

# Gasoline fuel cell systems

A. Docter<sup>\*</sup>, A. Lamm

*Daimler-Benz, Research and Technology, Fuel Cell Systems, D-89013 Ulm, Germany*

Accepted 28 June 1999

## Abstract

For different types of hydrocarbon fuel reformer concepts, thermodynamic equilibrium calculations were conducted. These simulations allow to estimate the potential energy efficiency of these reformers and thus help to choose the right technology before further development work starts. According to the simulation results, autothermal-reforming can yield higher energy efficiencies than partial oxidation. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Hydrogen; Fuel cell; Hydrocarbon; Fuel processing; Reforming; Thermodynamic simulation

## 1. Introduction

Today, reforming processes are well-established in the oil and chemical industry for stationary applications. Such plants have gas capacities up to 100,000 Nm<sup>3</sup>/h and huge dimensions. Furthermore, since several years there is a great effort in developing small fuel processing systems for mobile applications. This development activities have to be considered in connection with the worldwide increasing activities in the field of PEM Fuel Cells.

Regarding the existing reforming processes to generate hydrogen rich-gas on board of a car, methanol yields the highest vehicle efficiencies among all available liquid fuels. A first vehicle with fuel cell propulsion and gas processing system based on methanol as fuel (NECAR III) has been presented by Daimler-Benz on the automotive fair of Frankfurt in 1998.

The energy efficiency of a car with a fuel cell propulsion system based on gasoline as fuel will be lower than the efficiency of systems based on methanol but higher than the efficiency of a car with an internal combustion engine. However, the somewhat lower vehicle efficiency in the case of a fuel cell propulsion system with gasoline processor in comparison with a methanol system can be compensated by the higher efficiency of the energy conversion chain (well to tank). Furthermore, the energy

density of gasoline is higher than the energy density of methanol. The biggest drawback of a methanol-based fuel cell vehicle is the missing methanol infrastructure. Today, methanol is not available — despite some rare exceptions — and if a methanol infrastructure will be build up is still not clear.

## 2. Fuel cell systems

PEM fuel cells generate electric power, water and waste heat from air and hydrogen or from a hydrogen-rich gas. A hydrogen-rich gas can be produced in a so-called reformer or fuel processor from alcohols or hydrocarbons. The production of hydrogen-rich gases in an industrial scale is almost only done by processing crude oil, its products or of natural gas. Well-established processing technologies are steam-reforming, partial oxidation and autothermal-reforming. What all technologies have in common is that the reforming process consists of similar steps. In the first step, the hydrocarbon is transferred into a gas containing large quantities of hydrogen and carbon monoxide. This gas — commonly referred to as synthesis gas — is further processed in two shift reactors. In these reactors, the carbon monoxide is transferred into hydrogen by the water-gas shift-reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ ). The difference between the three reforming technologies lies in the concentration of the CO in the synthesis gas, the temperature the first reactor is working on and in the composition of the educts, but the basic structure of a

<sup>\*</sup> Corresponding author

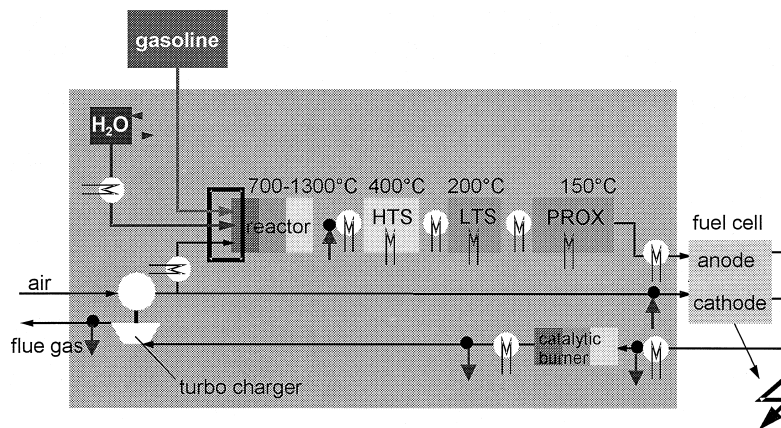


Fig. 1. Basic concept for a fuel cell system with a gasoline fuel processor.

reformer is independent of the reforming technology applied. Because of the similar structure of the reformer, the following fuel cell system design suits all reforming technologies (Fig. 1).

