

Process simulation of hydrogen production by steam reforming of diluted bioethanol solutions: Effect of operating parameters on electrical and thermal cogeneration by using fuel cells.

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ABSTRACT

The possibility to exploit diluted bioethanol streams is discussed for hydrogen production by steam reforming. An integrated unit constituted by a steam reformer, a hydrogen purification section with high- and low-temperature water gas shift, a methanator reactor and a fuel cell were simulated to achieve residential size cogeneration of 5 kW electrical power + 5 kW thermal power as target output. Process simulation allowed to investigate the effect of the reformer temperature, of bioethanol concentration and of catalyst loading on the temperature and concentration profiles in the steam reformer. The net power output was also calculated on the basis of 27 different operating conditions. $P_{\text{electrical}}$ output ranging from 3.3 to 6.0 kW were obtained, whereas the total heat output $P_{\text{thermal, total}}$ ranged from 3.9 to 7.2 kW. The highest overall energy output corresponded to $P_{\text{electrical}} = 4.8$ kW, $P_{\text{Thermal, FC}} = 3.1$ kW, $P_{\text{heat recovery}} = 4.1$ kW, for a total 12 kW energy output. This was achieved by feeding a mixture with water/ethanol ratio = 11 (mol/mol), irrespectively of the catalyst mass, and setting the ref split temperature so to have an average temperature of 635°C in the ESR reactor.

Keywords: H₂ production; Bioethanol; Steam reforming; Process simulation; Process intensification; process optimisation; Combined heat and power cogeneration; Fuel processor; Fuel cells.

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1 - INTRODUCTION

The production of syngas from renewable sources is attracting attention as a mean to improve the sustainability of refinery processes such as the Fisher Tropsch synthesis, or as a way to obtain an interesting energy vector such as hydrogen after purification from CO. Among the different possibilities [1], ethanol steam reforming (ESR) is in a very advanced research stage. Insights on the mechanism were discussed by Benito et al. [2], including its specific application to fuel cell systems [3]. Different active phase were proposed, based on either noble [4] or transition metals (Ni and Co, predominantly) [5–11]. Also immobilised catalyst formulations were proposed, such as monoliths [12], as well as microreactors [13].

Different demonstrative projects have investigated the feasibility of electrical and thermal energy cogeneration based on fuel cells, fed with hydrogen or reformat produced from bioethanol, as described below.

Aicher et al. proposed a 250W fuel cell fed through an autothermal reformer intended for portable applications [14]. Other systems differ for the reformat purification from CO by means of preferential oxidation [15–17]. Different scale of production were considered, up to steam reforming and hydrogen separation units at industrial level (100,000 N m³/h) [18] or even in microreactors, adapted to micro-fuel cell devices [19,20]. Computational fluid dynamics simulation of ESR in catalytic wall microchannels has been also performed on a Co₃O₄-ZnO catalyst [21].

Membrane reactors were proposed attractively to improve H₂ purification from CO and CO₂ [22]. Besides the trivial advantage to eliminate a poison for the FC catalyst, this method is also interesting to increase H₂ concentration in the reformat with advantages on the volumetric efficiency of the fuel cell and on its voltage. This is a very challenging point due to the lacking knowledge and technology availability for fuel cells efficiently working with reformat with respect to a rather consolidate technology based on pure hydrogen feed.

On this basis, we tested an integrated fuel processor + fuel cell suitable for the cogeneration of 5 kW_{electrical} + 5 kW_{thermal} power as a target for residential size units [23,24]. The system was constituted by six reactors connected in series, *i.e.* prereformer, reformer, high- and low-temperature water gas shift (HT-WGS and LT-WGS) and two methanators, extensively described in the cited references.

This system was designed to produce up to 7 Nm³/h H₂ with residual 20 ppmv CO. Therefore, the reformat was suitable to feed a Proton Exchange Membrane Fuel Cell (PEM-FC) of the mentioned size. After preliminary testing, we tried to optimise the system identifying possibly redundant equipment (e.g. the pre-reformer and the second methanator) and improving heat integration of the system [25,26]. In addition, we investigated the possibility to use diluted bioethanol solutions to feed the system, as a cheaper feedstock with respect to anhydrous ethanol. This opened the possibility to use much less expensive separation devices for the purification of bioethanol, such as a flash drum, efficiently leading to 15-25 vol% bioethanol solutions [24]. Therefore, in the present work we made a parametric investigation considering the effect of temperature of the steam reforming reactor, of space velocity and of water/ethanol ratio on the fuel cell output, both in terms of electrical and thermal efficiency. The work was based on process simulation using the Aspen Plus[®] simulation tool.

2 – MODELS AND METHODS

The Aspen ONE Engineering Suite[®] (Aspentech Inc.) was used for process simulation, in particular the Aspen Plus[®] tool. The flowsheet, represented in Fig. 1, included the following units. All the simulations were carried out at atmospheric pressure.

- a) A *steam reformer*, modelled as a multitubular reactor, with the ESR catalyst inside the tubes and hot gases deriving from ethanol combustion in the shell side. Details on the kinetic model and relative parameters used for the simulation of this block are extensively described elsewhere [25,27,28]. Proper models were used to compute the pressure drop across the tubes and the global heat exchange coefficient U, as described in the cited references. The feed was constituted by ethanol + water in specified amounts (with a ratio varied during testing) at a temperature of ca. 280°C, reached after preheating in multiple heat exchangers for internal energy recovery. Different catalyst mass was overall located inside the reactor. Therefore catalyst mass variation with fixed flowrate allowed to explore the effect of the Gas Hourly Space Velocity (GHSV), keeping a minimum variation (except possibly for products distribution) for the downstream sections.

