic property. Advantageous for the greenhouse emissions are not only the high H/C mole ratio of this fuel compared with gasoline. But also the CO<sub>2</sub> neutral generation by the photosynthesis process helps to reduce the formation of carbon dioxide. For the establishment of bio-ethanol as fuel on the energy market the cost reduction during the last years plays a decisive role. 1974 the production of a litre ethanol from wood cost \$ 2.50. Optimised technical procedures and new raw materials reduced the cost of the ethanol production up to 0.30 \$/litre. In 10 years researchers expect production costs of about 0.22 \$/litre [1]. Apart from the possibility to replace petrol by ethanol in internal combustion engines ethanol can be used for the generation of a hydrogen rich synthesis gas in a steam reformer process. The hydrogen can be taken as feed stream in a PEM fuel cell with applications in stationary grid-independent CHP-Units.

During the research project an allothermal steam reformer, which can be fed with bio-ethanol was designed and investigated. The main idea was to develop a compact reforming reactor with an internal heat management for the evaporation and superheating of the feed stream. The heat for the endothermic reforming reaction is supplied with an internal porous burner. The reformer concept will be optimised in respect of the activity of the reforming catalyst, the heat transfer between the porous burner and the reforming reaction zone and the heat losses across the reformer shell.

In the preliminary stages of the project a catalyst screening has been made to find out the catalyst material with the highest activity in regard to the bio-ethanol steam reforming reaction and the most significant selectivity in respect of the hydrogen formation. Based on the result of this catalyst screening, a commercial nickel catalyst is used for the bio-ethanol steam reforming process. At the maximum operation point the compact steam reformer generates a hydrogen rich product gas with a thermal energy content of about 4,2 kW<sub>H<sub>2</sub>,therm.</sub>. The heat supply for the reforming reaction and the evaporation and superheating of the reactants is realised with a porous burner. The main convenience of this burner concept is the 3-dimensional reaction zone. This property makes it possible to modulate the burner in a range of 1 up to 18. Moreover this expanded reaction area has a positive influence on the NO<sub>x</sub> and the CO formation. The high heat capacity of the porous SiSiC-ceramic in the combustion chamber allows it to use both gaseous and liquid fuels for the porous burner.

This research project was developed during my graduation work at the Fraunhofer Institute for Solar Energy in Freiburg [1]. Moreover basic investigations were made during the project Bio-ethanol I (JOR3-CT97-174), which was funded by the European Commission [2].

Key words: biomass conversion, hydrogen, liquid biofuels

**Introduction:**

The steam reforming process of ethanol is defined by an endothermic reaction corresponding to equation 1:



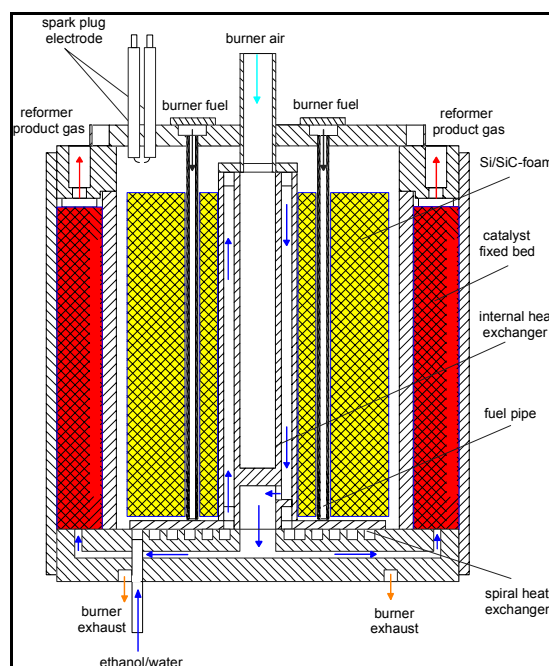
This main reaction can be characterised by following both equations



Possible side reactions are the methanation by hydrogenation of carbon monoxide, carbon dioxide or carbon, preferring at low temperature. The formation of acetaldehyde and ethylene are possible side reactions too, taking place at temperatures lower than 650 °C. Additional the carbon formation has to be avoided at the steam reforming process, building by the endothermic Boudouard reaction, the thermal methane cracking and the heterogeneous water gas reaction.

