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Thermodynamic analysis of ethanol processors for fuel cell applications

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Abstract

A thermodynamic analysis of hydrogen production from ethanol has been carried out with respect to solid polymer fuel cell applications. Ethanol processors incorporating either a steam reformer or a partial oxidation reactor connected to water gas shift and CO oxidation reactors were considered and the effect of operating parameters on hydrogen yield has been examined. Employment of feeds with high $H_2O/EtOH$ ratio results in reduced energy efficiency of the system. When hydrogen, non-converted in the fuel cell, is used to supply heat in the steam reformer, the effective hydrogen yield is essentially independent of the temperature of the reformer and the water gas shift reactor. Optimal operating conditions of partial oxidation processors have been determined assuming an upper limit for the preheat temperature of the feed. Results are discussed along with other practical considerations in view of actual applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ethanol; Reforming; Partial oxidation; Hydrogen production; Thermodynamic analysis

1. Introduction

Solid polymer fuel cells (SPFC) are the most attractive type of fuel cell for mobile and small-scale, stationary applications [1]. Chemical storage of hydrogen in liquid fuels is considered to be one of the most advantageous short- and mid-term options for supplying hydrogen to the SPFC. A variety of liquid fuels, such as methanol, ethanol and hydrocarbons are suitable for this purpose. In all cases, a fuel processor unit is required to transform the liquid fuel to a hydrogen-rich stream containing only trace amounts of CO (∼10 ppm) to avoid poisoning of the electrocatalyst of the fuel cell [2].

Among liquid fuels, ethanol is a promising source of hydrogen, as it can be readily produced from renewable sources (biomass). It is also less toxic than methanol or hydrocarbons. The overall reaction of hydrogen production from ethanol corresponds to the formation of 6 mol of H_2 per mol of ethanol:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{1}$$
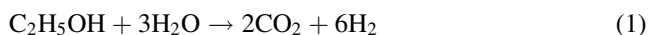
This reaction, however, has to be carried out in two steps: (i) a high-temperature endothermic step (steam reforming), in

which ethanol is converted to a gaseous mixture of H_2, CO, CO_2, CH_4 and unreacted H_2O and (ii) a subsequent, low-temperature step (water gas shift reaction), in which CO is reacted with H_2O towards H_2 and CO_2. Because the shift reaction is equilibrium-limited, CO conversion is not complete and an additional step of CO removal is necessary (e.g. by selective CO oxidation). As a consequence, the fuel processor consists, in general, of a steam-reforming/POX reactor, a WGS reactor and an oxidation reactor for selective oxidation of CO. Vasudeva et al. [3] and Garcia and Laborde [4] have carried out thermodynamic analysis of the steam reforming of ethanol. The thermodynamics of ethanol reforming have been also examined by other investigators [5–7] in relation to applications in molten carbonate fuel cells. It has been found that the only gaseous products at equilibrium are H_2, CO, CO_2 and CH_4. Formation of elemental carbon is predicted only at low $H_2O/EtOH$ ratios (<2) and temperatures lower than 900 K [3].

As steam reforming of ethanol (and of all other fuels, too) is an endothermic process, heat must be supplied to the system. This can be accomplished by an either external or internal mode of heat supply. In the case of the external mode, a fuel is combusted externally to supply the required heat for reforming (conventional steam reformer SR). In the case of the internal mode, air is co-fed with ethanol and water and the required heat is produced by combustion of a

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Nomenclature	
P	operating pressure (atm)
R	water to ethanol (H_2O/EtOH) molar ratio of feed (-)
S_{OX}	oxidation selectivity of CO in the SOX reactor (-)
T_{OPT}	optimal temperature of POX reactor (K)
T_{POX}	temperature of POX reactor (K)
T_{REF}	temperature of steam reformer (K)
T_{WGS}	temperature of WGS reactor (K)
Y_{H2}	hydrogen yield (mol H_2/mol EtOH)
Y_{H2}^{eff}	effective hydrogen yield of ethanol processor with a steam reformer (mol H_2/mol EtOH)
Φ	fuel equivalence ratio $\Phi=(\text{EtOH}/O_2)_{feed}/(\text{EtOH}/O_2)_{stoich}$ (-)
Φ_o	fuel equivalence ratio for a thermoneutral process (-)

fraction of ethanol. The POX reactor is simpler in construction and exhibits faster response characteristics under transient conditions and, for this reason, appears to be the reactor of choice in vehicle applications. On the other hand, the POX-fuel processor has to process higher volumetric flow rates and produces a gas stream of lower H_2 concentration due to the effect of nitrogen dilution. Mitchell et al. [8] have reported on the performance of a catalytic POX reactor for hydrogen production from ethanol for fuel cell applications.

In the present work, a thermodynamic analysis of ethanol processors, incorporating either a steam reformer or a POX reactor, has been undertaken with the goal to determine optimal operating conditions of the separate reactor units comprising the system.