Fuel, water and air are fed into the reformer in a controlled manner. The operating temperature of the first reactor lies between 700°C and 1300°C, depending on the technology applied. The lower temperature corresponds to steam-reforming, the highest to partial oxidation. Autothermal-reforming works at temperatures somewhere between these temperature boundaries. The hot synthesis gas has to be cooled down to the working temperature of the high temperature shift reactor, which lies in the range of about 400°C. This cool down has to be done quickly to kinetically inhibit coke formation by the Bourduard reaction ( $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ ). The easiest way to achieve this is to inject liquid water. It is possible to match the amount of water needed for quenching with the amount of water needed for the shift-reaction. The second shift-reaction takes place at about 200°C. Behind this low temperature shift reactor, the CO concentration lies in the range of 0.5 up to 1.0%. CO can be removed from the synthesis gas by preferential oxidation down to concentrations smaller 10 ppm. This gas enters the anode side of the fuel cell, while the pressurized and humidified air enters the cathode side. The off gas of anode and cathode side are mixed and fed into a catalytic burner, which converts the hydrogen left over by the fuel cell into water and heat. A turbo charger can be used to recover a part of the energy by the combustion of the hydrogen to power the compression of the air.

There are numerous possible variations of thermal system integration. The first reactor can be heated as well as cooled, whereas the shift reactors and the PROX can either be used adiabatic or isothermal. Between the reaction steps the gas has to be cooled. On the other side air, water and fuel can be preheated or in the case of water and fuel, be vaporized and overheated. Thermal integration is a key issue for the system design. The system design has to fulfill different mostly conflicting requirements. First of

all, a high system efficiency. It is obvious that for a high system efficiency a sophisticated thermal integration is necessary. But such a thermal integration is likely to result in a complex and therefore large and heavy system which shows a poor dynamic behavior. Besides these issues the system has to operate safely and reliably, therefore demanding the prevention of any soot or coke formation. To prevent coke formation in any operating point of the system, the reformer has to be operated in a certain manner, corresponding to the air and the water fed into the first reactor. The first step in designing a fuel cell system with reformer is to choose the right reforming technology. The second step is to describe the behavior of the reactor in terms of its input qualities. This has to be done experimentally as well as theoretically by means of calculation of thermodynamic equilibria.

### 3. Fuel processing

An important criterion for choosing a reforming technology is the reforming or thermal efficiency, which describes the relation of the lower heating values of the hydrogen produced to the lower heating value of the fuel processed. Since almost the complete amount of CO can be converted to  $\text{H}_2$ , the amount of  $\text{H}_2$  and CO produced in the first reactor limits the maximum amount of  $\text{H}_2$  to be generated in the reformer. In this article, these efficiency is defined as follows:

$$\eta_{\text{ref}} = \frac{(n_{\text{CO}} + n_{\text{H}_2})h_{\text{H}_2\text{-heating}}}{n_{\text{fuel}}h_{\text{fuel-heating}}}. \quad (1)$$

Steam-reforming of hydrocarbons usually takes place at temperatures around 700°C. From all reforming technologies, steam-reforming seems to guarantee the highest reforming efficiencies. But the drawback is that this reaction is endothermic and therefore the reactor needs to be heated. In large chemical plants, this is no problem since normally,

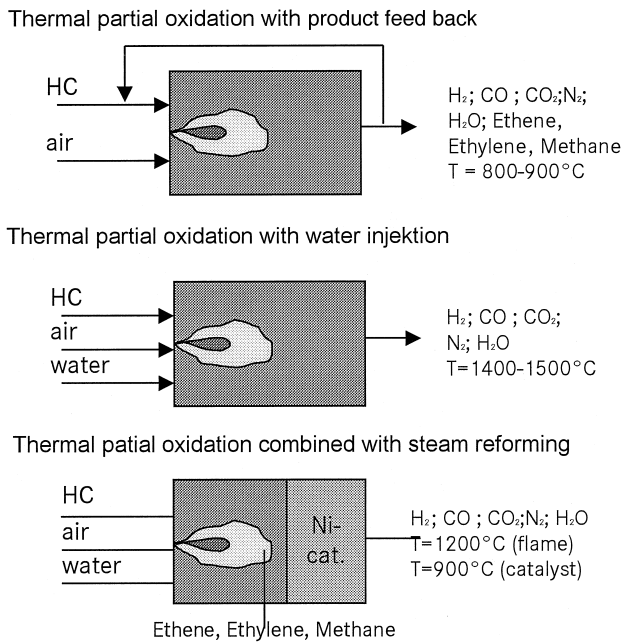


Fig. 2. Examples for reforming reactor types.