- b) A *burner* was modelled as external unit to compute the heating of the ESR reactor. In order to use diluted bioethanol solutions as feed for the reformer, the same feed could not be used as fuel, due to insufficient heating value. Therefore, part of the produced reformat was split (REF Split block in Fig. 1): after separation of excess water, a portion was sent to the fuel cell and a portion to the burner to sustain the ESR reactor. The burner was considered an adiabatic unit reaching equilibrium composition. Its hot products were fed in the shell side of the reformer co-currently with the feed leading to the desired reactor temperature. This was one of the variables tested, together with the GHSV and the water/ethanol ratio.
- c) The product of the ESR reactor was first purified from CO in a high temperature water gas shift reactor (HTWGS), followed by a low temperature one (LTWGS) and a methanator (METH). All these reactors were modelled as Gibbs reactors, operating isothermally at 350, 280 and 210°C, respectively. The heat available through cooling of the outlet of the HTWGS reactor, as well as the heat generated by the reactor was used to preheat the feed through proper heat exchangers placed in the flowsheet. The same holds for heat recovery from the LTWGS and METH blocks. Final cooling of the reformat stream to 80°C allowed conditioning the feed for the FC. Condensed water was then separated. This low enthalpy duty remained available as water at 65-80°C, which was summed to the FC cooling water (outflowing in the same temperature range) to increase the thermal output of the system and therefore the overall efficiency. This contribution was particularly relevant when using very diluted bioethanol feed.
- d) As for the FC, the problem was to properly model two different outputs, one in terms of electrical work (W), besides the heat developed by the reaction and withdrawn by circulating cooling water (Q). The block was modelled as a Gibbs reactor. After calculating the enthalpy variation of this unit (ΔH) we referred to literature data to define the electrical efficiency and the selection of 40% efficiency was based on ref. [29]. So, we calculated $W = 0.4 \cdot \Delta H$ and $Q = 0.6 \cdot \Delta H$. The electrical and thermal power outputs were calculated accordingly.

3 - RESULTS AND DISCUSSION

3.1 – Effect of operating parameters on plant performance

The profiles of temperature and mole fraction of selected species along the reactor are reported in Fig. 2. The heat supply from the burner was in the form of co-current flow of hot gases. This allowed to reach the desired temperature in the first 5 cm and a substantially flat profile in the remaining portion (total tube length 0.5 m). The concentration profiles of course depended on catalyst loading, which was varied between 1 and 5.5 kg. An increase of catalyst mass increased the final ethanol conversion. These values were set considering examples of fuel processors approximately of this size. Of course, increasing the catalyst mass, the size of the reformer increases. However, given the multitubular structure of the reformer, at this stage this point is accomplished by increasing the number of tubes constituting the reactor. We will deepen the specific reactor design at a later stage, provided that a specific plant configuration is optimised.

By keeping constant the catalyst mass at the highest value, and the water ethanol in the feed, the temperature was increased by increasing the reformat split ratio to the burner. This allowed to increase the temperature along the reactor, to fully convert ethanol well before reactor outlet and to achieve substantially the equilibrium gas composition (Fig. 3).

The isolation of the effect of the water/ethanol ratio was much more complex. Indeed, when increasing the amount of water in the feed we were forced to increase the reformat split ratio due to the need to vaporise more water. That is, increase the amount of reformat to the burner in order to supply additional heat to the reformer. This change increases the heat available to the reformer and this in turn can dramatically affect the temperature profile. Thus, the distinction between the water/ethanol ratio and the temperature effects was done through a careful selection of the reformat amount to be burnt in the burner. Indeed, the reformat split ratio was a very sensitive parameter, in turn heavily affecting the reformer temperature. The effect of the water ethanol feeding ratio on reactor profiles is summarised in Fig. 4, using as parameter the Ref Split setting and trying to maintain as constant as possible the reactor temperature. When using the lowest catalyst loading (to highlight the effect of cofeeding water on conversion), we observed markedly increasing ethanol and CO conversions with increasingly diluted feed. Besides the obvious advantage to use a lower

catalyst amount, the partial conversion of CO by thermodynamically favouring the WGS reaction was also beneficial. This latter aspect allows to simplify the purification section.

Through a sensitivity analysis on the system, we definitely found that many parameters were correlated. Furthermore, a slight variation of the reformat split ratio definitely induced very marked effects on the system performance.

When comparing the effect of the various variables on the power output of the system, we focused on the following results. The first interesting output was the net electrical power of the cell, obtained as difference between the FC output and the electrical consumption of the pumps and compressor. Then we considered the thermal output. This was calculated as the sum of the heat removed by cooling the fuel cell, plus the heat recovery accomplished by condensing the excess water contained in the feed after the methanator. In both cases heat is available in form of water flow at 65-80°C. These two last figures are considered separately and then summed in the total thermal power output datum.

All these data were not affected by catalyst loading in the steam reformer if full ethanol conversion is achieved. Indeed, provided that ethanol conversion is 100%, the hydrogen flowrate to the cell is fixed, so that the power output is given. Of course if the ethanol conversion is lower than 100% the net cell output decreases, but this is not a really significant case from the applicative point of view.

3.2 – Process intensification

The objective of this investigation was to explore the parametric dependence of the plant power output during cogeneration and the corresponding efficiency on important process variables, such as the water/ethanol ratio, GHSV (catalyst mass) and the temperature of the steam reformer. The final aim was to improve process efficiency, *i.e.* process intensification.

The increase of water/ethanol ratio promotes the ethanol conversion and the CO elimination through WGS. Furthermore, it helps preventing coke, whose accumulation was recently modelled in a heat integrated reformer [30]. Therefore, diluted bioethanol streams would be beneficial from the point of view of plant performance and catalyst durability. In addition, feeding diluted bioethanol would allow also to decrease the huge impact of ethanol distillation on its purification costs. A simple flash drum

would be sufficient to obtain 0.15-0.25 vol% bioethanol solutions in a quite simple and cost-saving way [28]. Nevertheless, we already demonstrated that feeding more and more diluted bioethanol streams to the reformer requires additional heating to vaporise the increased amount of water. Therefore, in our process layout the REF SPLIT block should be carefully set to an optimised value depending on the water/ethanol ratio in the feed. The higher the water content, the higher is the reformat fraction to be sent to the burner instead than to the fuel cell. This decreases the electrical power output and the electrical efficiency of the system. Nevertheless, in the water separation drum we recover a higher amount of hot water that contributes to an increase of the thermal power output. The overall efficiency was found to increase when increasing the water/ethanol ratio [27].