**Design of the steam reformer**

The general concept of the bio-ethanol steam reformer was described in [3]. Figure 1 illustrated the further development of the bio-ethanol steam reformer.



**Figure 1:** Construction of the bio-ethanol steam reformer

Some modifications are made at the actual design of the reactor. The ethanol water mixture enters the reactor at the bottom of the shape by the spiral heat exchanger.

There the liquid reactants are heated up before they are evaporated in the internal heat exchanger, which is placed in the centre of the reactor shape. After this the gaseous phase streams radial to the annular gap where the catalyst fixed bed is arranged. The reactants enter the reforming zone at the bottom, and the hydrogen rich product gas leaves the reactor at the top. As steam reforming catalyst the commercial nickel catalyst G90-B from the company Süd-Chemie has been selected after testing of different catalyst samples [3].

The necessary heat of the endothermic steam reforming reaction is supplied by a porous burner. The Si/SiC-ceramic foam encloses the internal heat exchanger. As burner fuel hydrogen and a mixture of hydrogen and ethanol with different concentrations are used. Moreover a hydrogen-carbon dioxide mixture simulating the offgas of a PEM-fuel cell is used for the oxidation reaction in the porous burner.

In the case of hydrogen the burner is used in a non premixed operation mode. The fuel enters the combustion zone through the 8 vertical pipes, which are arranged circularly in the ceramic foam. Air enters the burner through the central pipe separated from the fuel and streams radial through 64 bores in the case of the internal heat exchanger into the combustion zone.

#### Porous burner investigations

Figure 2 shows the hydrogen emission in the exhaust of the porous burner in dependence of the porous body temperature. In this operation mode the burner works with hydrogen as burner fuel at 4 different power levels and with an air ration of 1.2. The performance data corresponds with the thermal energy of the hydrogen stream, calculated with the lower heating value.

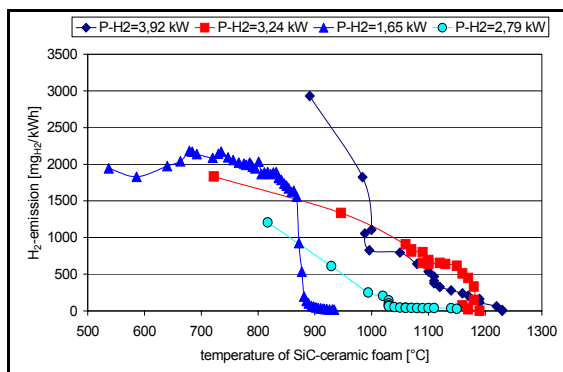


Figure 2: H<sub>2</sub> emission of the porous burner [4]

The plot at a burner performance of 1,65 kW shows a sudden decrease of the hydrogen emissions in a temperature range of 900 °C. At this temperature the oxidation reaction is kinetically limited by a slow reaction rate below 900 °C. Above this temperature the hydrogen emission decreases below a value of 100 mg<sub>H2</sub>/kWh. In the upper power range the hydrogen emissions decrease not as fast but more regular and the hydrogen emissions fall below the limit of 100 mg<sub>H2</sub>/kWh in a temperature range of 1200 °C. This behaviour makes clear that in the higher power range the reaction rate is limited by the mixing process of the combustion reactants.

In the case of the reformer operation mode the hydrogen emission of the porous burner varies in the range of 10 – 35 mg/kWh. Figure 3 shows the hydrogen content of the burner exhaust in dependence on the S/C-ratio of the reformer reactants. The higher hydrogen emission at the low S/C level results from the lower temperature of the SiC-foam in the burner chamber.