waste heat from other chemical processes is available. In a fuel cell car, this would have to be done by combustion of the anode off gas or the fuel itself. Thus, connecting the tail end of the fuel cell system with its front end, which results in time delays during load changes. So far, no sulfur tolerant steam-reforming catalyst has been found, resulting in the need for a very efficient and therefore probably large unit for removing the sulfur from the fuel. The time needed to heat up the desulfurization unit and the steam-reforming reactor to its working temperature by external heating through the combustion of fuel seems to be difficult and slow. From our point of view, steam-reforming is only suitable for transport applications with dynamic requirements less tough than for passenger cars, e.g., like trains and ships. Partial oxidation as well as autothermal-reforming systems promise to have a much better dynamic than a steam-reforming system since they do not require external heating and can be heated up internally relatively quick by combusting fuel. The sulfur

tolerance is also better, but depends on the technology applied as will be discussed later on. Partial oxidation as well as the hybrid technology autothermal-reforming can take place in gas phase reactions as well as in catalytic reactions. Some examples are shown in Fig. 2.

In the upper two partial oxidation reactors, gas phase reactions take place. The reactor at the top shows a principle developed by Mercedes Benz in the 1970s, the so-called “Spaltvergaser”, intended to reform the fuel into a gas much better combustible than the fuel itself to improve the emissions of a Mercedes Benz IC-engine. To prevent coke formation, a part of the reformat was fed back into the reformer. The system worked well for its purpose but because of the low working temperatures and the short residence times of the gas inside the reactor, a lot of by-products not wanted in fuel cell systems like ethane, ethylene and a large amount of methane were produced.

The system in the middle uses water to prevent coke formation and operates at a very high temperature thus resulting in good gas phase kinetics and therefore generating a reformat of good quality.

The third system uses also water in addition to air, but operates at temperatures comparable to the first system, also resulting in unwanted by-products, but by means of a steam-reforming catalyst, the unwanted by-products can be processed to  $H_2$  and CO.

A first simple approach to estimate the potential of the thermal efficiency of the different reforming technologies can be gained by the following simple stoichiometric calculations as seen in Table 1.

For example, let us view the processing of gasoline. Gasoline is a mixture of many different hydrocarbons. In this work, gasoline is represented by  $C_7H_{12}$ , which represents german gasoline (“Normalbenzin”) quite well [1]. Using this model substance, it can be seen that partial oxidation can give only a maximum thermal efficiency of 78%. In the case of autothermal-reforming, the efficiency depends respectively on the amount of air used, the amount of fuel burnt to feed the endothermic steam-reforming reaction and to preheat the educt to the reactor temperature. As will be shown later, theoretical values for  $a$  lie between 3.0 and 3.5 resulting in efficiencies between 84

Table 1

Comparison of stoichiometric-reforming reactions. Lower heating value gasoline: 4050 kJ/mol. Lower heating value hydrogen: 242 kJ/mol

Technology	Reformer efficiency $\eta$
Partial oxidation	$\eta = 78\%$ for $C_7H_{12}$
Reforming reaction	$C_nH_m + n/2O_2 + n/2 * 3,7N_2 \rightarrow nCO + m/2H_2 + n/2 * 3,7N_2$
Shift-reaction	$nCO + m/2H_2 + n/2 * 3,7N_2 + nH_2O \rightarrow nCO_2 + (n + m/2)H_2 + n/2 * 3,7N_2$
Gross-reaction	$C_nH_m + n/2O_2 + n/2 * 3,7N_2 + nH_2O \rightarrow nCO_2 + (n + m/2)H_2 + n/2 * 3,7N_2(2)$
Autothermal-reforming	$\eta = 78-84\%$ for $C_7H_{12}$
Reforming reaction	$C_nH_m + aO_2 + a3,7N_2 + (n - 2a)H_2O \rightarrow nCO + (n - 2a + m/2)H_2 + a3,7N_2$
Shift-reaction	$nCO + (n - 2a + m/2)H_2 + a3,7N_2 + nH_2O \rightarrow nCO_2 + (2n - 2a + m/2)H_2 + a3,7N_2$
Gross-reaction	$C_nH_m + aO_2 + a3,7N_2 + (2n - 2a)H_2O \rightarrow nCO_2 + (2n - 2a + m/2)H_2 + a3,7N_2(3)$

