



Hydrogen for fuel cells from ethanol by steam-reforming, partial-oxidation and combined auto-thermal reforming: A thermodynamic analysis

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ABSTRACT

Thermodynamics of hydrogen production from ethanol by steam-reforming, partial-oxidation and combined auto-thermal reforming was investigated as a function of steam-to-ethanol ratio (0.00–10.00), oxygen-to-ethanol ratio (0.00–2.50) and temperatures (200–1000 °C) at atmospheric pressure.

Thermodynamically ethanol is fully converted already at low temperatures. Main product at low temperatures is methane, which changes to hydrogen with increased temperature. At elevated temperature also carbon monoxide content increases, which is in accordance with the water-gas-shift reaction. Coke-formation is a serious issue, especially at low steam-to-ethanol (S/E) ratios. Coke-formation free steam-reforming is possible above $S/E > 3$. Steam-reforming achieves the highest hydrogen-yield, which is almost up to the theoretical value at high steam-to-ethanol ratios.

Pure partial-oxidation shows similar trends of hydrogen and carbon monoxide content with temperature and oxygen-to-ethanol (O/E) ratio; therefore high hydrogen content is always accompanied by high carbon monoxide content. Partial-oxidation shows a low hydrogen yield and the avoidance of coke formation demands high temperatures or high O/E ratios, whereas nitrogen dilution increases strongly with O/E ratios.

Increasing O/E-ratio from 0.00 to 0.75 in auto-thermal reforming shows no strong effect on the hydrogen and carbon monoxide formation at temperatures below 600 °C and over the whole S/E-ratio range. Auto-thermal operation reduces the coke-formation and reduces energy demand for the reforming process.

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1. Introduction

Energy security and climate change are very popular issues these days and their imperatives require a large-scale substitution of petroleum-based fuels as well as improved efficiency in energy conversion. Multinational research efforts to develop technologies for renewable energies and for increasing the efficiency of energy-use are in progress, whereas fuel cells for mobile and stationary applications are highly valued due to their high theoretical efficiency and only steam as a by-product in case of fuel cells operating with hydrogen as fuel [1,2]. However the realisation of fuel cell-based energy systems is depending on renewable sources for hydrogen, since hydrogen is no primary energy carrier itself and is as “clean” or “dirty” as the primary energy, where it is converted from [3].

Ethanol is considered to be a promising candidate as a source for renewable hydrogen with several advantages compared with other

fuels, such as methanol, gasoline, LPG, methane and dimethyl-ether. Ethanol production by fermentation of glucose is a mature process and process-economics are known. It has attractive attributes such as lower CO₂ emissions, environmental friendliness and ease of storage and distribution. Moreover ethanol is today's most available bio-fuel and its production increased from 18 billion l year⁻¹ in year 2000 to 33 billion l year⁻¹ in year 2004, which is about 3% of the worldwide gasoline-consumption [4]. Major research in biomass is directed towards the better transformation of cellulose to sugar for ethanol-production [5]. Current ethanol-production from corn or sugar cane can have green-house gas emissions only slightly lower to conventional gasoline, but requires much less petroleum inputs in the production compared to gasoline. Next generation of ethanol production from cellulosic materials can reduce both green-house gas emissions and petroleum inputs substantially [6]. The usage of ethanol in conventional vehicles is increasing in America, Asia and Europe. Therefore it is very reasonable to investigate different options of hydrogen production from ethanol since supply and infrastructure for ethanol-distribution is building up today.

Most of the research of hydrogen production by ethanol reforming is undertaken in development of catalysts for ethanol-reforming

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[7–15]. Different catalyst systems as non-noble metals, Ni and Co, as well as noble metals, Rh and Pt, on different catalyst supports are researched. The ethanol steam-reforming occurs at higher temperatures compared to methanol steam-reforming and gives higher carbon monoxide content in the effluent [16]. Most of the studies are dealing with steam-reforming, whereas few publications deal with auto-thermal reforming and partial-oxidation reforming [17–21].

The durability of ethanol-reforming catalysts is one of the key factors for the practical use. Coke-formation and metal sintering are known as the main reasons for deactivation. Choosing appropriate reforming operation conditions can suppress such deactivation. Several reports calculated the thermodynamic compositions of the ethanol steam-reforming process [22–26], dealt with coke-formation, but did not include a thorough investigation of partial-oxidation and auto-thermal operation of ethanol reforming.

1.1. Scope

This paper tends to explore the different options in the process for reforming ethanol to a hydrogen-rich feed for fuel cells using steam-reforming, partial-oxidation as well as the combined processes. This study presents the equilibrium compositions of ethanol reforming as a function of the steam-to-ethanol ratio (0.00–10.00), and oxygen-to-ethanol ratio (0.00–2.50) and temperature (150–1000°C) at atmospheric pressure. The species considered are hydrogen, carbon monoxide, carbon dioxide, methane, water, ethanol, ethylene, ethane, acetaldehyde, acetic acid as well as solid carbon.

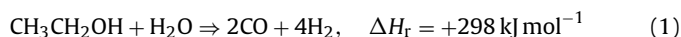
2. Hydrogen production by ethanol reforming

This paragraph discusses the implications of the generation of hydrogen-rich feed streams for fuel cells by reforming. The operation-mode for the reformer can be very different, with wide implications on the composition of the reformer effluent and the energy demand, necessary to generate the hydrogen-rich feed.

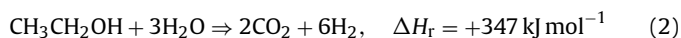
Possible operational modes are:

- steam-reforming;
- partial-oxidation;
- auto-thermal reforming.

Steam-reforming is an endothermic process

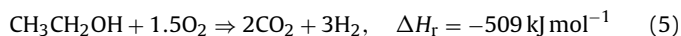
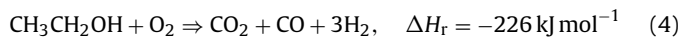
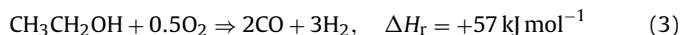


Complete steam-reforming operation is given by the following reaction

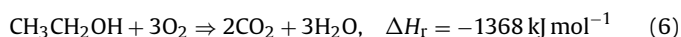


whereas the maximum hydrogen-yield of ethanol steam-reforming can be fixed by 6 mole H₂/mole ethanol.

Partial-oxidation is as indicated by the name, the incomplete oxidation of the feed. This incomplete oxidation generates heat and fractionates the feed to smaller molecules.



As the oxygen content in the feed stream is increased, the feed is completely oxidised and the maximum heat output is achieved.



Auto-thermal reforming is the combination of these two processes of steam-reforming and partial-oxidation, in order to achieve a minimum energy input necessary to maintain the required reformer temperature.

The space of operation for a fuel processor for hydrogen production is depicted in Fig. 1.

The selection of operation conditions of a reformer is depending on various targets. Main target is a high hydrogen yield, simultaneously with low carbon monoxide content. Maximum hydrogen efficiency and low carbon monoxide content is possible for steam-reforming operation. However, steam-reforming is an endothermic process and therefore energy demanding. This energy has to be transferred into the system from outside. In case of mobile reformers start-up-time and start-up-energy-demand should be as low as possible. Therefore the partial-oxidation or auto-thermal operation is preferred as the process is exothermic. It is inherent to these reforming processes that carbon monoxide is generated. The production of carbon monoxide needs to be avoided, as it is an inefficient by-product, which impacts the mass and size of the fuel processor. In a fuel processing system the reformer is followed by water-gas-shift reactors to reduce the carbon monoxide contents to the desired level. The mass and size of the water-gas-shift reactor directly corresponds to the level of carbon monoxide content in the reformer outlet stream. In case of mobile reformers size and weight of the fuel processor is limited. The definition of an ideal operation point for the chosen fuel reformer is therefore a multivariate optimisation problem.