2. Description of ethanol processors

A schematic diagram of an ethanol processor utilizing the internal mode of heat supply is shown in Fig. 1. The EtOH/H_2O/air feed is initially directed to the POX reactor, which operates at autothermal temperatures higher than 900 K and produces a gaseous stream containing H_2, CO, CO_2, CH_4, H_2O and N_2. After cooling, this stream enters the WGS reactor, where a large fraction of CO is reacted with H_2O towards CO_2 and H_2. The WGS reactor may actually consist of two units, namely the high and low temperature shift reactors. The products of the WGS reactor exit at temperatures around 473 K and enter the selective oxidation (SOX) reactor, where the remaining CO is totally oxidized with the addition of small amounts of air to CO_2 (residual CO ~10 ppm) at temperatures in the range of 373–473 K. The CO-free, hydrogen-rich stream is then fed to the fuel cell, where hydrogen is electrochemically oxidized to H_2O with simultaneous production of electrical energy. At first glance, an obvious operating window of the POX reactor is the one which minimizes formation of CH_4 byproduct, because methane retains four hydrogen atoms in its molecule and its formation corresponds to a loss in hydrogen yield. In addition, methane is not converted downstream the POX reactor and will be finally exhausted to the atmosphere (unless an energy-consuming aftertreatment unit is installed). Although methane is not considered as an air pollutant, it is still a greenhouse gas with global warming potential (GWP) of 21 over a 100-year period.

The ethanol processor utilizing the external mode of heat supply is shown in Fig. 2. The WGS and SOX reactors are the same as in the previous case, whereas the POX reactor has been replaced by a steam reformer. In principle, any type
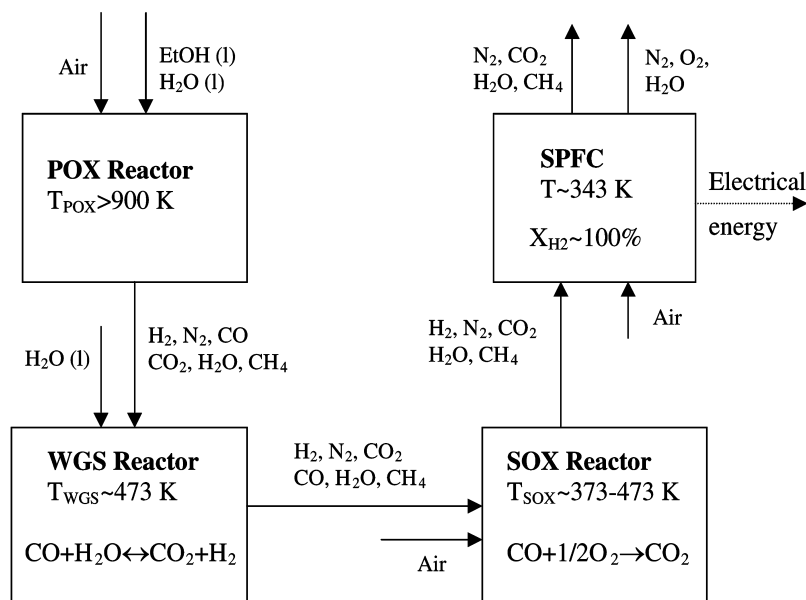

Fig. 1. Schematic diagram of ethanol processor incorporating a partial oxidation (POX) reactor.
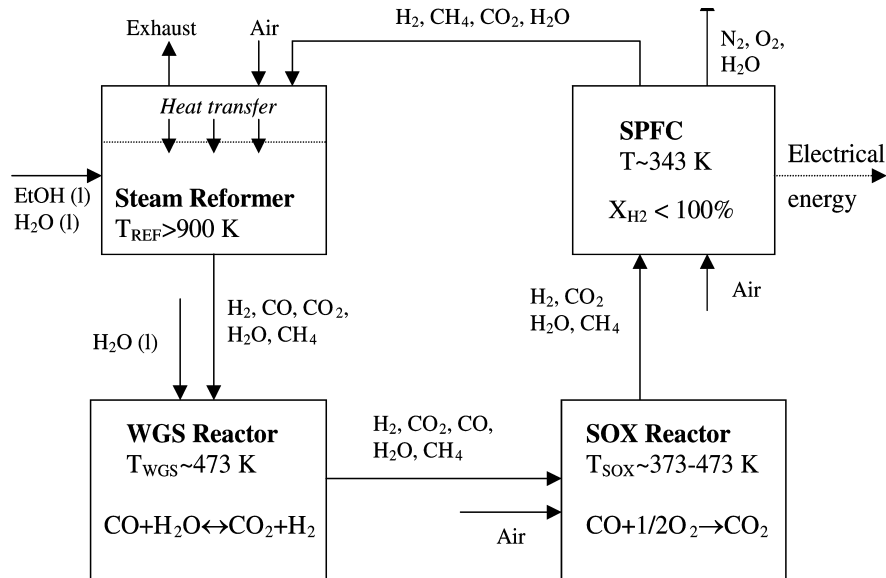
Fig. 2. Schematic diagram of ethanol processor incorporating a steam reformer.

of fuel, such as ethanol or natural gas, may be used to supply heat in the reformer. An interesting situation arises, however, when hydrogen, non-converted in the SPFC, is recycled and burned in the reformer. In this case, the SPFC will operate under conditions of incomplete fuel utilization (conversion of H_2, $X_{H2} < 100\%$), which offer the possibility to obtain higher conversion efficiencies to electrical energy. In addition, this mode of operation gives larger flexibility in the window of operating conditions of the reformer. As methane is recycled and burned as a fuel in the reformer, one can tolerate higher amounts of methane produced and the overall heat requirements can be satisfied by adjustment of hydrogen conversion in the SPFC.