and 78%. A prediction of possible values for  $a$  out of a stoichiometric calculation is not possible, but calculations of the thermodynamic equilibrium in an adiabatic reactor allow to predict the optimal operating condition for an autothermal reactor and possible values for  $a$ . Background literature to equilibrium calculations for gasoline and diesel reformer can be found in Refs. [2–6] and for methanol reformer in Refs. [7–9].

#### 4. Simulation results

The thermodynamic equilibrium in a reformer reactor depends on the following parameters:

- Preheat temperatures of the reactor feed air, water and fuel
- Pressure inside of the reactor
- Chemical composition of the fuel
- Heat loss of the reactor
- Relation of fuel to air and to water.

If these parameters are given, the thermodynamic equilibrium of the system can be calculated by means of minimizing the Gibbs energy. The equilibrium describes the temperature of the system and the product composition. This calculations can be done with commercially available software. In this case, all calculations were conducted with AspenPlus™. For all calculations, it was assumed that the reactor is adiabatic and the pressure inside is 5 bars. It is assumed that at the exit of the reactor, the gas is in thermodynamic equilibrium. In reality, this is only the case if all necessary reactions can take place because the right catalyst are used or in the case of gas reactions, the residence times are long enough. As a model for gasoline, a mixture of 35% Hexane (C<sub>6</sub>H<sub>14</sub>), 25% Hexene (C<sub>6</sub>H<sub>12</sub>) and 40% Xylol (C<sub>8</sub>H<sub>10</sub>) was used. This mixture possess the same sum of C and H atoms as gasoline (german ‘‘Normalbenzin’’) and has also the same heating value. The ratios between the fuel and air and between the fuel and water, respectively are expressed in terms of the air ratio  $\phi$ :

$$\phi = (n_{\text{air}}/n_{\text{fuel}})_{\text{real}} / (n_{\text{air}}/n_{\text{fuel}})_{\text{complete combustion}} \quad (4)$$

and the steam to carbon ration S/C:

$$S/C = n_{\text{H}_2\text{O}} / n_{\text{C within the fuel}} \quad (5)$$

##### 4.1. Processor syngas quality

S/C was varied between 0 (partial oxidation) and 2. For each S/C, the air ratio was varied between 0 and 1. This procedure was followed for several preheat temperatures of the feed which might be possible to realize inside a reformer. Fig. 3 shows two diagrams with product concentrations and the reactor temperature in terms of the air ratio  $\phi$ . Fig. 3 shows diagrams for S/C = 0 and for S/C = 0.7. The concentration of the products H<sub>2</sub>, CO,

CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and elementary C are shown in molecular ratio to the fuel. C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> were also considered in the equilibrium calculations, but were not predicted as products. Carbon as well as CH<sub>4</sub> vanish at higher temperatures, which can only be achieved by combusting a larger fraction of the fuel by the use of a larger air ratio. S/C affects the reactor temperature, the composition and the formation of coke and CH<sub>4</sub>. A higher S/C shifts the coking boundary to lower air ratios and it affects also the reformer efficiency. In each of these two diagrams, an optimal air ratio can be identified which gives the highest reformer efficiency for the S/C chosen, while in both cases the optimal air ratio  $\phi_{\text{opt}}$  is very close to the theoretical coking boundary.