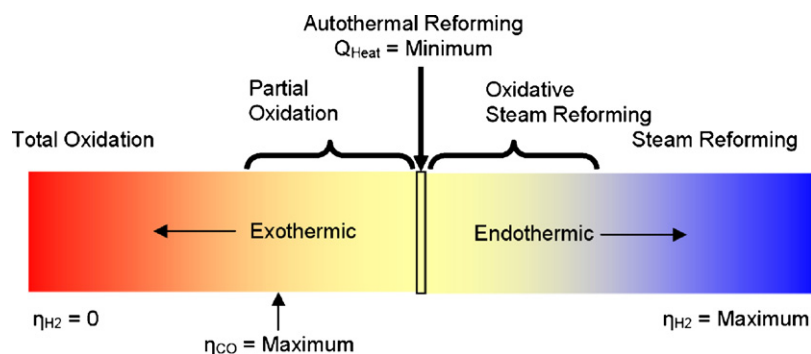


Fig. 1. Different operating conditions for ethanol reforming.

3. Modelling methodology

3.1. Thermodynamic formulation of equilibrium—Gibb's free energy

Chemical equilibrium calculations have traditionally been made through the use of equilibrium constants of known reactions, a procedure still useful for simple problems. However, when the equilibrium composition is determined by a number of simultaneous reactions, the computations required become complex and tedious. A more direct and general method for solving these complicated problems is the direct minimization of the Gibb's function of the system.

The total Gibb's free energy G of the system, comprised of n_i mole of each of S species, may be expressed as

$$G = \sum_{i=1}^S n_i \left[\bar{G}_i^0 + R_g T \ln \left(\frac{f_i}{f_i^0} \right) \right] + n_s G_s \quad (7)$$

where \bar{G}_i^0 is the free energy of the i th species at normal temperature and pressure (standard conditions SC); f_i^0 and f_i are the fugacity of the i th species at SC and operating conditions. n_s is the number of carbon molecules in case of coke formation and G_s is the free energy of the solid carbon [27].

All species different from solid carbon are at the gaseous state. Assuming the reaction at the pressure P one can write

$$\frac{f_i}{f_i^0} = y_i \gamma_i P = \frac{n_i}{n} \gamma_i P \quad (8)$$

where n is the total number of molecules in the gaseous phase and γ_i is the activity coefficient of the i th species.

The aim is to calculate the different values of n_i and n_s which minimizes G at constant T and P , subject to the constraints of elemental balances:

$$\sum_{j=1}^N a_{ij} = b_j \quad (9)$$

for $i=1$ to S , $j=1-N$, where a_{ij} is the number of atoms of the j th atomic element in a mole of i th species; N the number of elements and S is the number of species present in the reaction mixture.

All equilibrium calculations were calculated with vapour phase constituents, except the coke-formation. For the equation of state used, the Peng–Robinson equation was and the minimization was performed by using Aspen Tech™ [28], a commercial flow sheeting software with the ability to perform multi-component equilibrium calculations.

3.2. EtOH processing: reactions, temperature and pressures

The major gas species involved in the thermodynamic analysis are hydrogen, carbon monoxide, carbon dioxide, methane, water, ethanol, ethylene, ethane, acetaldehyde, acetic acid as well as solid carbon. This study presents the equilibrium compositions of ethanol-reforming as a function of the steam-to-ethanol ratio (0.00–10.00), and oxygen-to-ethanol ratio of (0.00–2.50) and temperature (150–1000 °C) at atmospheric pressure.

3.3. EtOH-SR: thermodynamically feasible products

Main reforming products are hydrogen, methane, carbon dioxide, carbon monoxide and water. Depending on the catalyst used and the completeness of conversion, the product distributions in the reformat stream may be different than assumed above. The

Table 1

Expanded product set applied in the estimation of thermodynamically feasible products for ethanol reforming

Expanded product set
Ethanol ^a
Water ^a
Hydrogen ^a
Carbon dioxide ^a
Carbon monoxide ^a
Methane
Ethane
Ethylene
Acetylene
Acetaldehyde
Acetic acid
Acetone
Ethyl acetate
Diethyl ether
Ethylene glycol
<i>n</i> -Propanol
<i>iso</i> -Propanol
<i>n</i> -Butanol
<i>iso</i> -Propyl-methyl-ether
<i>iso</i> -Propyl-alcohol

^a Basis sets of products.

standard product set was expanded to include products that might be generated by intermediates or products from side reactions. The expanded product-set is shown in Table 1.

The estimation of thermodynamically feasible products is started with the expanded product set given in Table 1. The reaction product with the largest mole fraction, besides the basis product set, was removed to give the next expanded product set, and then the calculation was repeated and so on. Solid carbon was excluded as a thermodynamically viable species in all product sets.

3.4. Ethanol conversion, coke formation and hydrogen yield

To evaluate the performance of the ethanol reforming system the equilibrium conversions of ethanol, the coke-formation and the yield of hydrogen are defined as follows. Equilibrium conversion of EtOH

$$X_{\text{EtOH}} = \frac{F_{\text{EtOH}_{\text{in}}} - F_{\text{EtOH}_{\text{out}}}}{F_{\text{EtOH}_{\text{in}}}} \quad (10)$$

Coke-formation rate

$$\text{Cokeform} = \frac{F_{\text{C}_{\text{out}}}}{F_{\text{EtOH}_{\text{in}}}} [\text{mole C/mole EtOH}] \quad (11)$$

H₂ yield

$$\text{H}_2\text{-yield} = \frac{F_{\text{H}_2}}{F_{\text{EtOH}_{\text{in}}}} [\text{mole H}_2/\text{mole EtOH}]. \quad (12)$$

4. Results

4.1. Thermodynamically feasible products

The thermodynamic compositions for steam-reforming of the expanded product set (Table 1) were investigated to determine the sequence of other thermodynamically viable products. The species included are ethane, ethylene, acetylene, acetaldehyde, acetic-acid, acetone, ethyl acetate, diethyl ether, ethylene glycol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-propyl-methyl-ether and *iso*-propyl-alcohol.

The results for the calculation cases of the thermodynamically most feasible products are shown in Table 2. Methane is favoured over the whole temperature range investigated. Removing methane

Table 2

Thermodynamic calculation cases of the expanded product sets for evaluation of feasible products with a steam-to-ethanol ratio of 6.00, an oxygen-to-ethanol ratio of 0.00 and atmospheric pressure

Case	Most abundant	Species excluded
1	Methane	None
2	Ethane	Methane
3	iso-Propyl-alcohol	Ethane + Methane
4	n-Butanol	iso-Propyl-alcohol + Ethane + Methane
5	n-Propanol	n-Butanol + iso-Propyl-alcohol + Ethane + Methane
6	Ethylene	n-Propanol + n-Butanol + iso-Propyl-alcohol + Ethane + Methane
7	Diethyl ether	Ethylene + n-Propanol + n-Butanol + iso-Propyl-alcohol + Ethane + Methane
8	Acetic acid	Diethyl ether + Ethylene + n-Propanol + n-Butanol + iso-Propyl-alcohol + Ethane + Methane

as possible species ethane is the second favoured species but only in a lower temperature range. For the other thermodynamic cases 3–8, the products approach practically zero concentration as the temperature goes above 250 °C. The concentrations of the most abundant species as a function of temperature are shown in Fig. 2.

Known products of ethanol steam-reforming are acetaldehyde, ethylene and acetone [8,29]. Acetaldehyde, ethylene and acetone are in the expanded product set for the estimation of the thermodynamically feasible products but all three species do not show up as any thermodynamically viable species. This occurrence can be explained by the fact, that the reforming reactions are in practice kinetically controlled. Acetaldehyde, ethylene and acetone can be considered as intermediates of an incomplete reforming reaction and are in fact no thermodynamically stable products.