Thus, according to such a preliminary investigation there is room for choosing the desired electrical and thermal output and consequently the optimal bioethanol concentration to achieve it. However, this conclusion is complicated by the mutual connection of the governing parameters of the steam reformer: as already discussed the reformer temperature and the vaporisation of excess feeding water both rely on the setting of the REF SPLIT valve.

A further step towards process intensification would be the decrease of the reformer operating temperature. Ethanol is fully converted at relatively low temperature when active catalysts are adopted. In spite of this, methane can form through ethanol thermal decomposition and it is much harsher to convert, requiring higher temperature. The variation of reformer temperature is accomplished by changing the amount of reformat fed to the burner. Then, again, by properly setting the REF SPLIT valve, which affects also the vaporisation of water. Thus, a careful choice of the operating value of this block should be carried out depending on both desired reformer temperature and water/ethanol ratio.

Additionally, the GHSV was very broadly varied (keeping fixed the bioethanol flowrate and varying the catalyst mass between 1 and 5.5 kg). Of course, a decrease of the catalyst mass, provided that full ethanol conversion can be achieved is desirable to decrease the impact of catalyst cost on the system. The catalyst was selected based on the availability of reliable kinetic data in the literature and consisted of Ni/Al₂O₃ [26,27]. The GHSV value did not affect the final composition of the gas mixture fed to the fuel cell, because the gas purity was rectified through the series of Gibbs reactors,

working at equilibrium at their respective temperature, which constitute the purification section (HTWGS, LTWGS, METH). However, a variation of products distribution with catalyst mass (*i.e.* GHSV in the reformer), provided that full ethanol conversion was achieved in every case, modified the performance of the hydrogen purification section. Indeed, if more CO was fed to the HTWGS reactor, the reactor would convert a higher amount of CO to achieve the equilibrium composition and thus, being the reaction exothermal, a higher amount of heat would be transferred to the feed through the appropriate heat exchanger. So, a lower amount of heat would be needed through the burner, allowing a higher amount of reformat to be fed to the FC.

In turn, the CO concentration outflowing the reformer was mutually affected by temperature, GHSV and water/ethanol ratio, the three parameters confirming very correlated also from this point of view. In order to keep all this into account, we selected as summarising parameter the split ratio of the reformat to the burner as parameter (REF SPLIT). The plant optimisation was carried out with respect to this parameter.

Finally, a careful optimisation of the heat exchange network should be carried out in each configuration, as exemplified recently by Francesconi et al. [30].

3.3 – Process optimisation

The hydrogen flow from the different reactors and fed to the cell is summarised in Fig. 5, as a function of the REF SPLIT ratio. The latter value was optimised case by case. It can be observed that H₂ flow increased as expected passing from the SRE to the HTWGS to the LTWGS reactors. We would expect that the amount of H₂ fed to the FC decreased with increasing the water/ethanol ratio in the feed since it was necessary to vaporise a higher amount of water. However, as we said before, the reformat split valve setting also influenced the reactor temperature. Indeed, the temperature of the ERS reactor increased due to the higher amount of reformat to the burner from 630 to 773°C (Table 1). This increased the ethanol conversion with consequent increase of the H₂ flow rate, electrical power output and thermal output of the cell. In turn, the amount of heat recovered in the condenser decreased, so that the overall thermal power output remained substantially unaltered by this parameter (Table 1).

As a final result of 27 simulations by varying all the mentioned variables, we obtained $P_{\text{electrical}}$ output ranging from 3.3 to 6.0 kW, whereas the total heat output $P_{\text{thermal, total}}$ ranged from 3.9 to 7.2 kW.

The highest overall energy output corresponded to $P_{\text{electrical}} = 4.8$ kW, $P_{\text{Thermal, FC}} = 3.1$ kW, $P_{\text{heat recovery}} = 4.1$ kW, for a total 12 kW energy output. This was achieved by feeding a mixture with water/ethanol ratio = 11 (mol/mol), irrespectively of the catalyst mass, and setting the ref split temperature so to have an average temperature of 635°C in the ESR reactor.

4 - CONCLUSIONS

A parametric study has been carried out on an integrated unit for electrical and thermal power cogeneration though process simulation. The system was constituted by a steam reformer of bioethanol, followed by a high and a low temperature water gas shift reactor and a methanator. The reformat was used to feed a fuel cell with a target size $5 \text{ kW}_{\text{electrical}} + 5 \text{ kW}_{\text{thermal}}$. The effect of catalyst loading, reactor temperature and water/ethanol ratio in the feed was investigated. The amount of catalyst determined the ethanol conversion in the steam reformer. However the latter parameter could be effectively enhanced also by increasing the temperature or, much better, by increasing the water amount in the feed. This allowed the proposal of diluted, much less expensive, bioethanol solutions for this application.

The reformer temperature and of the water/ethanol ratio in the feed were tightly connected and ultimately governed the setting of the reformat splitting ratio, *i.e.* the amount of reformat used in the burner to sustain the steam reformer. This parameter was the most sensitive for the regulation of the plant. The overall power output of the cogeneration system was enhanced by using diluted bioethanol.

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TABLES

Table 1: Simulation results with constant catalyst mass = 5.5 kg, corresponding to GHSV = 1.4 h⁻¹ (w/w). Water/ethanol = 5 mol/mol. T = average ESR temperature; P = power.

Ref. Split	T ESR (°C)	Ethanol conversion (%)	P _{electrical} (kW)	P _{thermal} (kW) FC	P _{thermal} (kW) Heat recovery	P _{thermal} (kW) total
0.258	630	93.9	5.4	3.0	0.89	3.9
0.276	687	100	6.5	3.7	0.42	4.1
0.300	773	100	6.6	3.8	0.26	4.0

FIGURES

Fig. 1: Process flowsheet.