Equilibrium compositions in the reformer or the POX reactor have been calculated by taking into account the fact that the only products at equilibrium are H_2, CO, CO_2 and CH_4 in the temperatures and feed compositions of practical interest [3]. Based on that, reaction (2) was taken to proceed quantitatively to the right and the final equilibrium composition was found by solving for the equilibrium of reactions (3) and (4). In the case of the WGS reactor, the equilibrium composition was calculated using reaction (4).

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \qquad (2)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (4)$$

In the case of the POX reactor, the irreversible combustion of ethanol was also taken into account:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad (5)$$

The inlet to the system was assumed to be at 298 K with ethanol and water in the liquid state. Hydrogen-rich product gas was assumed to exit the system at a temperature of 343 K, in view of the fact that typical temperatures of SPFC

operation are also $\sim$343 K. The validity of thermodynamic predictions was checked by comparison with existing literature data regarding steam reforming of ethanol [3–7].

3. Results

3.1. Ethanol processor with steam reformer

3.1.1. Effect of operating parameters

The main operating parameters of the system are: the $H_2O/EtOH$ ratio (R) of the feed, the exit temperatures of the reformer, T_{REF}, and the WGS reactor, T_{WGS}, the pressure, P, and the selectivity of CO oxidation in the SOX reactor, S_{OX}. The last parameter is defined as the ratio of oxygen consumed for CO oxidation to the total consumption of oxygen for CO and H_2 oxidation. Current catalytic systems for selective CO oxidation exhibit selectivities of the order of 0.5 [9,10]. The effect of reformer exit temperature, T_{REF}, on hydrogen yield, Y_{H2}, is presented in Fig. 3. Results in Fig. 3
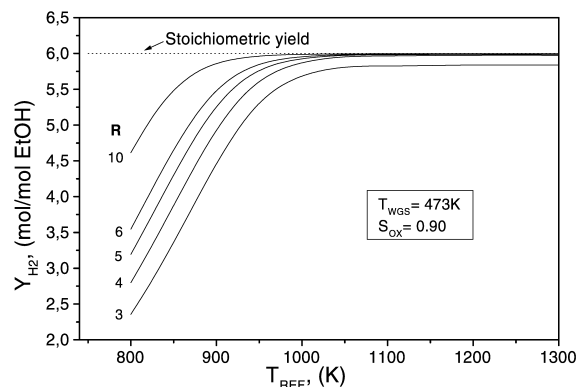

Fig. 3. Effect of reformer temperature, T_{REF}, on hydrogen yield.

have been obtained for $T_{WGS}=473$ K and $S_{OX}=0.9$. It can be observed that Y_{H2} increases with increasing reformer temperature and tends towards the stoichiometric value ($Y_{H2}=6$) for $T_{REF}>1000$ K and $R>6.0$ or 1100 K and $R>4.0$. Hydrogen yield increases also with increase of R, as expected from the equilibrium reactions (3) and (4). Employment of R values higher than 5.0 does not result in any significant gain in hydrogen yield, as long as the reformer temperature is higher than ~1000 K. It has to be noted that processing of feeds with high R values requires a larger reactor size due to the larger gas volumes involved. The thermodynamically-predicted molar fraction of CH_4 decreases with increase of reformer temperature and of the R value and becomes lower than 100 ppm at $T_{REF}>1180$ K when $R=3$ and at $T_{REF}>1120$ K when $R=5$.

The effect of the temperature of the WGS reactor, T_{WGS}, on the predicted hydrogen yield is presented in Fig. 4 for R values in the range of 3–5 and $T_{REF}=1000$ or 1100 K. As the WGS reaction is exothermic, increase of its temperature leads to a decrease of hydrogen yield. It can be, however, observed that T_{WGS} has a stronger effect on hydrogen yield when R is small. This is explained by taking into account that H_2O is in excess when $R>3$ and this helps in shifting the WGS equilibrium towards the right. Comparison of the curves for $R=3$ and $T_{REF}=1000$ K or 1100 K shows that the reformer temperature simply shifts vertically the equilibrium curve without affecting its shape. From a practical point of view, employment of a feed with R ~4–5 permits operation of the WGS reactor at higher temperatures without a significant loss in hydrogen yield. This, in turn, makes feasible the use of a smaller WGS reactor due to the higher activity of the shift catalyst.

The effect of the oxidation selectivity, S_{OX}, in the SOX reactor on hydrogen yield is presented in Fig. 5. It can be observed that the oxidation selectivity does not influence significantly the hydrogen yield obtained, as long as the R value of the feed is ~4.0 or higher. This is explained by noting that the residual CO concentration entering the SOX reactor is very low at such values of R so that its oxidation leads to small loss of hydrogen even if it is carried out with a
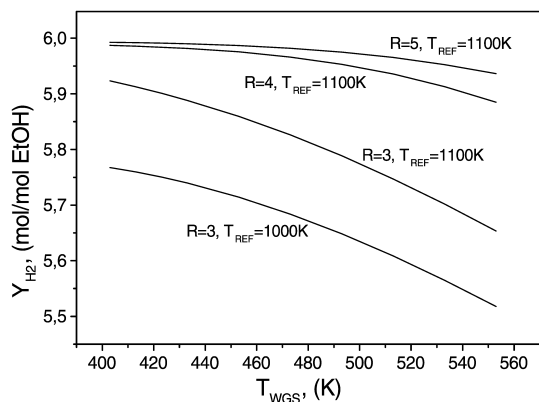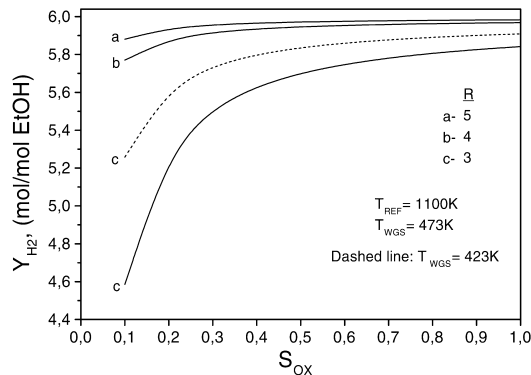