4.2. Coke formation

Coke-formation is of importance in reforming hydrocarbon and oxygenates feed-stock for the production of hydrogen. High temperatures associated with steam-reforming to produce hydrogen also favour the formation of carbon. Four reactions may be involved [30,31]

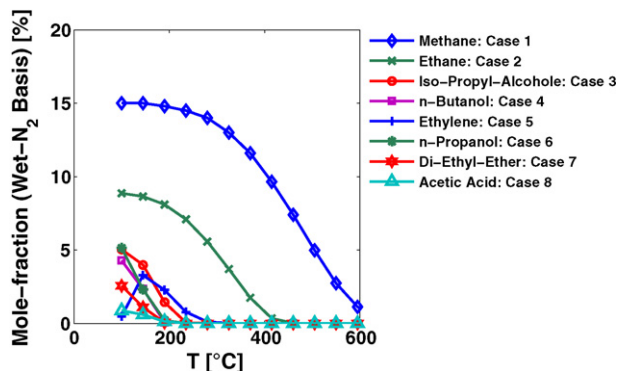


Fig. 2. Concentrations of the most abundant species for the thermodynamic cases 1–8 as a function of temperature at a steam-to-ethanol ratio, $S/E = 6.0$ and an oxygen-to-ethanol ratio, $O/E = 0.0$.

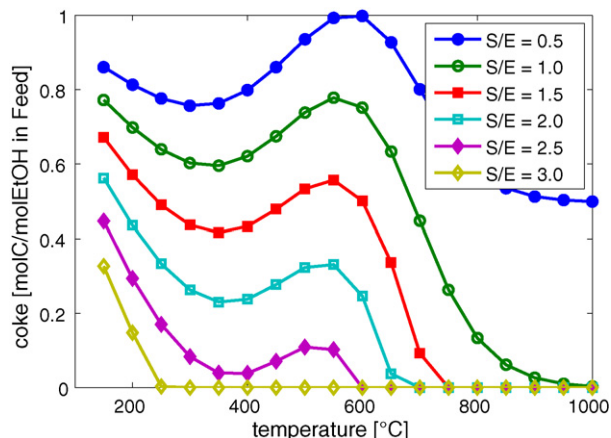


Fig. 3. Thermodynamically predicted coke-formation for different S/E -ratios (mole $\text{H}_2\text{O}/\text{mole EtOH}$) in a fuel processor in steam-reforming operation (oxygen-to-ethanol ratio, $O/E = 0.00$).

These reactions are in equilibrium and the formation of coke via reactions (14) and (15) becomes less favoured as the temperature increases. However coke-formation via reactions (13) and (16) becomes increasingly important at higher temperature and depending on the catalyst used the coke-formation can rapidly deactivate the catalyst and block the reactor. Catalyst systems with acidic properties are prone to coke-formation via polymerization according reaction (16) as it is reported [32]. The reactions are reversible and may also form the basis of a method to remove carbon by gasification.

Fig. 3 shows the coke-formation (mole coke/mole ethanol in feed) for different steam to ethanol ratios S/E in steam-reforming operation. Low water content in the feed-stock tends to result in more pronounced coking. The coke-formation does not show a monotone behaviour but two regions with strong coking. This is due to different coking mechanisms as mentioned beforehand.

From the thermodynamic evaluation one can assume that a safe steam-reforming operation is possible using a steam-to-ethanol ratio higher than $S/E = 3$.

Furthermore the behaviour of the coke-formation in case of partial-oxidation and/or steam-reforming has been evaluated. Fig. 4 shows the temperature of the coke-formation-boundary for different steam-to-ethanol ratios over different oxygen-to-ethanol ratios.

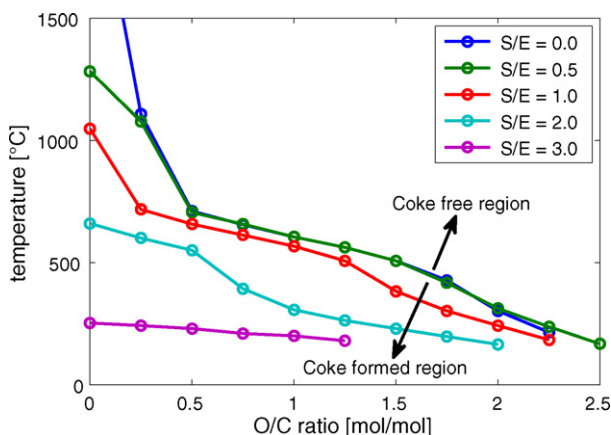


Fig. 4. Coke-formation boundary for ethanol steam-reforming and partial-oxidation as a function of steam-to-ethanol ratio, S/E (mole $\text{H}_2\text{O}/\text{mole EtOH}$) and oxygen-to-ethanol ratio, O/E (mole $\text{O}_2/\text{mole EtOH}$).

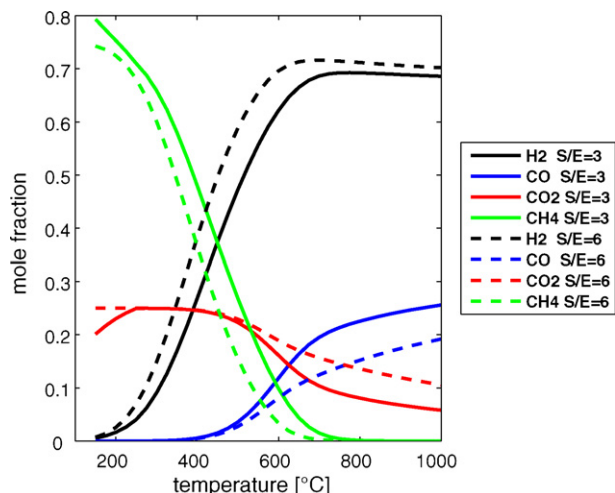
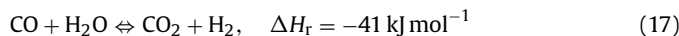


Fig. 5. Reformate product composition in mole-fraction on dry basis for steam-reforming of ethanol at steam-to-carbon ratio, S/E = 3 and 6, oxygen-to-carbon ratio, O/E = 0 and atmospheric pressure.

The line for S/E = 0 corresponds to partial-oxidation operation and a vertical line at O/E = 0 corresponds to steam-reforming operation. Pure partial-oxidation of ethanol for hydrogen production needs high O/E levels in order to be above the coke-formation boundary. The addition of small amounts of water to the feed reduces the carbon-formation boundary at very low oxygen-levels in the feed. At high oxygen levels no influence of small S/E is seen, the curves are actually overlapping. From Fig. 4 it can be concluded that coke is formed during ethanol-reforming in the following order: partial-oxidation > steam-reforming > auto-thermal-reforming. Using combined partial-oxidation and steam-reforming operation it is possible to be in the coke-free region using an O/E = 0.50–1.00 and S/E = 2.00–3.00 at reforming temperatures above 400 °C.

4.3. EtOH–SR

The thermodynamically predicted equilibrium conversion of ethanol in steam-reforming operation is always at 100%. Fig. 5 shows the changes of the equilibrium product distribution over changing steam-reforming temperature. At low temperatures methane and carbon dioxide are the mostly occurring products besides small contents of hydrogen and almost no carbon monoxide. When the steam-reforming temperature is raised the methane content decreases whereas the hydrogen content increases concurrently. Reasonable hydrogen concentrations can be achieved using steam-reforming temperatures of 550 °C. At higher temperatures $T > 500$ °C the carbon monoxide content is strongly increasing, which can be attributed to the thermodynamics of the water–gas-shift reaction. Increasing the steam-to-ethanol ratio moves the aforementioned temperature points to slightly moderate temperatures.



Increasing steam-to-ethanol ratio also has beneficial influence on the carbon monoxide content in the reformer effluent, since this means increasing the water level inside the reforming mixture. Therefore the water–gas-shift reaction (17) is influenced to react towards less carbon monoxide according the thermodynamical equilibrium. The decrease of carbon dioxide content at steam-to-ethanol ratios of S/E = 3 towards low temperatures is according to coke-formation at this operating conditions.

The influences of steam-to-ethanol ratio and reforming temperature on the equilibrium products of steam-reforming of ethanol are shown in Fig. 6a–d.

The hydrogen content in the effluent, shown in Fig. 6a, is at high levels of a mole fraction of 0.60–0.70 for a reforming temperature above $T = 600$ °C and increases very slightly with rising the steam-to-ethanol ratio. A very slight reduction of the hydrogen content is occurring for increasing the temperature at high level, which is effected by the water–gas-shift reaction. The minimum valley in hydrogen content approaching steam-to-ethanol = 0 at high temperatures is due to coke-formation in this region.