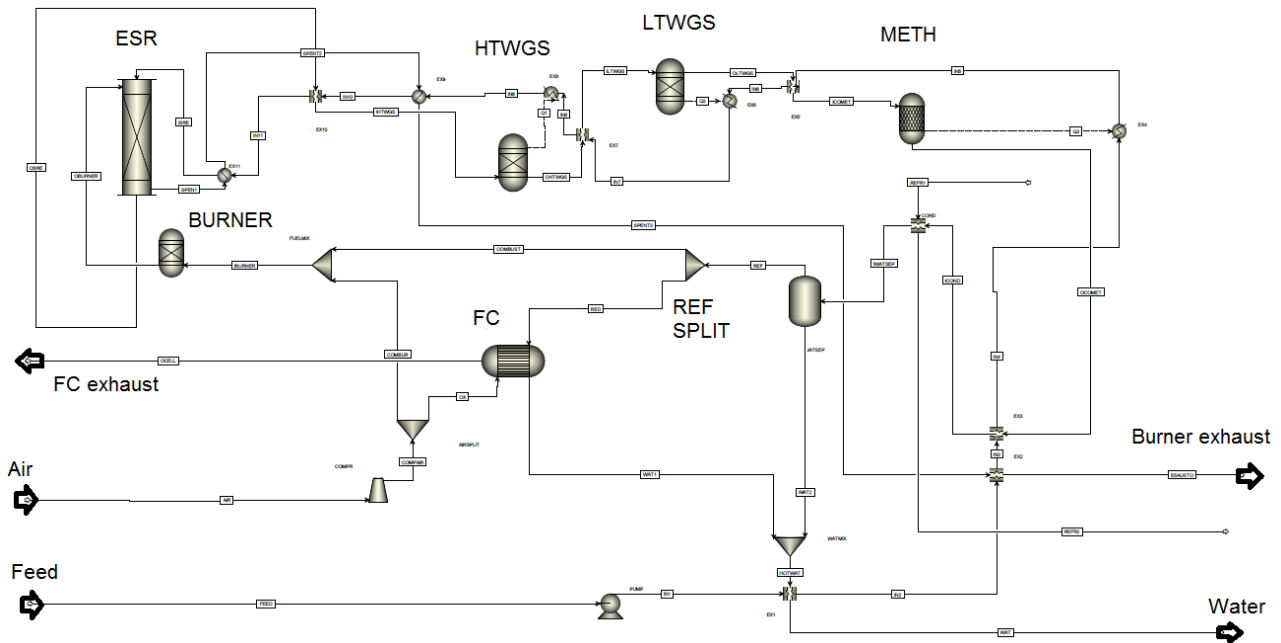
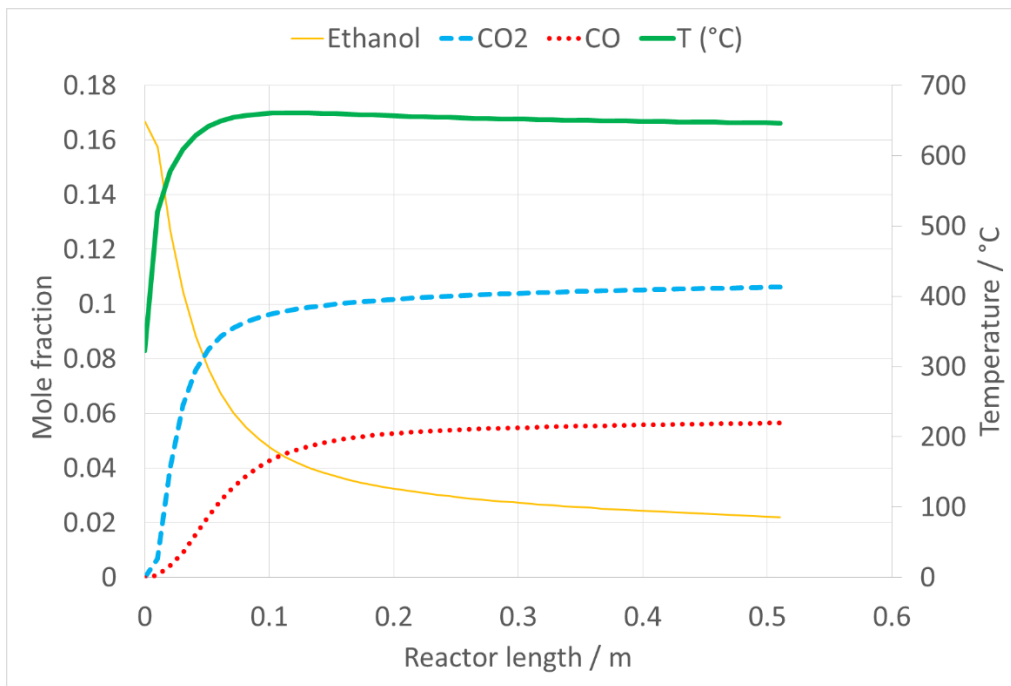
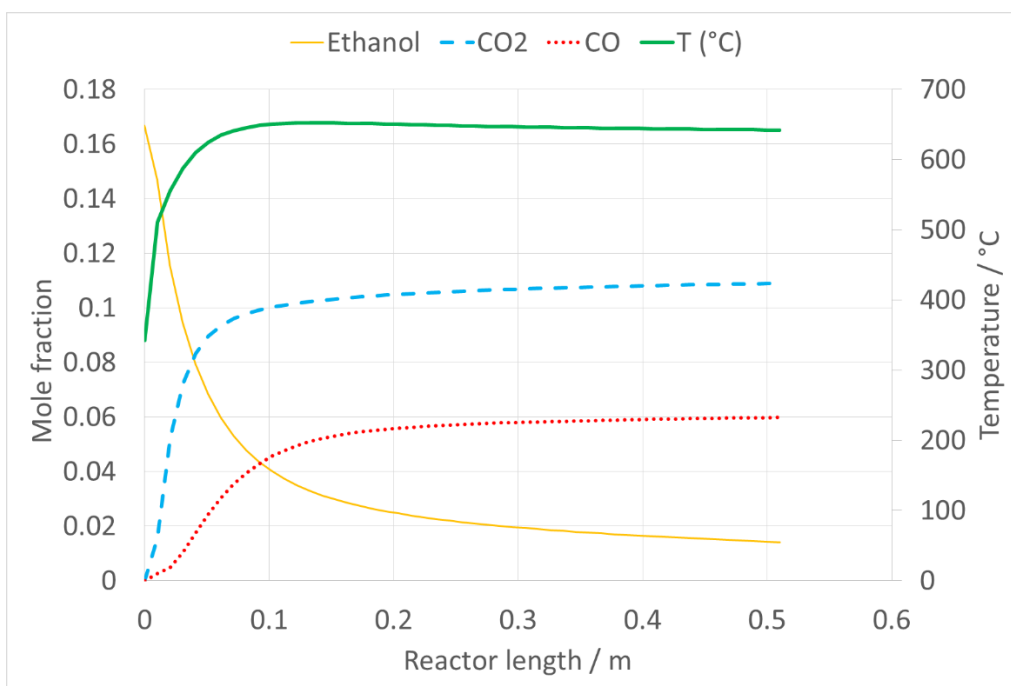