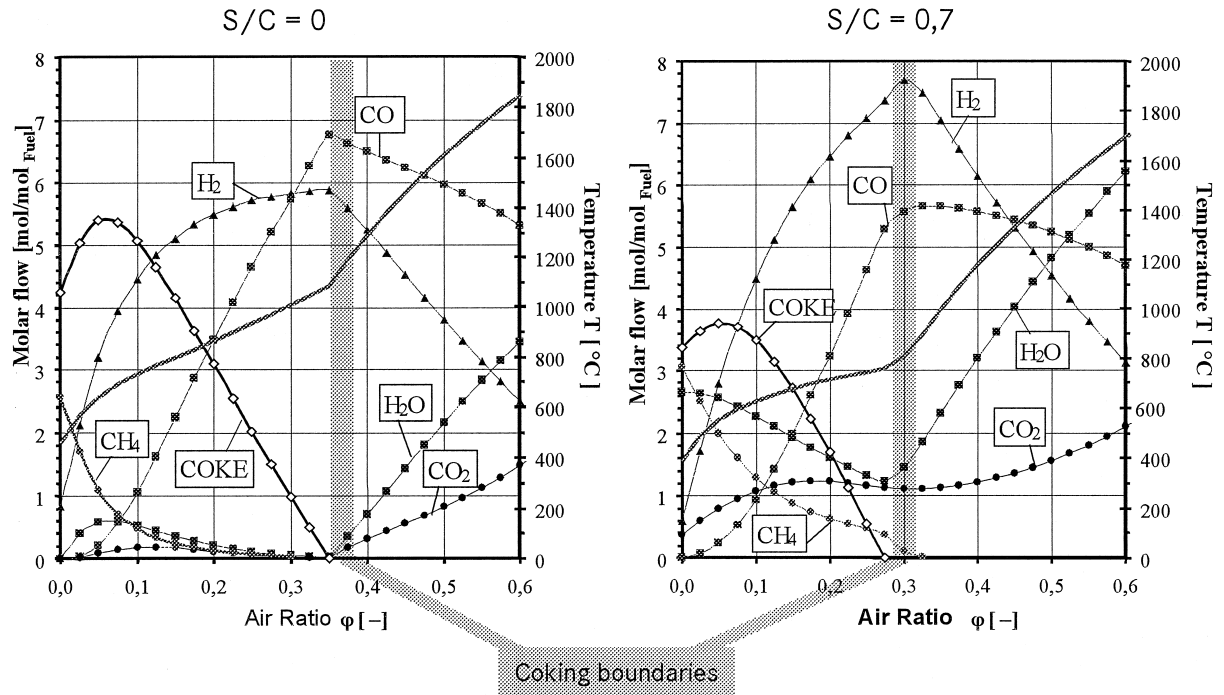
An air ratio  $\phi = 0$  corresponds to the pure thermal cracking of the fuel and  $\phi = 1$  corresponds to the complete combustion of the fuel. Autothermal hydrocarbon-reforming is likely to take place at air ratios between 0.25 and 0.35.

From a thermodynamic point of view, the formation of solid carbon — soot or coke — depends on the ratio of carbon and hydrogen in the hydrocarbon fuel as well as on the air ratio and the steam to carbon ratio and the reactor temperature. But the reactor temperature also depends on the air and steam to carbon ratio. In reality, coke formation can also appear at conditions which are theoretically free of carbon. This might be due to non-ideal mixing of the fuel with the air and the steam or locally too low reactor temperatures. On the other side, some catalysts might be able to enhance only the reforming reactions but to suppress the coke formation reaction. However, theoretical coking boundaries give starting values for experimental reactor tests.

##### 4.2. Fuel processor efficiency

The reforming efficiency is directly proportional to the amount of hydrogen and carbon monoxide generated. Not only a high reforming efficiency is wanted, but also a higher hydrogen concentration than carbon monoxide concentration, since the volume and weight of the shift reactors HTS and LTS are directly proportional to the CO-concentration in the reformat. The fuel cell works more efficiently if the hydrogen content of the reformat after the CO clean up is higher. From Eqs. (2) and (3), it can easily be seen that the amount of CO<sub>2</sub> depends only on the chemical structure of the fuel. The water concentration has to match a specified value to ensure a sufficient humidification of the fuel cell. Therefore, the diluting component in the reformat which can be adjusted is only nitrogen. The concentration of nitrogen in the reformat only depends on the air ratio  $\phi$ . Thus, the air ratio has to be as small as possible.