The carbon monoxide content, shown in Fig. 6b, has a maximum at low steam-to-carbon ratios and high temperatures. Aiming for a high hydrogen content and a low carbon monoxide content is a contradiction, because the reforming temperature has to be high enough to obtain a reasonable hydrogen concentration and on the other side the reforming temperature has to be as low possible to keep the carbon monoxide content small. The carbon dioxide and methane content of the reformer effluent for different steam-reforming operations are shown in Fig. 6c and d. The methane content at low temperatures is very high and is strongly decreasing with increased temperature. For a given temperature the methane content strongly decreases at a rising steam-to-ethanol ratio. The carbon dioxide content is almost constant at high level, for temperatures below 600 °C and steam-to-ethanol ratios above S/E = 4. Below this steam-to-ethanol ratio the carbon monoxide content strongly decreases due to coke-formation.

Fig. 7 shows the hydrogen-yield and coke-formation for ethanol-steam-reforming. The function of the hydrogen yield has a relatively flat top plateau with hydrogen yields above 4 moles H_2 /mole EtOH for reforming temperatures above 550 °C and steam-to-ethanol ratios of S/E = 3. The hydrogen yield for steam-reforming approaches a maximum of almost 5.5 moles H_2 /mole EtOH for temperatures around 600–700 °C and high steam-to-ethanol ratios above S/E = 6. Increasing the reforming temperature reduces the hydrogen yield via consumption of hydrogen in water–gas-shift equilibrium reaction. Rising the steam-to-ethanol ratio increases the water content in the reforming mixture and has the twofold effect of supply more water for steam-reforming reactions and shifting the water–gas-shift equilibrium towards hydrogen and water. The coke-formation for steam-reforming operation at low steam-to-ethanol ratios is still considerable. Increasing the steam-to-ethanol ratio above S/E = 3 seems to be necessary to avoid coke formation in the steam reformer. As conclusion of the results for steam-reforming of ethanol–water feeds it can be said, that a reformer effluent with high hydrogen content and a high hydrogen yield is possible for reforming temperatures between 550 and 650 °C and steam-to-ethanol ratio above S/E = 4. With this condition, a hydrogen-yield > 4 mole H_2 /mole EtOH and a carbon monoxide content in the reformer effluent below 0.1 mole fraction is possible, without the danger of coke-formation.

4.4. EtOH–POX

Hydrogen production by partial-oxidation of pure feed-stocks is an interesting application for on-board fuel cell applications. The pure feed-stock has a higher energy content compared to fuel–water mixtures used in steam-reforming and a maximum energy per weight ratio for the fuel can be achieved. Furthermore the pure partial-oxidation operation has the advantage of lower energy-needs in the evaporation of the fuel, since no water needs to be evaporated.

Partial-oxidation operation is achieved by using air as an oxygen carrier, since pure oxygen is not economical. A major disadvantage of any partial-oxidation operation or air-addition is the nitrogen

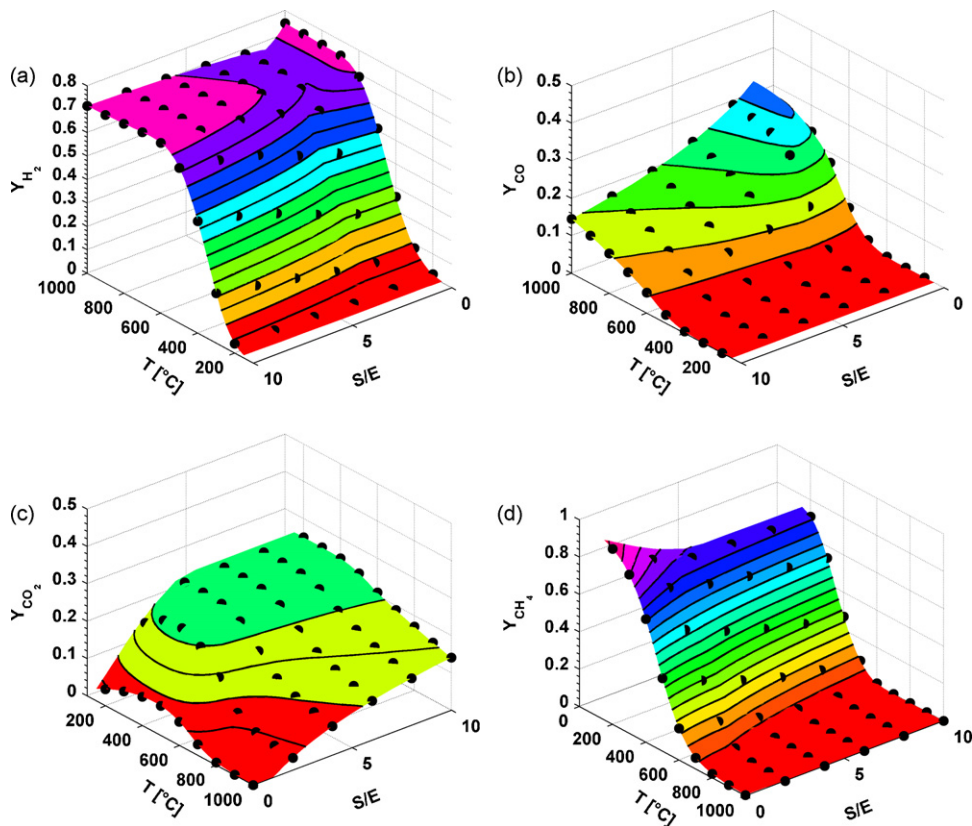


Fig. 6. Plots of the thermodynamic equilibrium product mole fractions of hydrogen, carbon monoxide, carbon dioxide and methane on a dry-basis for steam-reforming with $S/E = 0.0$ – 10.0 and $O/E = 0.0$.

dilution of the hydrogen containing effluent. This nitrogen dilution is deteriorating fuel cell operation, because increased nitrogen content lowers the open-circuit voltage of the fuel cell and at higher current densities a mass transport limitation is experimentally observed for proton exchange membrane fuel cells [33].

Fig. 8 shows the effect of nitrogen dilution, whereas the nitrogen-content in the reformer effluent on dry basis is shown for different partial-oxidation operations with O/E -ratio from 0.00 to 3.00 [mole O_2 /mole EtOH].

The increase of oxygen-to-ethanol ratio above $O/E = 1.5$ seems an unrealistic operating point, since the nitrogen dilution is already very high with a nitrogen content $y_{N_2} = 0.6$ on a dry basis.

The results of the thermodynamic calculation for the partial-oxidation case are shown in Fig. 9. The data shows the hydrogen

and carbon monoxide content in the reformer effluent on dry basis (Fig. 9a and b) and the coke-formation as well as the hydrogen yield for partial-oxidation operation with no water addition $S/E = 0$ (Fig. 9c and d).

The maximum hydrogen yield of partial-oxidation operation reaches only H_2 -Yield_{theo,PoX} = 3 mole H_2 /mole EtOH and is therefore much lower than the maximum reachable hydrogen yield for steam-reforming H_2 -Yield_{theo,SR} = 6 mole H_2 /mole EtOH. It is interesting to notice that conditions for high hydrogen content in the reformer effluent are in coincidence with high carbon monoxide content in the reformer. This means that a reasonably high hydrogen content in partial-oxidation of ethanol is possible at temperatures above 600°C and furthermore oxygen-to-ethanol ratios below 1.50. When lowering the oxygen-to-ethanol ratio the

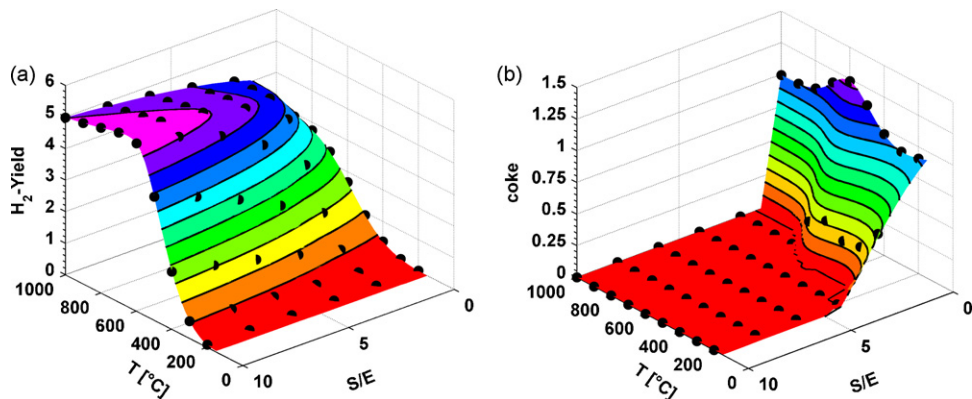


Fig. 7. Hydrogen-yield and coke-formation for steam-reforming operation with $S/E = 0.0$ – 10.0 and $O/E = 0.0$.