Fig. 5. Effect of oxidation selectivity of CO in the selective oxidation reactor, S_{OX}, on hydrogen yield.

low selectivity of the order of 30%. The equilibrium molar fraction of CO at the WGS reactor exit, is, for example, 0.11% for $R=5$, $T_{REF}=1100$ K and $T_{WGS}=473$ K. On the other hand, the selectivity of CO oxidation strongly influences hydrogen yield for $R=3$, especially when S_{OX} is smaller than 0.6. In this case, the effect of S_{OX} can be attenuated by operating the WGS reactor at low temperatures (Fig. 5, the $T_{WGS}=423$ K curve) in order to achieve higher equilibrium conversion of CO in this reactor.

Increase of pressure has a negative effect on hydrogen yield because it shifts reaction (3) towards the right. The predicted hydrogen yield is presented in Fig. 6 as a function of operating pressure in the range of 1–5 atm, which is of interest in the context of this work. It can be observed that hydrogen yield decreases linearly with increasing pressure in this range. The strongest effect of pressure appears at low values of R and low reformer temperatures. For example, increase of pressure from 1 to 5 atm for $R=3$ causes a decrease in hydrogen yield of 0.9% for $T_{REF}=1100$ K and of 0.1% for $T_{REF}=1200$ K. The corresponding values for $R=5$ are 0.35 and 0.05%, respectively. Overall, it can be said that the negative effect of pressure is small in this pressure range and it can be counteracted, if needed, by an increase of reformer temperature or of the R value of the feed.
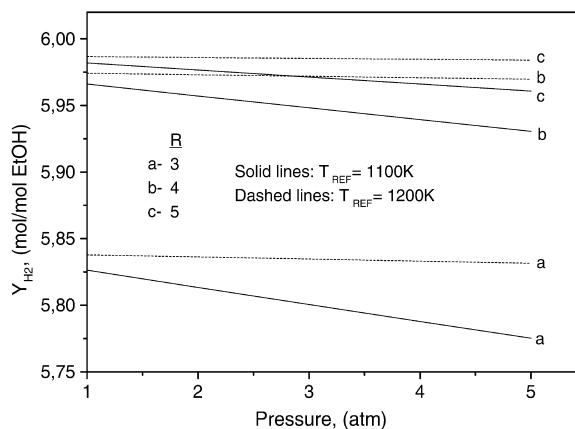

Fig. 4. Effect of temperature of water gas shift reactor, T_{REF}, on hydrogen yield.

Fig. 6. Effect of pressure on hydrogen yield ($T_{WGS}=473$ K, $S_{OX}=0.9$).

3.1.2. Coupling of ethanol processor to a SPFC

Coupling of the ethanol processor to a SPFC implies, as shown in Fig. 2, that the SPFC operates at hydrogen conversions less than unity and the SPFC exhaust gas is used as a fuel to supply the required heat in the steam reformer. The required conversion level of hydrogen in the SPFC depends on the operating parameters of the ethanol processor, and especially on the reformer temperature and the R value of the feed. The effective hydrogen yield of the system, Y_{H2}^{eff}, is equal to the normal hydrogen yield (e.g. Fig. 3) minus the amount of hydrogen, which has to be burned in the reformer to supply the required heat. Y_{H2}^{eff} has been calculated as a function of R and T_{REF}, assuming an ideal system and an overall thermoneutral process at $P=1$ atm (EtOH and H_2O enter the system at 298 K in the liquid state, exhaust gas exits the system at 343 K) and the results are presented in Fig. 7. It can be observed that the effective hydrogen yield decreases linearly with increasing R, when R is larger than ~3.0. A maximum in hydrogen yield is evident, which increases in magnitude and shifts towards lower R values with decreasing reformer temperature. The predicted decrease in hydrogen yield with increasing R is due to the increased energy requirements for water evaporation, which overwhelm the marginal increase of hydrogen production with increasing R (Fig. 3). When R becomes smaller than the stoichiometric value of 3.0, the amount of unreacted CO starts to increase and this factor finally predominates leading to a maximum in hydrogen yield. The maximum appears at smaller R values as T_{REF} decreases because additional water is produced in the reformer together with methane at low reformer temperatures. Another important remark is that Y_{H2}^{eff} increases only marginally with reformer temperature, when $R>2.9$. This confirms what was mentioned in a previous section regarding the flexibility in the operating window of the reformer when the system is coupled to a SPFC. Calculations performed with variation of the WGS reactor temperature in the range of 423–523 K also showed that the effect of T_{WGS} on effective hydrogen

yield is minor (less than 1% change in hydrogen yield). Therefore, the reformer may operate at any temperature above 950 K and the WGS reactor at any temperature in the range of 423–523 K in the coupled system, while maintaining, essentially, the same effective hydrogen yield.