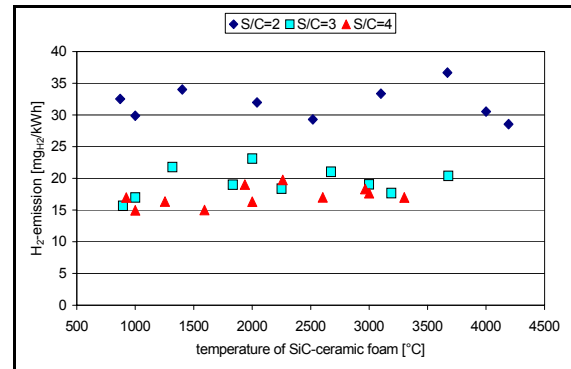


Figure 3: H<sub>2</sub>-emission of the porous burner in the steam reformer operation mode [4]

As a result of the low operation temperature of the porous burner the formation of NO<sub>x</sub> pollutions isn't highly pronounced. The maximum temperature of the SiC-foam during the investigations is 1240 °C. During the investigations of the nitrogen oxide emissions the burner performance is varied in range of 2,5–3,4 kW. The maximum NO<sub>x</sub>-concentration in the exhaust is lower than 10 mg<sub>NOx</sub>/kWh.

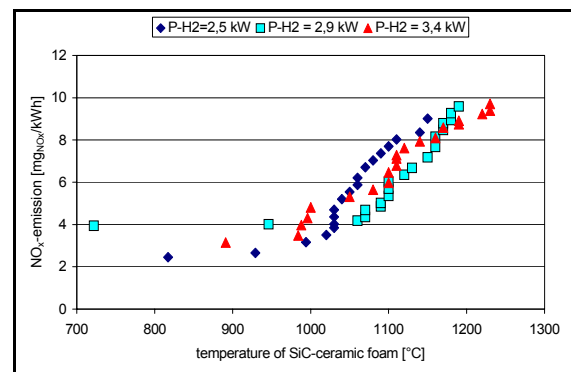


Figure 4: NO<sub>x</sub>-emission of the porous burner [4]

In the case of a hydrogen/ethanol-mixture as fuel two different operation modes of the porous burner are investigated. On the one hand ethanol streams with the hydrogen through the pipes into the combustion chamber (nv). On the other hand ethanol is premixed (v) with the air and enters the reaction zone through the central bore in the internal heat exchanger. The reformer works with a S/C ratio of 4 at 700 °C and supplies a hydrogen mole stream of 42,5 mole/h. Figure 5 presents the H<sub>2</sub>- and CO-emissions at different fuel mixtures. During the complete operation period the burner works with a constant fuel performance of 3450 kW. First this energy content is provided only by hydrogen. During the further handling the hydrogen is substituted by ethanol step by step. At the end the fuel ratio of ethanol to hydrogen is about 1.1. The hydrogen content in the exhaust is continuously on a low level increasing the ethanol content in the fuel mixture.

But the CO-emission increases remarkably if the ethanol rate rises. In the case of the non premixed operation mode the CO content increases to a maximum value of 366 mg<sub>CO</sub>/kWh. If the burner works in the premixed operation mode the maximum CO content is reduced to 123 mg<sub>CO</sub>/kWh.

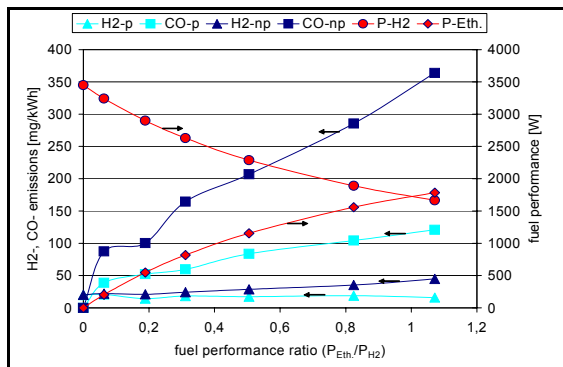


Figure 5: H<sub>2</sub>- and CO-emission using a hydrogen/ethanol mixture as burner fuel [4]

At high fuel performance ratio the liquid ethanol evaporates partially in the porous body. Therefore the temperature decreases and that is why the CO content in the exhaust increases in the case of the non premixed operation mode.