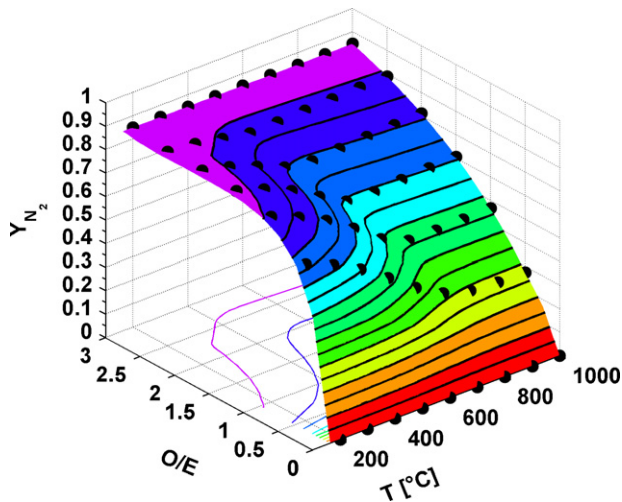


Fig. 8. Nitrogen dilution of hydrogen effluent for partial-oxidation. Nitrogen content on dry basis for different oxygen-to-ethanol ratios, $O/E=0.0\text{--}2.5$ at a steam-to-ethanol ratio of $S/E=0.0$.

operating temperature has to be increased to stay away from the coke-formation boundary. Whereas lowering the oxygen-to-ethanol ratio and increasing the operating temperatures inevitably lead to high carbon monoxide content in the effluent.

The window of reasonable operation conditions for pure partial-oxidation of ethanol is limited to $O/E=0.80\text{--}1.50$ and temperatures above $T=600\text{ }^\circ\text{C}$ and rather high carbon monoxide content in the reformer effluent.

4.5. EtOH–auto-thermal reforming

The auto-thermal reforming operation is a combination of steam-reforming and partial-oxidation operation. As discussed before, the steam-reforming operation leads to the highest hydrogen-yield and therefore to the highest hydrogen efficiency. The coke-formation in steam-reforming operation gives severe limitations on the operation conditions for a fuel-reformer. The combination of steam-reforming with partial-oxidation, the so called auto-thermal operation might give a possibility for reducing the stringent coke-formation boundary in steam-reforming, a further option is the reduction of carbon monoxide content in the reformer effluent and therefore a simplified gas-processing in the water–gas-shift reactors.

Using air as oxygen-carrier increases the nitrogen-content in the reformer effluent strongly as can be seen in Fig. 8.

In order to evaluate the auto-thermal operation mode, the results are shown for steam-to-ethanol ratios of $S/E=0.00\text{--}10.00$, oxygen-to-ethanol ratios of $O/E=0.00\text{--}0.75$ and a temperature of $T=200\text{--}1000\text{ }^\circ\text{C}$.

Fig. 10a–d shows the hydrogen-content in the reformer effluent on a dry nitrogen-free basis according Eq. (18)

$$y_{\text{H}_3\text{-figure}} = \frac{y_{\text{H}_2}}{1 - y_{\text{H}_2\text{O}} - y_{\text{N}_2}} \quad (18)$$

The hydrogen-content is shown on that basis since the nitrogen dilution hides the effects of an increased oxygen-to-ethanol ratio on the hydrogen content. It is interesting to notice, that increasing the oxygen-to-ethanol ratio does not strongly modify the hydrogen content on a dry nitrogen-free basis. Taking the reformer temperature below $500\text{ }^\circ\text{C}$ and looking on different oxygen-to-ethanol

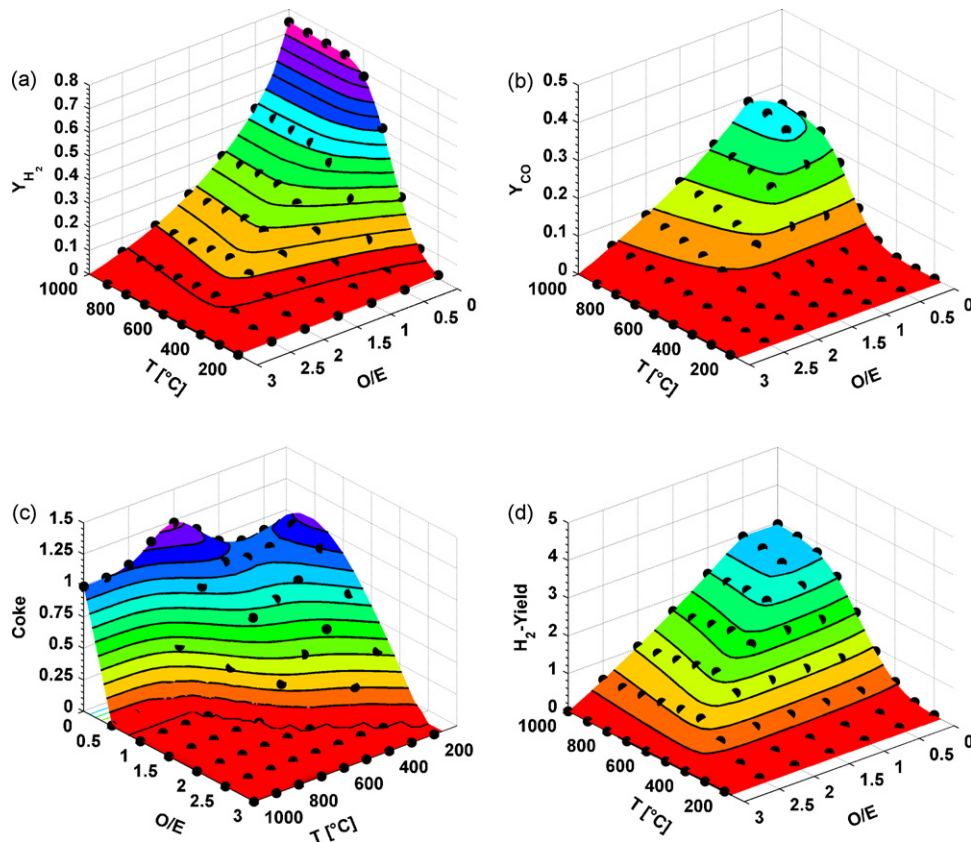


Fig. 9. Plots of the thermodynamic equilibrium product mole fractions of hydrogen and carbon monoxide on a dry nitrogen-free basis and hydrogen-yield [mole H_2 /mole EtOH] and coke formation [mole C/mole EtOH] for pure partial-oxidation with steam-to-ethanol ratio $S/E=0.0$.