3.2. Ethanol processor with POX reactor

When the ethanol processor incorporates a POX reactor in the place of the steam reformer, an additional parameter of the system is the EtOH/air equivalence ratio, Φ, of the feed, defined as: $\Phi=(EtOH/O_2)_{feed}/(EtOH/O_2)_{stoich}$ [8]. A value of $\Phi=1$ corresponds to the stoichiometric combustion mixture of ethanol and oxygen (air). Values of $\Phi>1$ correspond to rich mixtures. An indication of the required quantity of oxygen for the operation of the POX reactor is provided by the following equation:

$$C_2H_5OH \ (l) + 0.608O_2 + 1.784H_2O \ (l)$$
$$\rightarrow 2CO_2 + 4.784H_2, \quad \Delta H(298\,K) = 0 \tag{6}$$
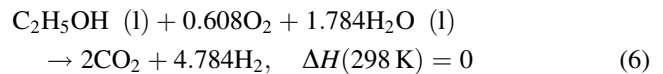
Eq. (6) shows that 0.608 mol of oxygen per mol of ethanol — corresponding to a Φ value of 4.93 — are required for a thermoneutral overall reaction at 298 K. The thermodynamic behavior of the POX-ethanol processor is similar to the one of the processor incorporating a reformer, as the main difference is the presence of N_2 which acts as a diluent.

It is understandable that the amount of air necessary to achieve an overall thermoneutral process depends on the R value of the feed. The equivalence ratio, Φ, which is just sufficient for a thermoneutral process for a specific R value, will provide the maximum hydrogen yield in an ideal system. Employment of higher equivalence ratios is not interesting from a practical point of view because it will result in a heat-deficient process, while smaller equivalence ratios will result in lower hydrogen yields, because of the larger than necessary fraction of ethanol consumed (in practice, smaller equivalence ratios will have to be used, of course, to account for heat losses and non-ideal heat exchangers). Therefore, the ideal behavior of a POX processor can be mapped by calculating the equivalence ratio for a thermoneutral process, Φ_o, as a function of R. The results of this calculation are presented in Fig. 8, assuming a POX reactor temperature of 1200 K (T_{pox} has only a minor effect on Φ_o, as long as it is >1100 K). Curves plotted as solid lines have been obtained assuming that extra water is added to the WGS reactor to maintain an effective $H_2O/$ EtOH ratio equal to 3.0, as long as R is smaller than ~1.9. The curve plotted as a dashed line corresponds to an effective $H_2O/EtOH$ ratio of 4.0 at R values smaller than ~2.4. It can be observed that all curves practically coincide at R values higher than 2.5, in which region Φ_o decreases with increasing R. This is expected, because larger amounts of air are needed to account for the heat requirements of a feed containing a lot of water. Φ_o remains practically
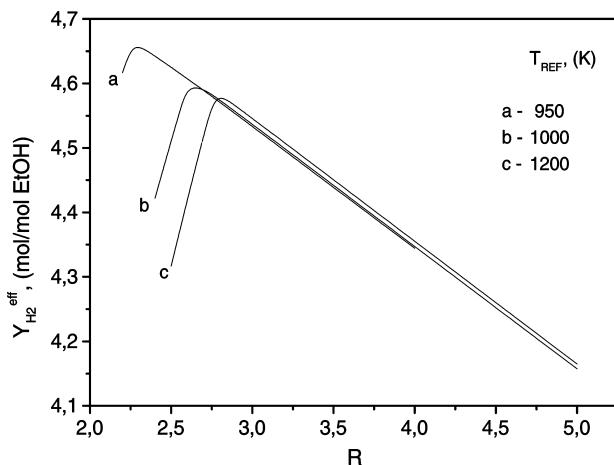
Fig. 7. Effective hydrogen yield, Y_{H2}^{eff}, as a function of R in the coupled system ethanol processor-SPFC (T_{WGS}=473 K, S_{OX}=0.9).
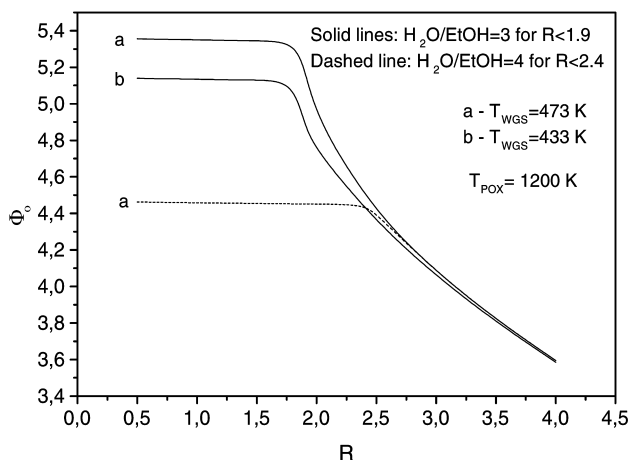
Fig. 8. Equivalence ratio of feed corresponding to a thermoneutral process, Φ_o, as a function of R.

constant at R values smaller than 2.4 (dashed line curve) or 1.9 (solid line curves), because the total amount of water entering the system remains constant in this case. Comparison of curves a and b shows that Φ_o decreases with decreasing temperature of the WGS reactor. This is explained as follows: The concentration of residual CO exiting the WGS reactor decreases with decreasing WGS reactor temperature and this leads to smaller heat production in the SOX reactor, which has to be compensated by use of lower equivalence ratios in the feed. Maximum hydrogen yields pertaining to the conditions of Fig. 8 are presented in Fig. 9. The following observations can be made:

- Hydrogen yield does not depend significantly on the temperature of POX and WGS reactors, as long as the R value of the feed is larger than ~2.5. This is because the high water content hinders methane formation in the POX reactor and facilitates CO conversion in the WGS reactor.
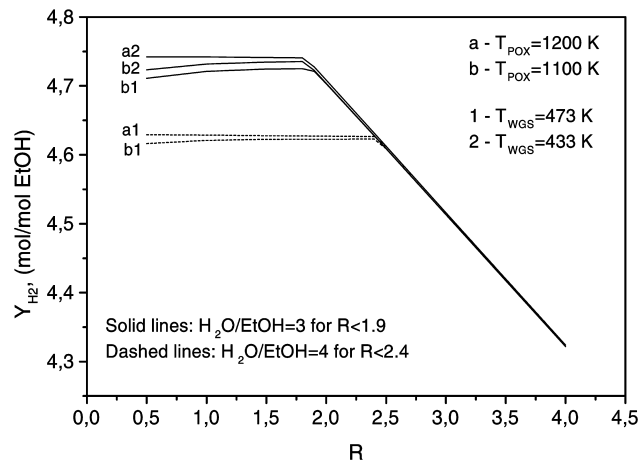- Keeping the effective $H_2O/EtOH$ ratio higher than the stoichiometric value of 3.0 results in lower hydrogen

yields (compare solid and dashed line curves). This happens because lower Φ values have to be employed at high effective $H_2O/EtOH$ ratios.
- Hydrogen yield increases with increase of POX temperature from 1100 to 1200 K and with decrease of WGS temperature from 473 to 433 K, when the R value of the feed is smaller than ~1.9. In this case, the effect of POX temperature becomes more significant at low R values.

Under the conditions pertaining to Figs. 8 and 9, methane concentration remains smaller than 100 ppm, as long as the POX temperature is 1200 K. When POX temperature is 1100 K, methane concentration lower than 100 ppm is obtained at R values larger than 2.5, while it becomes ~800 ppm at $R=0.5$.

Realisation of an autothermal ethanol processor requires heat exchange between the feed and the gas stream at various positions in the processor, so that heat available downstream the POX reactor can be transferred to preheat the feed. The final temperature of preheated feed has been calculated as a function of R, assuming complete heat transfer to the feed stream and it was found that (i) preheat temperatures increase with the exit temperature of POX reactor, (ii) preheat temperatures decrease with increase of R, because of larger enthalpy requirements in the case of feeds with high water content, (iii) under conditions of practical interest, preheat temperatures are higher than 700 K and can become as high as 1170 K in the case of feeds with low water content.

The achievable preheat temperature of the feed will depend, in practice, on the design and efficiency of heat exchangers incorporated in the processor. Another factor, which has to be taken into account, is that typical feeds to the POX reactor contain, generally, 10–20% ethanol and 10–15% oxygen. Flammable limits of ethanol mixtures in air are 3.3–19% v/v at 298 K and the autoignition temperature of ethanol is 696 K [11]. There exists, therefore, the possibility of development of explosive conditions, especially at high preheat temperatures. Setting of the maximum preheat temperature of the feed at 650 K, either as a safety precaution or as a practically attainable limit, has the following implications:

- Makes necessary the use of lower equivalence ratios in order to achieve adiabatic temperatures of the order of 1100–1200 K.
- Results in a heat surplus in the overall system.

The equivalence ratio, Φ, required to achieve autothermal operation of the POX reactor at adiabatic temperatures of 1100 and 1200 K is presented in Fig. 10A as a function of the R value of the feed assuming that the feed is preheated to 650 K. It can be observed that increase of the amount of water fed to the reactor necessitates the use of larger amounts of air to maintain adiabatic temperatures at the target range. Obviously, the amount of air increases (Φ decreases) with increase of the desired adiabatic
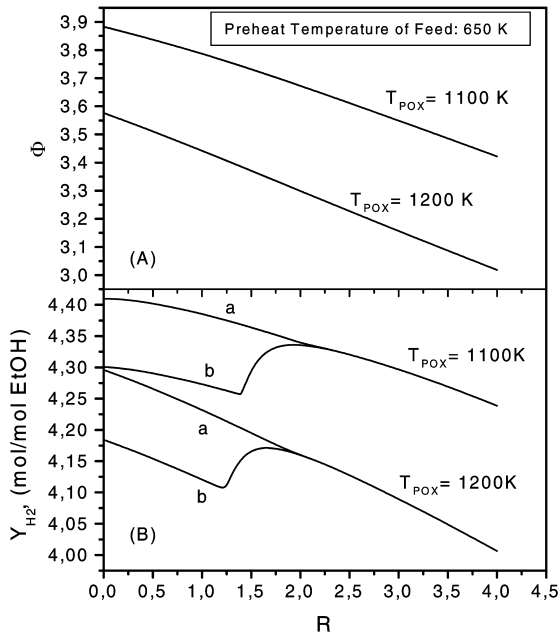

Fig. 9. Hydrogen yield obtained in the POX-ethanol processor as a function of R (corresponding Φ_o taken from Fig. 8).

Fig. 10. (A) Equivalence ratio, Φ, and (B) corresponding hydrogen yield, Y_{H2}, as a function of R for a preheat temperature of feed of 650 K. Curves a obtained assuming an effective $H_2O/EtOH$ ratio of 4.0, while curves b assuming an effective $H_2O/EtOH$ ratio of 3.0.