#### Energetic examination of the steam reformer

Figure 6 shows the composition of steam reformer product gas in dependence on the temperature at the top of the reforming catalyst zone. At a temperature of 600 °C the reformat gas contains a hydrogen content of 36 mole-%. With increasing temperature the hydrogen content rises up to 39 mole-% at 700 °C and 42 mole-% at 800 °C. Simultaneously the methane and water content in the reformat gas decreases.

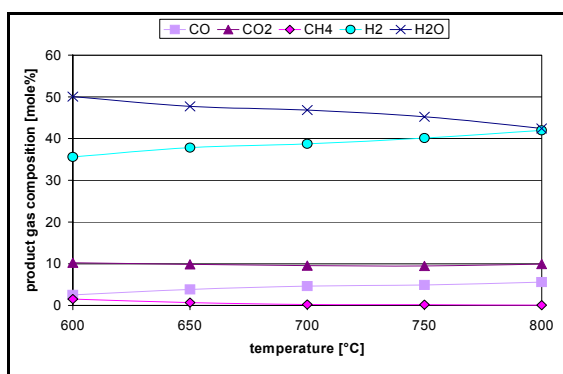


Figure 6: Composition of the reformer product gas [4]

The benefit of the steam reformer is the chemical enthalpy stream of the reformer product gas ( $P_{R,chem}$ ), based on lower heating value of hydrogen. Moreover the sensible heat of the reformer product gas ( $Q_{R,s}$ ) and the sensible heat of the burner exhaust gas ( $Q_{B,s}$ ) are considered. The chemical enthalpies of the burner ( $P_{B,chem}$ ) and reformer ( $P_{Ref,chem}$ ) inlet fuel streams are the inputs of this process. The following equation shows the definition of the efficiency of the ethanol steam reformer:

$$\eta = \frac{P_{R,chem} + Q_{R,s} + Q_{B,s}}{P_{Ref,chem} + P_{B,chem}}$$

The chemical enthalpy of the reformer product gas is calculated with the H<sub>2</sub> and CO mole stream because the carbon monoxide reacts in the equimolar homogeneous water gas reaction to carbon dioxide with formation of 1 mole hydrogen.

The efficiency of the steam reformer in dependence on the thermal performance of the reformer product gas is shown in Figure 7. Generally the efficiency increases with rising thermal performance of the reformer product gas. The comparison of the different S/C ratios shows that higher water content in the feed stream has a positive effect on the energy balance of the steam reformer. The efficiency at S/C = 4 is about 1.0 to 1.5 % higher in comparison with a S/C ratio of 2 at the same thermal product gas performance. At S/C = 2 the maximum efficiency is reached at a product gas performance of 3600 W. In the case of S/C = 4 the maximum is at 3300 W. The reason of this behaviour is the limited area of the pipe between the burner chamber and the reforming zone for the heat transfer. Therefore the heat losses by thermal conduction over the exhaust pipes increase.

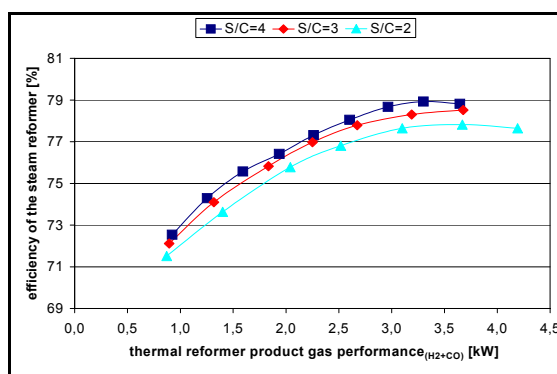


Figure 7: Efficiency of the ethanol steam reformer [4]

Figure 8 presents the comparison of the energy balance of the steam reformer at a temperature of 700 °C and at two different S/C ratios. In both cases the chemical performance of the reformer product gas ( $P_{Ref,chem}$ ) is in a range of 3000 W.

