



Addressing fuel recycling in solid oxide fuel cell systems fed by alternative fuels

Rokni, Masoud

Published in:
Energy

Link to article, DOI:
[10.1016/j.energy.2017.03.082](https://doi.org/10.1016/j.energy.2017.03.082)

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Rokni, M. (2017). Addressing fuel recycling in solid oxide fuel cell systems fed by alternative fuels. *Energy*, 137, 1013-1025. <https://doi.org/10.1016/j.energy.2017.03.082>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Addressing Fuel Recycling in Solid Oxide Fuel Cell Systems Fed by Alternative Fuels

M. Rokni

Department of Mechanical Engineering

Institution of Thermal Energy Systems, Copenhagen, Denmark

e-mail: MR@mek.dtu.dk

ABSTRACT

An innovative study on anode recirculation in solid oxide fuel cell systems with alternative fuels is carried out and investigated. Alternative fuels under study are ammonia, pure hydrogen, methanol, ethanol, DME and biogas from biomass gasification. It is shown that the amount of anode off-fuel recirculation depends strongly on type of the fuel used in the system. Anode recycling combined with fuel cell utilization factors have an important impact on plant efficiency, which will be analysed here. The current study may provide an in-depth understanding of reasons for using anode off-fuel recycling and its effect on plant efficiency. For example, it is founded that anode recirculation is not needed when the plant is fed by ammonia. Further, it is founded that when the system is fed by pure hydrogen then anode recirculation should be about 20% of the off-fuel if fuel cell utilization factor is 80%. Furthermore, it is founded that for the case with methanol, ethanol and DME then at high utilization factors, low anode recirculation is recommended while at low utilization factors, high anode recirculation is recommended. If the plant is fed by biogas from biomass gasification then for each utilization factor, there exist an optimum anode recirculation at which plant efficiency maximizes.

Keywords

SOFC, fuel cell, alternative fuels, anode recirculation, methanol, ethanol, ammonia, biogas.

1. INTRODUCTION

With an ever increasing demand for more efficient power production and distribution, some main research and development for the electricity production is identified as efficiency enhancements and pollutant reduction, especially carbon dioxide among others. Alternative fuels have also been recognized as potential element in decreasing emissions locally such final at end users.

Solid Oxide Fuel Cells (SOFCs) are recognized as one of the most promising types of fuel cells, particularly in terms of energy production. Besides pure hydrogen they can be fed variety of fuels such as Natural Gas (NG), ethanol, Di Methyl Ether (DME), methanol and syngas from gasification of biomass or municipal waste. They are expected to produce clean electrical energy at high conversion rates with low noise and low pollutant emissions [1]. They can tolerate sulphur compounds at concentrations higher than those tolerated by other types of fuel cells. Additionally, unlike in most fuel cells, carbon monoxide can be used as a fuel in SOFCs. Due to the above-mentioned advantages, SOFCs are considered to be a strong candidate for either hybrid systems or integration into currently deployed technologies. Therefore, SOFC plants have been the subject of many studies since the beginning of 90s. For

44 example [2] showed that electrical efficacy of a hybrid plant consisting SOFC, gas turbine
45 and steam turbine may reach about 70% which is encouraging to further investigate on such
46 plants.

47 Numerous studies on SOFC based systems have been considered in the literature among
48 them SOFC–gas turbines hybrid systems have extensively studied, for example the study of
49 [3] shows that plant efficiency reaches about 60% at full load while its part-load (until 50%)
50 efficiencies are also above 50%. In the study of [4], the net efficiency of a SOFC plant was
51 calculated to be about 28–29 % when it is fed by biogas from biomass gasification. A study
52 on biogas (assumed to be available in the gas grid without providing the source) fuelled
53 SOFC micro-CHP in [5] showed that an overall CHP efficiency of about 80% is achievable
54 for single-family detached dwellings. In another study carried out in [6], it was concluded that
55 a SOFC plant fed by biogas from organic wastes may reaches electrical efficiencies of about
56 34% at approximately 55% utilization factor. Biogas from wastewater treatment facilities was
57 used in the study of [7] to estimate electrical efficiency of a SOFC plant. The study showed
58 that plant efficiency would be about 41% if the utilization factor was selected to be 65%. A
59 study on syngas from municipal waste gasification carried out in [8] showed that plant
60 efficiency of such integrated gasification-SOFC plant approaches about 43% with utilization
61 factor of about 80%. These are some examples of many that have been explored by
62 researchers for utilization of waste to energy in sustainable modern societies.