Fig. 2: Temperature and composition profiles in the ESR reactor depending on the operating conditions. a) Water/ethanol = 5 mol/mol, catalyst mass = 1 kg, Ref Split = 0.258; b) Water/ethanol = 5 mol/mol, catalyst mass = 3 kg, Ref Split = 0.258; c) Water/ethanol = 5 mol/mol, catalyst mass = 5.5 kg, Ref Split = 0.258.

a)



b)



c)

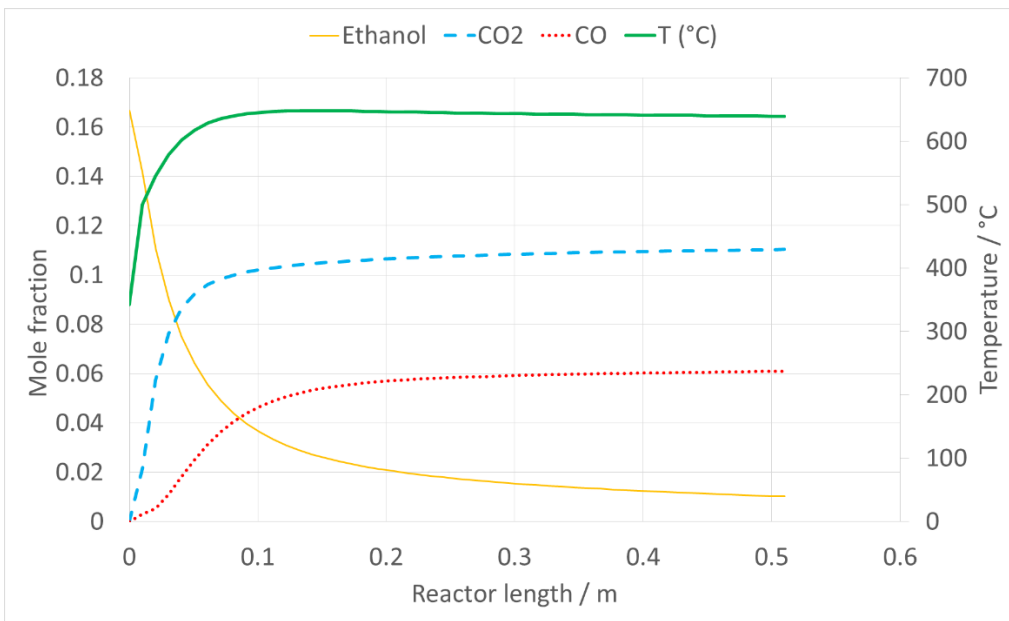
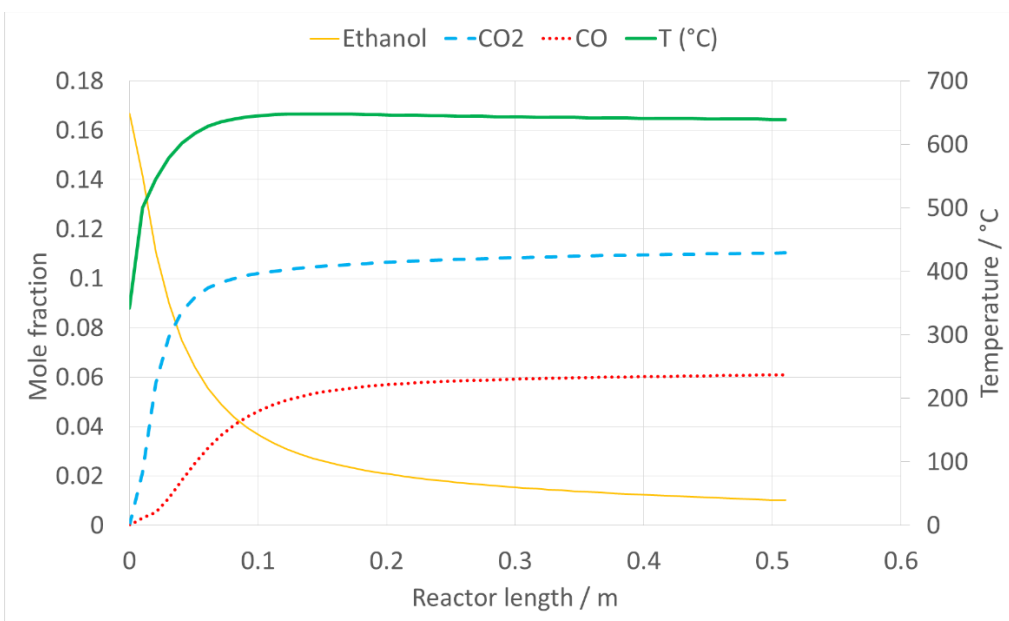
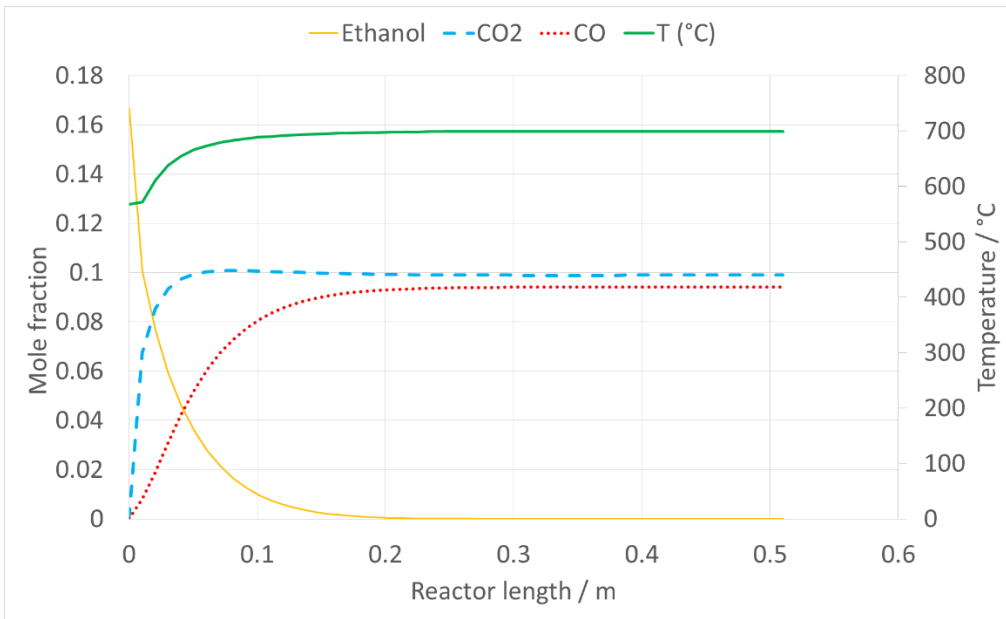