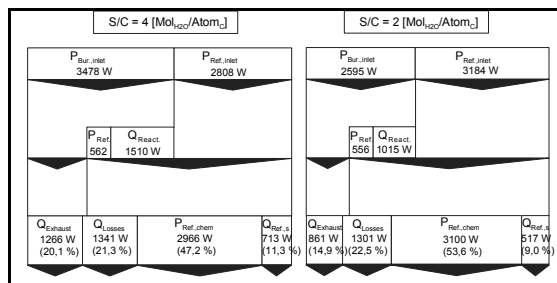


Figure 8: Energy balance of the steam reformer [4]

In this demonstration the differences will be clear. Due to the higher heat requirement for the evaporation of the water the heat for the reactants ( $Q_{React}$ ) is about 50 % higher at a S/C ratio of 4 then at 2. Therefore the burner inlet performance ( $P_{Bur,inlet}$ ) is about 34 % higher at this S/C ratio. The performance for the steam reforming reaction ( $P_{Ref}$ ) in both cases is almost identical.

Remarkable differences are the sensitive heat of the burner exhaust ( $Q_{\text{Exhaust}}$ ) and the reformat gas stream ( $Q_{\text{Ref,s}}$ ) at both S/C ratios. Both enthalpy streams are higher at S/C 4. The sensitive heat of the burner exhaust is 47 % higher and of the reformer product gas 38 %.

The heat for evaporation and heating of the reactants is mainly transported as radiation heat. In contrast to this process the reaction heat to the steam reforming catalyst is transferred by radiation and convective mechanism. Figure 9 shows the heat contribution of the different mechanisms in dependence on the reformer product gas performance in the range of S/C = 2 - 4.

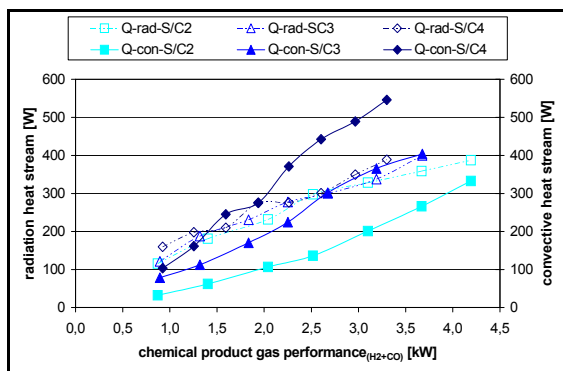


Figure 9: Heat transfer mechanism to the reforming zone

In particular at high S/C ratios the convective heat stream increases more than the radiation heat with rising reformat gas performance. For example at S/C = 4 the convective heat rises in a power range of 900- 3300 W from 103 – 546 W. Whereas the radiation heat increases only from 159 – 389 W. As result of the higher burner exhaust volume stream the convective heat is more pronounced with higher performance of the steam reformer.

#### Exergetic examination of the steam reformer

For a optimum fuel utilisation an exergetic consideration of the steam reformer is carried out. The exergetic balance of the steam reformer including the porous burner is illustrated in Figure 10. The reformer part of the exergetic balance is divided into the mixture of the reactants (E-M-Ref) the heat transfer to the liquid reactants (E-WT-VW), for the evaporation (E-WT-V) and the superheating (E-WT-Ü). Moreover the exergy for heating the reactants (E-WÜ-R), the exergy for the heat supply of the endothermal reforming reaction (E-WÜ-Ref) and the exergy of the chemical reaction (E-Ref) are considered. In the case of the burner the mixing of the burner reactants (E-M-Br) and the oxidation reaction (E-Ox) influenced the exergetic balance.