63 SOFC fed by different fuels have also studied by many researchers. In the study of [9], the
64 net efficiency of a 2 kW_{el} SOFC plant was calculated to be about 55% when the fuel was
65 methanol. If DME was used as fuel, then the study of [10] showed that the plant efficiency
66 will be about 50%. The study of [11] showed that plant net efficiency of about 53% is
67 achievable when the fuel of SOFC was bioethanol. In [12] an ammonia fed SOFC integrating
68 with gas turbine was studied and the results shown efficiencies close to 56%. Comparison
69 performance of SOFC plants fed by alternative fuels have also been studied in [13] in which a
70 single general modelling approach was used for the investigation. This single modelling
71 approach with the same simulating code was also evaluated to ensure accuracy of the
72 modelling and methodology used in the present study as documented in [13].

73 Despite extensive studies on SOFC based power plants, investigations on anode recycle
74 SOFC systems fed by NG is comparably limited. Anode off-fuel recycling (anode gas
75 recycle) is essential in SOFC systems fed by NG in order to provide steam for the steam
76 reforming reactions in a pre-reformer prior to the SOFC cells. Exclusively all studies on
77 anode recycling are about carbon formation and carbon deposition in the pre-reformer of a
78 natural gas (NG) feed SOFC stack. Most of these studies are on stack level and do not on
79 investigate the effect of anode recycling on system level and plant performances. For
80 example, the experimental studies of [14] showed that the limit for O/C ratio (oxygen-carbon
81 ratio) to avoid carbon formation depends on the purity of gas. Their study showed that the
82 limit of O/C ratio for carbon formation for nickel catalyst was between 0.9 and 1.0 for
83 Russian natural gas and between 1.0 and 1.25 for Danish natural gas. If precious metal
84 catalyst used, then the limit was between 0.5–0.75 irrespectively of natural gas composition.
85 The effects of SOFC anode recycle on catalytic diesel reforming and carbon formation was
86 also studied in [15] experimentally. This study showed that anode recycle is more effective
87 than reformer recycle when it comes to carbon formation in the reformer (off-fuel from
88 SOFC, not reformat gas out of reformer). Steam recycling for internal methane (and/or
89 natural gas) reforming in SOFCs to analyse the carbon deposition using computational fluid
90 dynamic was used in [16]. This study showed also that anode recycling is need to decreases
91 carbon formation when fuel is methane or natural gas. Electric power generation of 380W
92 SOFC stack fed by methane with and without and anode recycle was demonstrated in [17].
93 Their study showed that anode recycle increases stack efficiency by about 10% when anode

94 recycle is used. It was reported in [18] that cell voltage could be improved by anode off-fuel
95 recycle in solid oxide fuel cell fed by pure methane. The study was on a cell level (not system
96 level) with distinguished conclusion. The study of [19] showed that anode recycling enables
97 the operation of a SOFC stack at low fuel utilizations without sacrificing the electrical
98 efficiency of the stack. The maximum electrical efficiency of 57% was reached at 60% fuel
99 utilization when the fraction of recycled fuel was 66%. If no anode gas recycling was applied
100 then the maximum electrical efficiency was about 53% with about 77.5 % fuel utilization.

101 Despite many studies on anode recycling and carbon formation, studies on anode off-fuel
102 recycling on plant efficiency are very limited and exclusively all are about natural gas (and/or
103 methane) fed fuel. No study on of-fuel recycling with alternative fuels is found in the open
104 literature, which makes the basis of the current study. The effect of anode recycling on plant
105 efficiency using different types of fuels is investigated here which is completely novel and has
106 not been studies elsewhere. A single study with similar conditions and prerequisites will thus
107 reveal the importance of off-fuel recirculation on plant performance when the fuel is an
108 alternative fuel. The findings in the current study may help SOFC system developer on
109 boosting their plant efficiencies when alternative fuels are used. All foundlings are new and
110 have not been reported elsewhere.