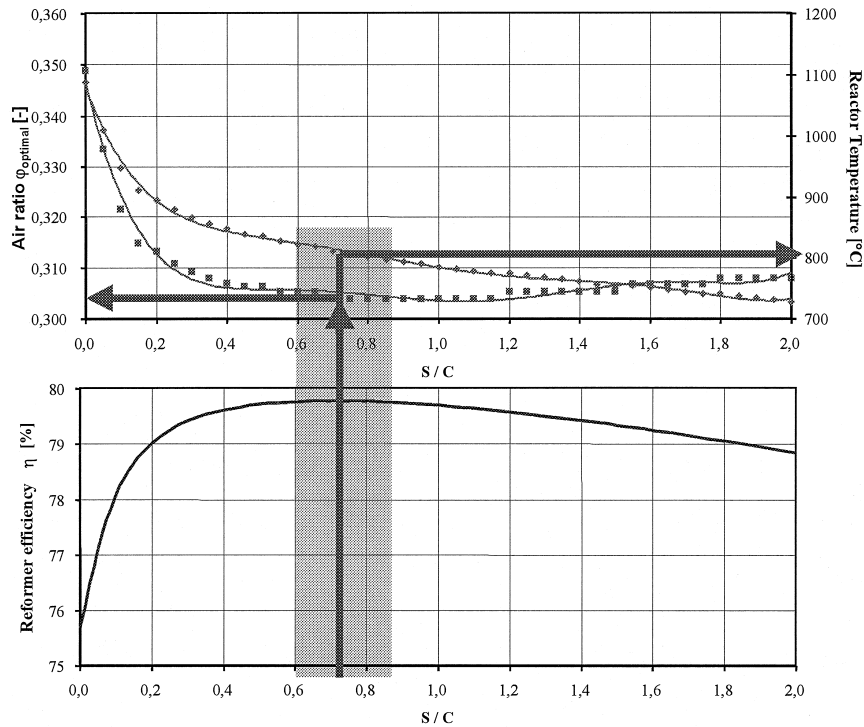
The upper diagram in Fig. 4 shows the dependence of the optimal air ratios  $\phi_{\text{opt}}$  and the corresponding reactor temperatures to the steam to carbon ratio S/C. With increasing S/C, the reactor temperature decreases continu-



Temperature of reactor feed:

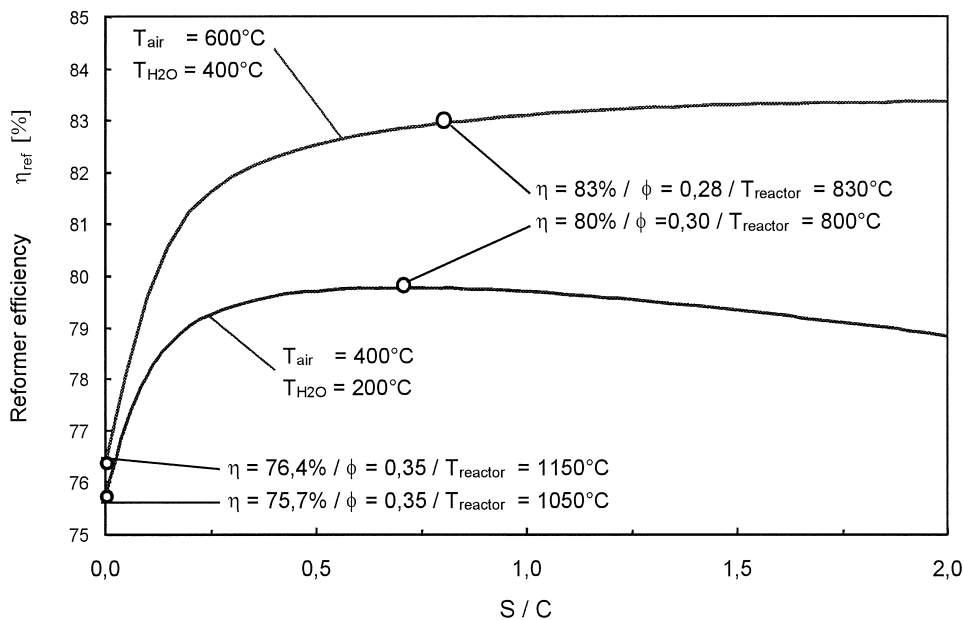
$$T_{air} = 400^\circ\text{C}, T_{H_2O} = 200^\circ\text{C}, T_{fuel} = 20^\circ\text{C}$$

Fig. 3. Product concentration of a partial oxidation reformer and an autothermal reformer depending on the air ratio  $\phi$  and the steam to carbon ratio  $S/C$ .