Fig. 3: Temperature and composition profiles in the ESR reactor depending on the operating conditions. a) Water/ethanol = 5 mol/mol, catalyst mass = 5.5 kg, Ref Split = 0.258; b) Water/ethanol = 5 mol/mol, catalyst mass = 5.5 kg, Ref Split = 0.276; c) Water/ethanol = 5 mol/mol, catalyst mass = 5.5 kg, Ref Split = 0.300.

a)



b)



c)

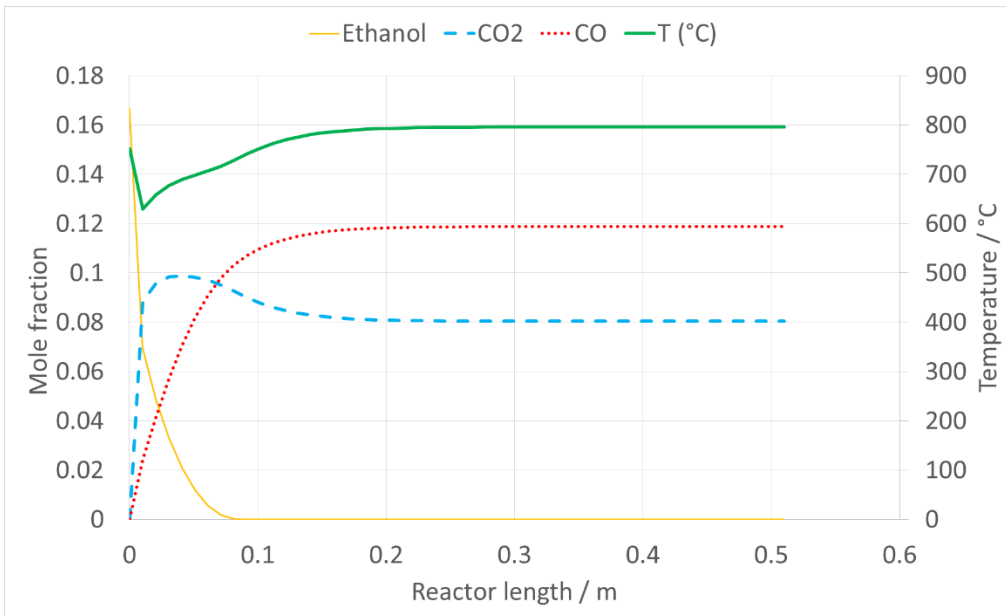
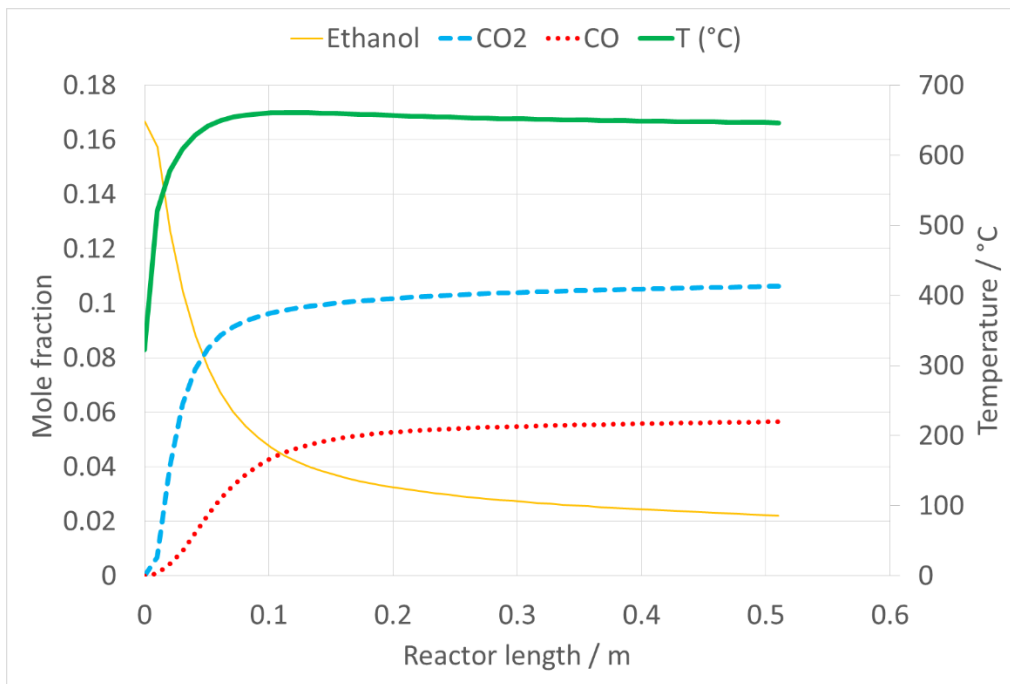
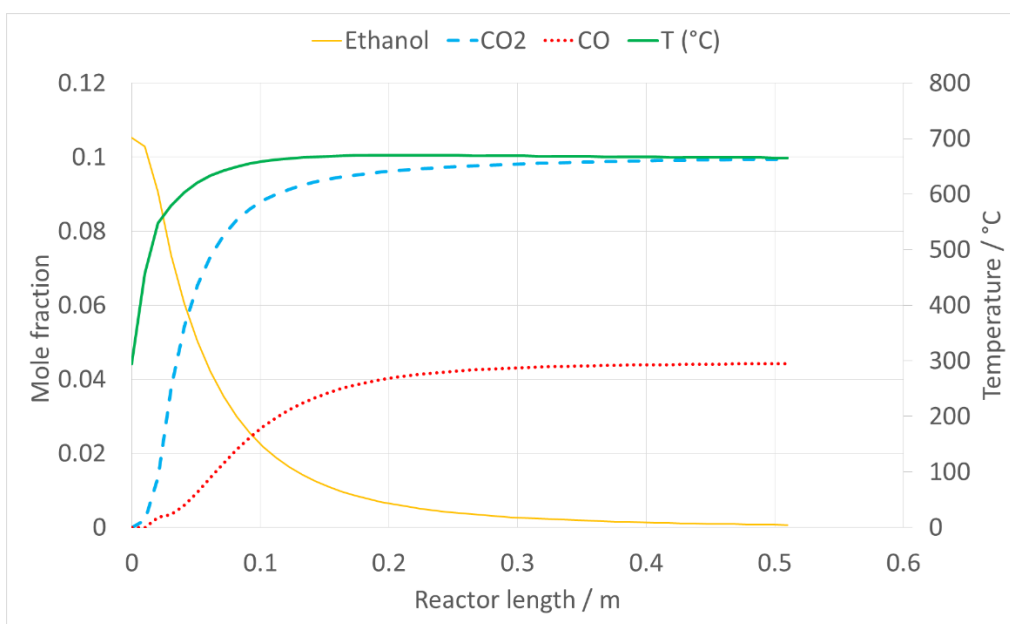


Fig.4: Temperature and composition profiles in the ESR reactor depending on the operating conditions. a) Water/ethanol = 5 mol/mol, catalyst mass = 1 kg, Ref Split = 0.258; b) Water/ethanol = 8.5 mol/mol, catalyst mass = 1 kg, Ref Split = 0.39; c) Water/ethanol = 11 mol/mol, catalyst mass = 1 kg, Ref Split = 0.463.

a)



b)



c)