Fig. 11. Optimal POX temperature, T_{POX}, and corresponding hydrogen yield, Y_{H2}, as a function of R calculated assuming a maximum preheat temperature of feed of 650 K (T_{WGS}=473 K, S_{OX}=0.9).

temperature. This trend translates into some interesting effects on the thermodynamically-predicted hydrogen yield.

Hydrogen yield is shown in Fig. 10B as a function of R, using the corresponding value of Φ for each value of R from Fig. 10A. Curves a have been obtained assuming that, as long as the effective $H_2O/EtOH$ ratio becomes lower than 4.0, water is added to the WGS reactor to maintain this ratio at the value of 4.0. In an analogous fashion, curves b correspond to an effective ratio of 3.0. In the case of curve b, for example, the point at which addition of water to the WGS reactor starts, is at $R\sim1.4$. For curve a, the corresponding value of R is at ~2.1. Curves a and b coincide at high R values, because at such values the effective $H_2O/EtOH$ ratio is larger than 4.0. It can be observed that hydrogen yield increases generally with decrease of the R value of the feed. This is a direct consequence of the fact that smaller amounts of air are required and hence, a smaller fraction of ethanol is consumed at low values of R. The behavior of curves b is explained by taking into account the two counteracting factors influencing hydrogen yield as R decreases, namely: the decrease of the required equivalence ratio and the decrease of the effective $H_2O/EtOH$ ratio. The former factor tends to increase hydrogen yield, while the latter tends to decrease it. As the effective $H_2O/EtOH$ ratio approaches the stoichiometric value of 3.0, its effect prevails and hydrogen yield starts to decrease. Hydrogen yield starts to increase again at effective $H_2O/EtOH$ ratios lower than 3, because it has been assumed that extra water is added to the WGS reactor to maintain the $H_2O/EtOH$ ratio at the stoichiometric value. It can be also observed in Fig. 10B, that hydrogen yield is higher when the POX reactor operates at a lower
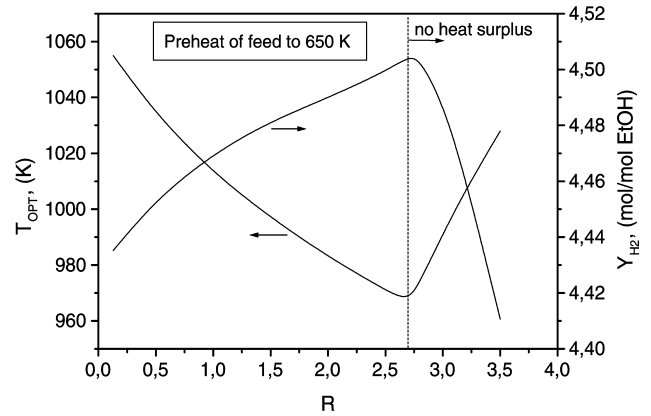
adiabatic temperature. This is because larger amounts of air are required for operation at higher temperatures and this leads to consumption of a larger fraction of ethanol.

It is evident that an optimal POX temperature exists for which hydrogen yield is maximized at a specific value of R. The optimal temperature is dependent on the R value of the feed and the optimization results are presented in Fig. 11, where the optimal exit temperature of the POX reactor and the corresponding maximized hydrogen yield are plotted as a function of the R value of the feed. These results have been obtained assuming that extra water is added to the WGS reactor to maintain an effective $H_2O/EtOH$ ratio equal to 4.0 for R values lower than ~2.4. Values of other parameters were: T_{WGS}=473 K and S_{OX}=0.9. It can be observed that T_{OPT} decreases and the corresponding hydrogen yield increases with increasing R up to the value of R=2.7, where a global optimum in hydrogen yield of 4.505 mol H_2/mol EtOH appears at T_{OPT}=967 K. At this point, the overall process is thermoneutral, that is the heat available in the system is exactly equal to the one required to preheat the feed to 650 K. At R values larger than 2.7, maximum hydrogen yields decrease and appear at higher optimal temperatures. In this region, the overall process remains thermoneutral, but the heat available is not sufficient to preheat the feed to 650 K, because of the high water content. Optimal hydrogen yields presented in Fig. 11 do not correspond to a condition where methane concentration is minimal. Actually, methane molar fractions are of the order of 1500–1800 ppm (0.15–0.18%). Therefore, imposing a constraint on the extent of preheat of the feed to the POX reactor results in optimal operating conditions, which do not coincide to those intuitively expected, i.e. high temperatures in order to minimize methane formation.

4. Discussion

Ethanol is an important candidate fuel for supplying hydrogen to fuel cells. It can be produced with existing

technologies from various types of biomass, available throughout the world. An interesting feature of ethanol is that it is produced as an aqueous solution containing ~8–10% v/v ethanol. As water is a co-reactant in the reforming process, ethanol does not have to be fully purified for use in ethanol processors. Based on the thermodynamic analysis of this work, employment of feeds with a $H_2O/EtOH$ ratio higher than 3.0 does not offer any significant advantage. A feed with a $H_2O/EtOH$ ratio equal to 3.0 corresponds to a ~52% v/v ethanol mixture. The production cost of such a mixture will be lower than that of purified ethanol (~95% v/v) due to reduced distillation costs. On the other hand, the cost of transportation of dilute ethanol to distribution points is higher and larger reservoir tanks are required in a vehicle for a specified autonomy range. A cost analysis would certainly be useful in identifying whether dilute ethanol mixtures present an economic advantage.