Temperatures of reactor feed:  $T_{air} = 400^\circ\text{C}, T_{H_2O} = 200^\circ\text{C}, T_{fuel} = 20^\circ\text{C}$

Fig. 4. Determination of the optimal operation conditions for a reformer.



Adiabatic reactor,  $T_{\text{fuel}} = 20^\circ\text{C}$

Fig. 5. Influence of preheat temperatures on reformer efficiency.

ously, in this case from  $1100^\circ\text{C}$  at a  $S/C$  of 0 down to  $740^\circ\text{C}$  at a  $S/C$  of 2. The air ratio decreases up to a certain value of  $S/C$  also, in this case till a  $S/C$  of 1.2, but at higher  $S/C$  values, the air ratio goes up again. The lower diagram shows the reformer efficiency in terms of  $S/C$ .

For this calculation, the reformer efficiency shows a maximum around a  $S/C$  of 0.7. The scope of the reformer efficiency curve proves that the reformer efficiency is directly coupled to the air ratio  $\phi$ , since it is obvious that the efficiency reaches its maximum at the minimum value of the air ratio and its minimum at the maximum of the air ratio.

The reformer efficiency curve depends on the temperature of the reactor feed as can be seen in Fig. 5, the higher the temperature of the reactor feed, the higher the reformer efficiency. The reason is that the higher the temperature of the feed, the less fuel has to be burnt to heat the feed to the necessary reactor temperature and the more fuel can be steam-reformed. Vaporizing of the fuel would also increase the reformer efficiency, since the heat of vaporization would be compensated for by the combustion of a fraction of the fuel. On the other side, vaporization of the fuel with a heat source downstream of the reactor leads to a slower load following and might be difficult, because the fuel can decompose and soot might be formed. Realistic values for the preheat of air and water are around  $200^\circ\text{C}$  and  $400^\circ\text{C}$  or vice versa. If higher preheat temperatures are wished, for example, higher than  $400^\circ\text{C}$ , more heat exchangers will have to be used increasing weight and volume of the reformer. A good trade-off between a moderate complex system and acceptable reformer efficiency seem to be preheat temperatures of air and steam

mixture around  $300^\circ\text{C}$  allowing reformer efficiencies around 80%.

## 5. Conclusion

Thermodynamic calculations have shown that autothermal-reforming theoretically yields higher reforming efficiencies than partial oxidation even at lower preheat temperatures. On the other side, a partial oxidation reactor has a simpler design since no water has to be added. From a systems design point of view, this is not necessarily an advantage, since within an autothermal reformer more heat can be reintegrated, for example, to vaporize the water and preheat the steam. In the case of a partial oxidation reformer, this energy is waste heat and has to be removed by the car cooling system, which has to be designed larger. Preheat temperatures around  $300^\circ\text{C}$  seem to be possible to achieve within a thermally integrated reformer system. The maximum achievable reformer efficiencies are around 80%.

Although purely theoretical thermodynamic calculations are useful and necessary to find the optimal operating points of potential reforming reactors. If the influence of the working parameters on the behavior of the reformer is known, a sensible system design is possible. Also, the theoretical values give excellent starting values for experimental reformer tests and input values for a more in-depth reformer simulation taking into account more reformer parameters like its geometry, the fluid flow, the temperature and concentration distribution and of course, the kinetic behavior of the reactions.

**References**

- [1] DGMK Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und E.V. Kohle, 1993.
- [2] T.G. Kreutz et al., Fuel Cell Seminar, Palm Spings, USA, 1996.
- [3] W.L. Mitchell et al., 30th Annual ISATA Conference, Florence, Italy, 1997.
- [4] J. Houseman, D.J. Cerini, SAE paper 740600, 1974.
- [5] M. Flytzani-Stephanopoulos, G.E. Voecks, *Energy Progress* 1 (1981) 52–58.
- [6] G.P. Purohit, J. Houseman, SAE Paper 800264, 1980.
- [7] A.D. Little, Phase I. Final Report, prepared for the US DOE, 1994.
- [8] R. Kumar et al., Argonne National Laboratory Report ANL-92/31 prepared for DOE, 1992.
- [9] B. Ganser, Bericht des Forschungszentrums Jülich 2748, 1993.