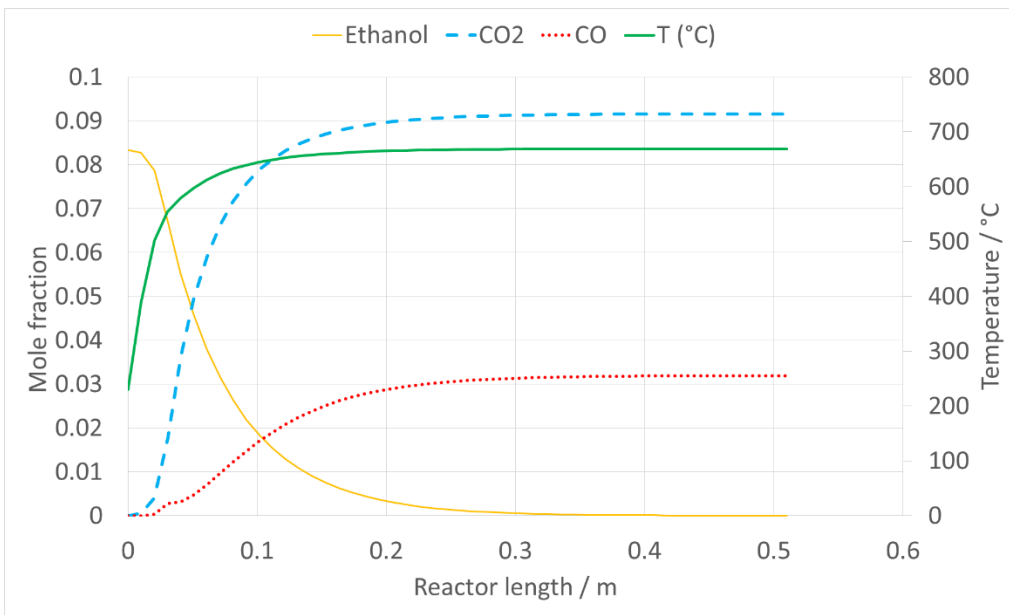
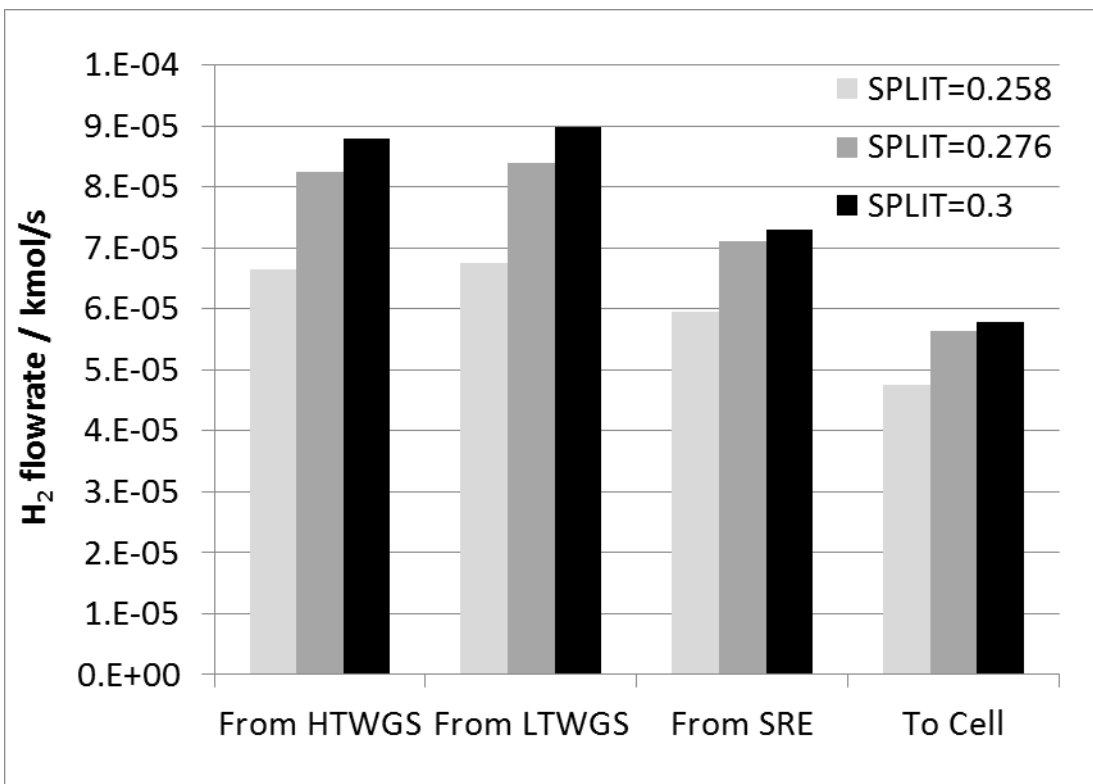
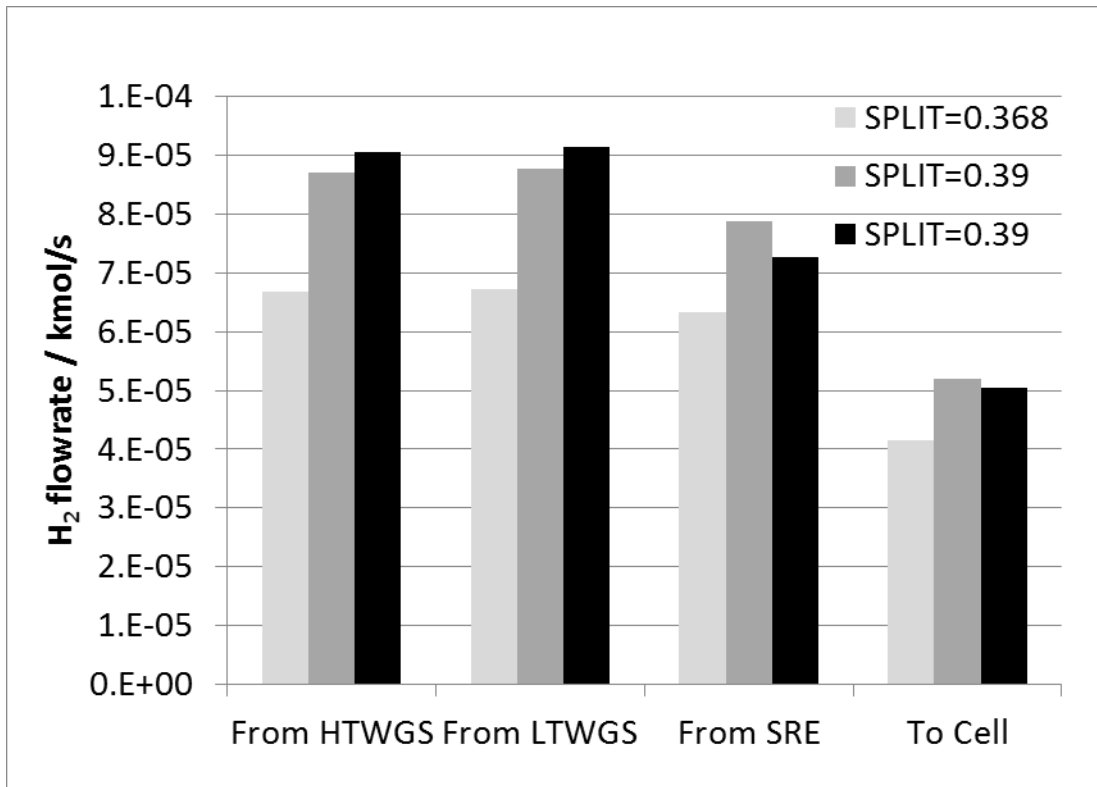


Fig. 5: H₂ flow (kmol/s) from the different reactors as a function of the split fraction of H₂ sent to the burner. Catalyst mass fixed at 5.5 kg, variable water/ethanol ratio: a) 5 mol/mol; b) 8.5 mol/mol; c) 11 mol/mol.

a)



b)



c)