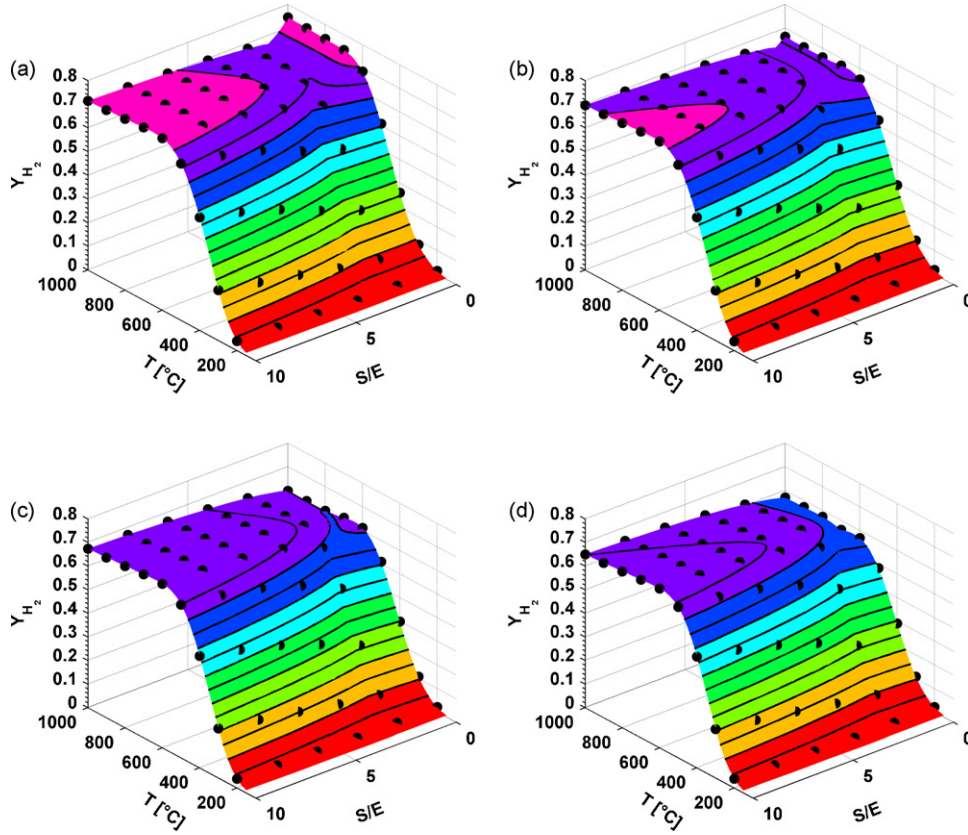


Fig. 10. Plots of the thermodynamic equilibrium product mole fractions of hydrogen on a dry nitrogen-free basis and for auto-thermal operation with steam-to-ethanol ratio, $S/E = 0.0$ – 10.0 and oxygen-to-ethanol ratio, $O/E = 0.00, 0.25, 0.50$ and 0.75 (a–d).

contents in Fig. 10a–d, $O/E = 0.00, 0.25, 0.50$ and 0.75 , one can see that the hydrogen content profile on a dry nitrogen-free basis stays almost constant.

Fig. 11a–d shows the carbon monoxide content on the dry nitrogen-free basis according Eq. (19)

$$y_{\text{CO-figure}} = \frac{y_{\text{CO}}}{1 - y_{\text{H}_2\text{O}} - y_{\text{N}_2}} \quad (19)$$

The carbon monoxide content on a dry nitrogen-free basis does not strongly change with the oxygen-to-ethanol ratio. For steam-to-ethanol ratios above $S/E = 4.00$ the carbon monoxide content profile on dry nitrogen-free basis is almost constant for the various oxygen-to-ethanol ratios. This means an increase of oxygen-to-ethanol ratio gives no real reduction of the carbon monoxide content in the effluent. The carbon monoxide content in the reformer effluent is only reduced to the dilution effect of the increased nitrogen-content in the reformer.

Fig. 12a–d shows the coke-formation (mole C/mole EtOH) for different auto-thermal operation modes. The increase of oxygen-to-ethanol ratio has a beneficial, even not very strong, effect on the coke-formation boundary. In order to reform feed streams with very low steam-to-ethanol ratio, high oxygen-to-ethanol ratios have to be chosen to avoid coke-formation. For example, in order to process feeds with a steam-to-ethanol-ratio of $S/E = 3.00$ the choice of a oxygen to ethanol ratio $O/E = 0.50$ allows a coke-free operation of the reformer down to temperature of $T = 300^\circ\text{C}$.

Fig. 13a–d shows the hydrogen yield for auto-thermal operation. The maximum hydrogen yield is decreased at higher oxygen-to-ethanol ratios, as expected. It is interesting to notice the hydrogen-yield profile, which at low reforming temperatures $T < 500^\circ\text{C}$, is almost not influenced by increasing the oxygen-to-carbon ratio.

As a conclusion it can be said that the benefit of the auto-thermal operation can be seen essentially in lower coke-formation boundary. The effects on the hydrogen and carbon monoxide contents are very low and mainly due to the increased nitrogen dilution, when oxygen-to-ethanol ratios were raised. Additionally auto-thermal operation lowers the energy demand for the reformer operation, since the partial-oxidation reaction is exothermal.

4.6. Reforming energy requirement

The reforming products for the three different options, steam-reforming, partial-oxidation and auto-thermal reforming have been analysed for isothermal conditions so far. In order to compare the three processes in their theoretical process energy requirements an approximate energy balance is made as shown in Fig. 14.

The process energy requirements for the reformer consist of the evaporation energy for of the ethanol–water feed and heating energy for heating up of feed gases and vapours from ambient to reformer temperature, the reforming energy for at reformer temperature and cooling energy of products from reformer temperature to 120°C . The energy for condensation of water in the reformer effluent is therefore not considered.

$$\dot{Q}_{\text{Process}} = \dot{Q}_{\text{Evaporation}} + \dot{Q}_{\text{Heating}} + \dot{Q}_{\text{Reformer}} - \dot{Q}_{\text{Cooling}} \quad (20)$$

The process energy needed is related to the moles of hydrogen in the reformer effluent.

$$\dot{Q}_{\text{Evaporation}} = \frac{\dot{n}_{\text{EtOH,in}}}{\dot{n}_{\text{H}_2,\text{out}}} \Delta H_{\text{vap,EtOH}} + \frac{\dot{n}_{\text{H}_2\text{O,in}}}{\dot{n}_{\text{H}_2,\text{out}}} \Delta H_{\text{vap,H}_2\text{O}} \quad (21)$$

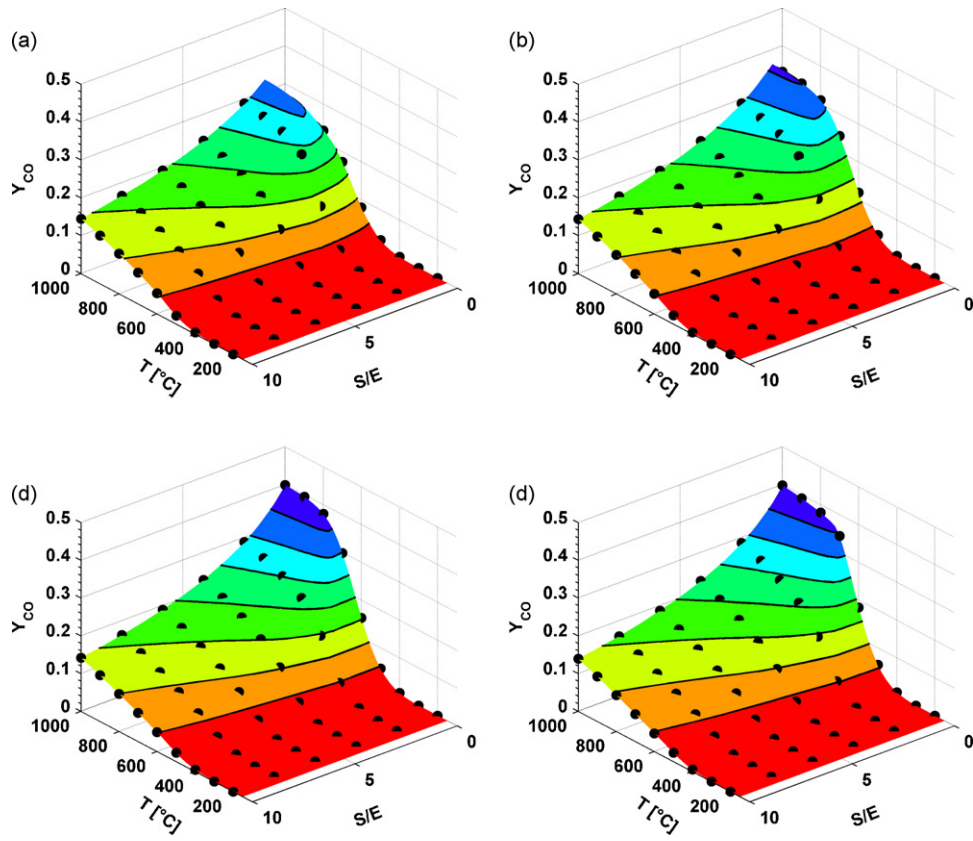


Fig. 11. Plots of the thermodynamic equilibrium product mole fractions of carbon monoxide on a dry nitrogen-free basis for auto-thermal operation with steam-to-ethanol ratio, $S/E=0.0-10.0$ and oxygen-to-ethanol ratio, $O/E=0.00, 0.25, 0.50$ and 0.75 (a–d).