Partial oxidation ethanol processors are considered to possess certain advantages for vehicle applications, namely fast start-up and fast response to load changes [8]. On the other hand, ethanol processors incorporating a steam reformer may be more attractive in small scale (0.1–1 MW), stationary applications, because steam reformers provide a product stream with a higher concentration of hydrogen compared to POX reactors. In such applications with slowly varying loads, the processor may operate in a more or less steady state, while load-leveling may be provided by electrochemical devices of energy storage. Coupling of the SPFC to the reformer, as shown in Fig. 7, offers a high degree of flexibility in the operating conditions of the system between two limiting cases. The first limiting case corresponds to high temperature operation (~1200 K), which produces a stream with minimal methane concentration. Hydrogen is converted in the SPFC at a level of ~78% and the hydrogen-containing SPFC exhaust is supplied as a fuel to the reformer. Operation of the SPFC at hydrogen conversion levels lower than 100% may lead to higher efficiencies of electricity production. The other limiting case corresponds to reformer operation at moderate temperature (~950 K), which produces a stream with higher methane concentration. Hydrogen is converted in the SPFC to a level of 86–99% and the methane-rich SPFC exhaust is again supplied as a fuel to the reformer. The flexibility in reformer operation resulting from its coupling to the SPFC enables use of feeds with low $H_2O/EtOH$ ratio. High $H_2O/EtOH$ ratios are required to ensure minimal formation of methane, but they also result in reduced energy efficiency. However, higher methane levels are acceptable in the coupled system, because methane is combusted as a fuel in the reformer. The coking behavior of the reforming catalyst defines the lowest acceptable values for the $H_2O/EtOH$ ratio and the reformer temperature, which ensure stable, long-term operation of the catalyst. If a feed of low water content is used, residual CO concentration increases and the design and heat management of the SOX reactor will be more challenging. Overall, coupling

of the reformer-processor to the SPFC makes possible the attainment of the same effective hydrogen yield irrespective of reformer and WGS reactor temperature. This is important, because it provides flexibility in the design and operation of the processor.

From a thermodynamic point of view, the performance of ethanol processors incorporating a POX reactor depends on the amount of co-fed air required to ensure self-sustained operation of the system. As it was shown in Fig. 8, the necessary amount of air increases (or alternatively, the equivalence ratio, Φ, decreases) with increase of the R value due to heat requirements for evaporation of the feed. Because of that, hydrogen yield is maximized when the feed has low water content. Results obtained under the constraint of a maximum preheat temperature of the feed of 650 K are the most interesting from a practical point of view. As it was shown in Fig. 11, maximum hydrogen yields in the range of 4.43–4.50 mol/mol EtOH may be obtained using feeds with an R value of 0.1–2.5 and exit POX temperatures in the range of 970–1050 K. Similar calculations can be carried out assuming a different allowable preheat temperature of the feed. It is understandable that as the allowable preheat temperature increases above 650 K, the predicted hydrogen yield will tend towards the values presented in Fig. 9. The following factors have, of course, to be taken into account for the selection of the operating conditions of a POX reactor:

- Operation of the POX reactor at the rather low exit temperature of ~1000 K will require a larger reactor size to account for decreased catalytic reaction rates. This may not be desirable in vehicle applications.
- Catalyst fouling due to coking may be an issue at low POX temperatures, especially with feeds of low R value.
- Methane formation is considerable at such conditions. Although methane emissions are not currently regulated, this can be an environmental issue.

Based on the above, POX temperature should be chosen to be at least 1100 K and probably around 1200–1300 K. At such temperatures, equilibration of the reaction mixture will be fast, while methane and coke formation will be minimized. Mitchell et al. [8] have reported results on the performance of an ethanol POX reactor, which demonstrate the importance of other factors besides thermodynamics in the design of an ethanol processor. For example, formation of soot was a problem, encountered when high fuel equivalence ratios were used. Soot-free operation of the burner was possible for fuel equivalence ratios lower than 3.0–3.7, depending on peak reactor temperature. Preheat temperatures up to 633 K were employed and reactant preheat was found to enhance yield, in accordance to the findings of this work.

Comparison of the performance of ethanol processors incorporating either a steam reformer or a POX reactor shows that the maximum hydrogen yield is larger when a POX reactor is employed. Results presented in Figs. 7 and 9

show that the maximum yield in the POX reactor is ~4.74 mol/mol EtOH obtained for $R<1.9$, while maximum yield in the steam reformer is ~4.65 mol/mol EtOH obtained for $R=2.3$. This difference is explained by noting that the maximum in the steam reformer appears at higher R values, i.e. employing a feed which has larger enthalpy requirements for evaporation.

5. Conclusions

Thermodynamic analysis of ethanol processor systems has shown that the most important parameter which affects efficiency is the R value of the feed. Employment of feeds with R values higher than stoichiometry results in reduced efficiency in hydrogen production, because of increased enthalpy needs for water evaporation. Regarding ethanol processors incorporating a steam reformer, use of the SPFC exhaust gas as an external fuel in the reformer gives large flexibility in the window of operating conditions of the system. In the case of ethanol processors incorporating a POX reactor, optimal operating conditions can be found as a function of the preheat temperature of the feed. In addition to

thermodynamics, other issues such as catalyst kinetics or safety aspects appear to play an important role in determining the operating conditions of the POX reactor.

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