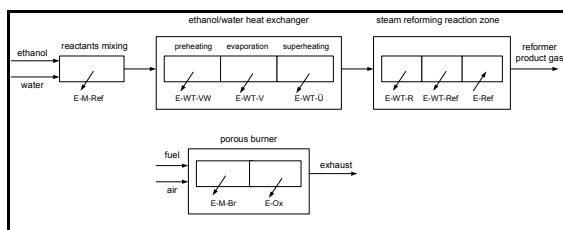


Figure 10: Exergetic balance of the steam reformer [4]

The exergetic balance of the steam reformer in dependence of the S/C ratio shows Table 1. The sum of the exergetic streams is negative. During the steam reforming process the exergy is reduced. The exergetic losses of the steam reformer increase from -494 to -904 W with rising S/C ratio.

Table 1: exergetic balance of the steam reformer

S/C ratio [mole <sub>H2O</sub> /atom <sub>C</sub> ]	2	3	4
Σ Exergetic streams [W]	-494	-697	-904

The exergetic streams of the different processes in dependence on the S/C ratio are presented in Figure 11. Only at the endothermal steam reforming reaction the exergy value increases. All other processes include exergetic losses, which is characterised by the negative value. The highest exergetic losses take place at the heat transfer during the evaporation of the liquid reactants ethanol and water and during the chemical oxidation reaction in the porous burner. Both processes represent 72 – 74 % of the exergetic losses in the steam reformer.

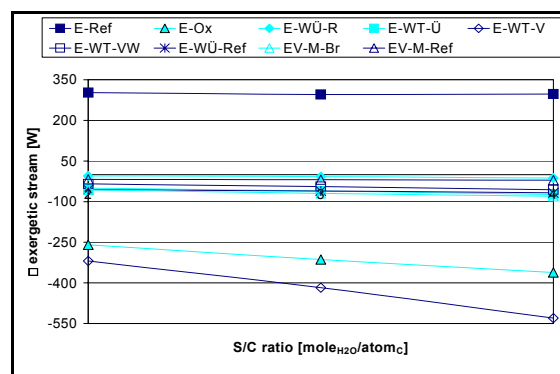


Figure 11: Exergetic streams of different processes [4]

For example the exergetic losses shall be reduced using the sensitive heat of the burner exhaust for the evaporation of the liquid reactants instead of the chemical enthalpy of the burner fuel. At a S/C ratio of 4 the exergetic loss is reduced from -545 to -366 W.

#### References:

- [1] CETEC: Camnet Energy Technology Centre [http://www.nrcan.gc.ca/es/etb/cetec/cetec01/html/docs/factsheet\\_ethanol\\_the\\_green\\_gasoline\\_e.html](http://www.nrcan.gc.ca/es/etb/cetec/cetec01/html/docs/factsheet_ethanol_the_green_gasoline_e.html)
- [2] Bio-ethanol as fuel for the fuel cell vehicles and small scale stationary power production; EU-Project JOR3-CT97-174 [http://dbs.cordis.lu/fep/cgi/srchidadb?ACTION=D&SESSION=85672004-4-1&DOC=30&TBL=EN\\_PROJ&RCN=EP\\_DUR:30&CALLER=PROJ\\_JOULE](http://dbs.cordis.lu/fep/cgi/srchidadb?ACTION=D&SESSION=85672004-4-1&DOC=30&TBL=EN_PROJ&RCN=EP_DUR:30&CALLER=PROJ_JOULE)
- [3] Hydrogen generation from Ethanol by allothermal Reforming; T. Rampe; P. Hübner; B. Vogel; A. Heinzel; FHG-ISE Freiburg; 2000;
- [4] Entwicklung eines Bioethanol-Dampfreformers zur Erzeugung von Wasserstoff für den Einsatz in einem PEM-Brennstoffzellen-BHKW; doctoral thesis; T. Rampe