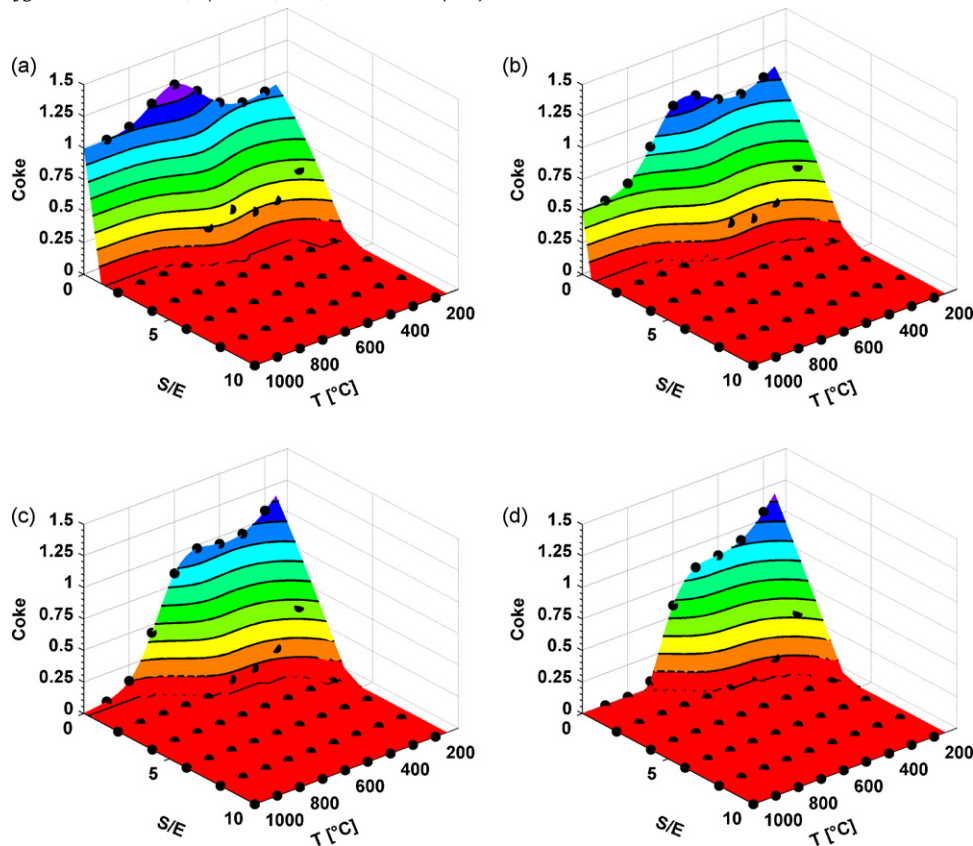


Fig. 12. Plots of the thermodynamic equilibrium coke-formation [mole C/mole EtOH] for auto-thermal operation with steam-to-ethanol ratio, $S/E=0.0-10.0$ and oxygen-to-ethanol ratio, $O/E=0.00, 0.25, 0.50$ and 0.75 (a–d).

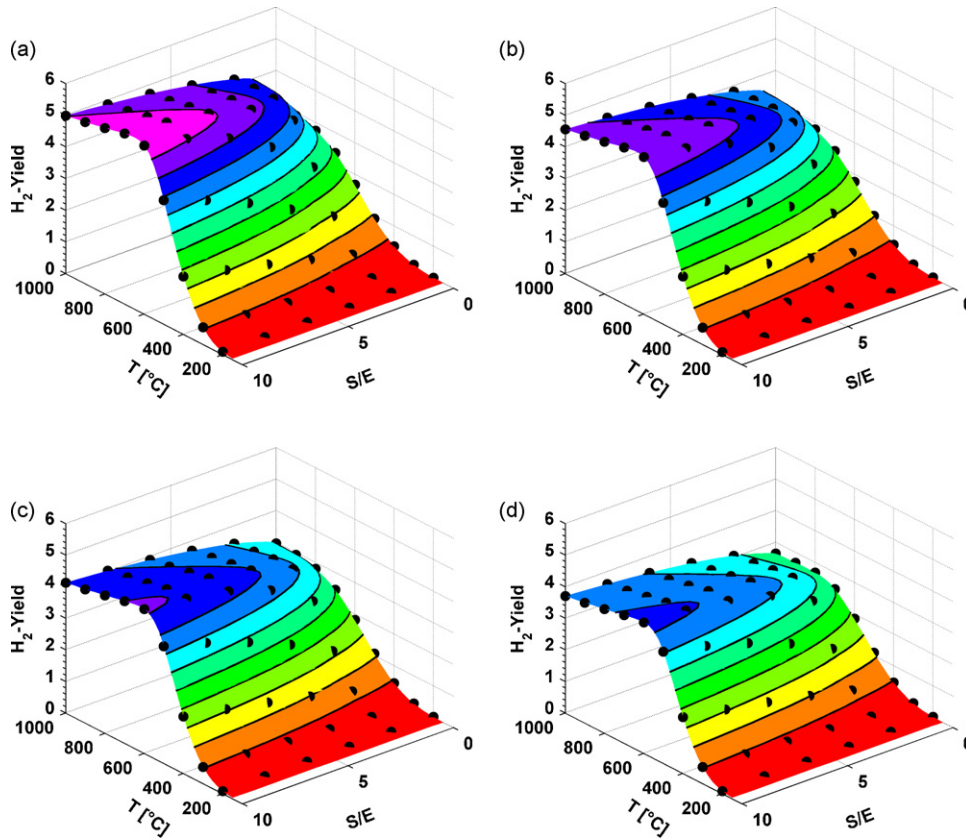


Fig. 13. Plots of the thermodynamic equilibrium hydrogen-yield [mole H₂/mole EtOH] for auto-thermal operation with steam-to-ethanol ratio, S/E=0.0–10.0 and oxygen-to-ethanol ratio, O/E=0.00, 0.25, 0.50 and 0.75 (a–d).

$$\dot{Q}_{\text{Heating}} = \sum_{i=1}^n \frac{\dot{n}_{i,\text{in}}}{\dot{n}_{\text{H}_2,\text{out}}} c_{p,i} (T_{\text{ref}} - T_0) \quad (22)$$

$$\dot{Q}_{\text{Cooling}} = \sum_{i=1}^n \frac{\dot{n}_{i,\text{out}}}{\dot{n}_{\text{H}_2,\text{out}}} c_{p,i} (T_{\text{ref}} - T_{\text{out}}) \quad (23)$$

$$\dot{Q}_{\text{Reforming}} = \sum_{i=1}^n \frac{\dot{n}_{i,\text{in}}}{\dot{n}_{\text{H}_2,\text{out}}} \Delta H_{f,i} - \sum_{j=1}^n \frac{\dot{n}_{j,\text{out}}}{\dot{n}_{\text{H}_2,\text{out}}} \Delta H_{f,j}, \quad (24)$$

where ΔH_{vap} is the enthalpy of vapourization, c_p the specific heat capacity and $\Delta H_{f,i}$ is the enthalpy of formation of species i . The index i corresponds to the feed stream to the reformer and out corresponds to the reformer effluent. T_{ref} is the temperature of the reformer, T_{out} is the temperature of the effluent after heat recovery due to cooling and T_0 is the ambient temperature.

Fig. 15 shows the different energy demands for steam-reforming and auto-thermal reforming. The energy is given as energy per mole hydrogen produced. Reasonable hydrogen yields are given at temperatures above 400 °C. Energy necessary for heating and cooling is

almost equal, which means that in a well-designed reformer with heat integration little energy is lost for heating and cooling. The largest amount of energy is necessary for reforming and evaporation. The energy needed for reforming is strongly reduced, when operating in auto-thermal mode. On the other hand increasing the oxygen-to-steam ratio raises the energy for evaporation since the ethanol is partly oxidised for in auto-thermal operation, and hence a higher feed flux is necessary in order to reach the same hydrogen flux in the reformer effluent.

The partial-oxidation operation has similar features as the auto-thermal operation, whereas the energy for reforming is more exothermic, as large amount of ethanol is oxidised, and due to the low amount of hydrogen produced the energy for evapora-

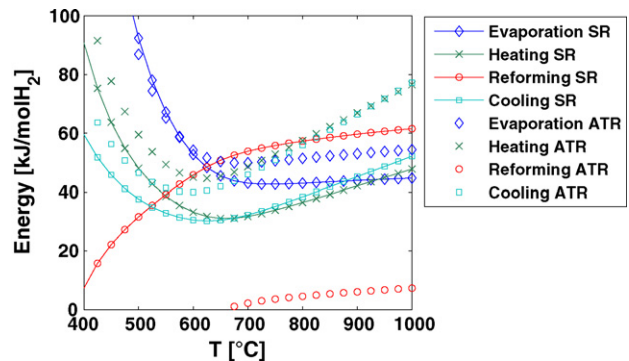


Fig. 15. Energy demands for evaporation, heating, reforming and cooling for ethanol steam-reforming SR (S/E=4.0) and auto-thermal reforming ATR (S/E=4.0 and O/E=0.25).

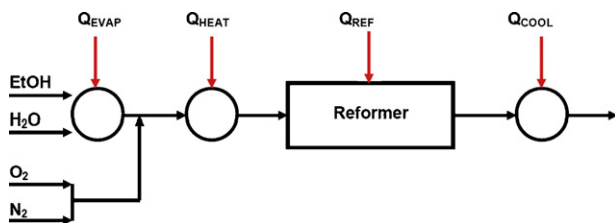


Fig. 14. Reformer energy balance.

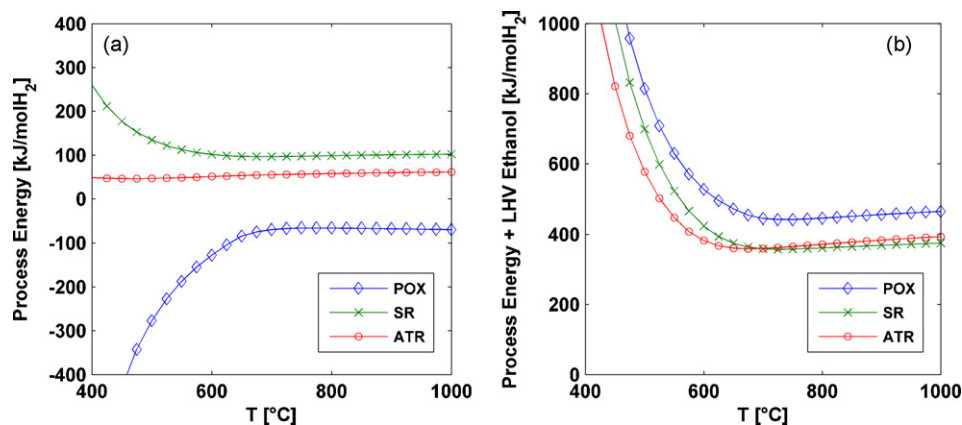


Fig. 16. (a) Total process energy required to produce one mol hydrogen in reformer effluent; (b) total energy demand, process energy plus lower heating value of ethanol in the feed, to produce one mole hydrogen in the reformer effluent. POX—partial-oxidation, SR—steam-reforming and ATR—auto-thermal reforming. Process energy is the sum of energy necessary for evaporation, heating, reforming and cooling.

tion strongly increases, based on the consideration of energy per hydrogen in effluent.

The total energy demand for reforming operation is shown in Fig. 16a and b. The comparison of steam-reforming, auto-thermal reforming and partial-oxidation in terms of energy demand is complicated, since in auto-thermal and partial-oxidation a part of the fuel is used for heat generation, which lowers the external energy demand. Fig. 16a shows the process energy necessary, whereas steam-reforming is clearly far off in energy demands compared to partial-oxidation. In Fig. 16b the process energy plus the lower heating value of the ethanol used is plotted in order to take care of chemical energy of ethanol used and the thermal energy. Here a complete different picture is drawn, whereas partial-oxidation is the most energy-demanding operation. This means from viewpoint of hydrogen content in the reformer effluent and total energy demands that following order in terms of efficiency, SR > ATR > POX, can be made.

5. Conclusions

Thermodynamic equilibrium of ethanol steam-reforming, partial-oxidation and auto-thermal reforming was studied by Gibbs enthalpy minimization including the possibility of solid coke-formation. The main product set is methane, hydrogen, carbon monoxide, carbon dioxide, water, ethanol, oxygen, nitrogen and solid coke. The study started with an expanded product set, including ethane, ethylene, acetylene, acetaldehyde, acetic acid, acetone, ethyl acetate, diethyl ether, ethylene glycol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-propyl-methyl-ether and *iso*-propyl-alcohol to evaluate the order of the thermodynamical stable products.

The thermodynamic compositions are evaluated for steam-to-ethanol ratios of $S/E=0.00$ – 10.00 , oxygen-to-ethanol ratios of $O/E=0.00$ – 3.00 and temperatures of $T=200$ – 1000 °C.

Based on the results following conclusions can be drawn:

- Thermodynamically, ethanol processed with steam and/or air will yield to the decomposition of ethanol over the whole temperature range studied. The main components at low temperature are methane and carbon dioxide. While increasing the temperature above 400 °C methane is reduced and hydrogen content rises strongly, additionally carbon monoxide evolves. At low temperatures and/or at low steam-to-ethanol ratios solid coke-formation is taking place.

- In steam-reforming operation a higher hydrogen-yield as in partial-oxidation operation is possible. Concurrent high hydrogen-content and low carbon monoxide content in the reformer effluent is possible. The favourable operation window for steam-reforming is at reforming temperatures between 550 and 650 °C and steam-to-ethanol ratios above $S/E=4$. With this condition, a hydrogen-yield >4 mole H₂/mole EtOH and a carbon monoxide below 0.1 mole fraction is possible, without the danger of coke formation.
- In partial-oxidation operation high hydrogen content appears in conjunction with high carbon monoxide content. The operation-window predicts reasonable a hydrogen yield at oxygen-to-ethanol ratio below $O/E=1.5$ and temperatures above $T=600$ °C. Additionally the coke-formation boundary requests oxygen-to-ethanol ratios $O/E>0.8$ in order to avoid coke-formation. From thermodynamical aspects pure partial-oxidation of ethanol for production of hydrogen rich feeds for fuel cells seem to be an unfavourable choice, merely due to high carbon monoxide content and the need of anhydrous ethanol feed, which is costly in production.
- Auto-thermal operation is the combined steam-reforming and partial-oxidation operation. Besides lowering the energy demand for the reforming operation the auto-thermal operation has the main advantage of reducing the coke-formation rate. Interestingly hydrogen and carbon monoxide content on dry nitrogen-free basis is almost not influenced by the auto-thermal operation, but the hydrogen and carbon monoxide content on dry basis is strongly reduced due to the nitrogen dilution.
- Comparison of the total energy demand, which is the process energy for heating, evaporation, reforming and cooling and the chemical energy, lower heating value, of ethanol used, shows clearly that steam-reforming is the least energy demand operation considering. The total energy demand is of the order POX > ATR > SR.
- The thermodynamically stable products as evaluated by the expanded product set are methane, ethane, *iso*-propyl-alcohol, *n*-butanol, *n*-propanol, ethylene, diethyl ether and acetic acid.

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