111 2. PLANT LAYOUT AND MODELLING METHODOLOGY

112 Figure 1 displays a typical SOFC plant with natural gas and/or methane as fuel. A similar
113 layout can also be seen in e.g. [1], [5] and [20]. Air is compressed and preheated in a cathode
114 preheater (CP) before entering the cathode side of the fuel cell. Natural gas (and/or pure
115 methane) is firstly reformed and then preheated in an anode preheater (AP) before entering the
116 anode side of the fuel cell. Depending on the utilization factor, a portion of the feed fuel will
117 leave the anode side without reacting inside the fuel cells. The remaining fuel (off-fuel) and air
118 (off-air) is then sent to a burner for further combustion. The off-gases after the burner is used to
119 preheat both incoming air and fuel into the fuel cell. In order to provide steam for the reformer
120 some of the off-fuel is recycled which calls for anode recirculation (or off-fuel recirculation).
121 Even though the main purpose of the off-fuel recirculation is to provide steam for the steam
122 reforming but it will also improve stack efficiency since more fuel is reacted inside the cells and
123 therefore more power will be generated (see e.g. [19]). On the other hand, since no external
124 steam is provided to the steam reformer (during normal operation) then it will be important that
125 steam-carbon-ratio (S/C-ratio) is approximately above 1.8 to avoid carbon deposition, which
126 has a significant effect on the reformer performance and lifetime, see e.g. [5]. However, most of
127 the researchers assumes the value of 2 to be on the safe side, such as in [5], [6], [21] and [22].
128 Note that it is generally believed that carbon deposition can be determined by S/C ratio but the
129 experimental study of e.g. [23] shows that not only S/C but also the extent of equilibrium in the
130 gas mixtures should be taken into account to control the carbon deposition (O/C ratio).
131 However, as shown in the study of [24] carbon deposition is not an issue in SOFC fed by wood
132 gas from biomass gasification.

133
134
135 *Figure 1. General fuel cell plant with anode off-fuel recirculation. CP: Cathode Preheater, AP:*
136 *Anode Preheater.*

137
138 However, when changing the fuel into alternative fuels such as ammonia, pure hydrogen,
139 methanol and ethanol then there is no problem on limiting the S/C (or O/C) ratio if a pre-
140 reformer is used (see e.g. the C–H–O ternary diagram in [5]). If biogas (from biomass
141 gasification) is used, then there will be enough steam in the gas and such problem does neither
142 exist, as discussed in [24]. For such alternative fuels the question will be if off-fuel recirculation

143 is needed or not and if it is needed then how it will effect on plant performance. This is the basis
144 of the present study, which is entirely new and not been studied elsewhere.

145 In this study, the thermodynamic results are obtained using the Dynamic Network Analysis
146 (DNA) simulation tool (see, e.g., [25]), established at DTU since 1983. The program has
147 continuously been developed to be generally applicable for different energy systems. It
148 includes a component library, thermodynamic state models for fluids and standard numerical
149 solvers for differential and algebraic equation systems. The component library contents
150 models for heat exchangers, burners, turbo machinery, decanters, energy storages, valves and
151 controllers, among many others. Figure 2 illustrates the calculation procedure used in the
152 program.

153
154 *Figure 2. Calculation procedure.*

155
156 DNA is a component-based simulation tool, meaning that the model is formulated by
157 connecting components together with nodes and adding operating conditions to create a
158 system. The equations include mass and energy conservation for all components and nodes
159 together with the relations for the thermodynamic properties of the fluids in the system. The
160 total mass balance and energy balance for the entire system is also included to account for
161 heat loss and heat exchange between different components. The program is written in
162 FORTRAN, and users can implement additional components and thermodynamic state
163 models to the libraries as well.

164 The main assumption within the calculations are

- 165 - No heat losses to the surroundings
- 166 - No resistance in the electrodes
- 167 - Constant utilization factor within all cells
- 168 - Constant current density for all cells
- 169 - Each cell is treated as a single point (eat and fluid flow is not calculated).

170 In reality, there exists some heat losses to the surrounding even though the stacks are well
171 insulated. However, heat losses after insulation are very small and therefore negligible, although
172 they can be accounted in the simulation. Resistance through the electrodes depends on the
173 selection of material and one can select the material for the electrodes so that their resistance is
174 very small and minor. Utilization may slightly varies from cell to cell, sometimes higher and
175 sometimes lower, and therefore the assumption of constant utilization factor may be eligible.
176 The same is true for the current density. The main limit of the modelling here is that the flow
177 dynamic in the cells is not accounted, since the focus is on the plant level with all components.
178 However, such technique is widely applicable/used for programs dealing with system level
179 rather than component level.

180 **3. MODELLING**

181 **3.1 Modelling of SOFC**

182 The SOFC model proposed in a previous study [26],[27] is adopted in this investigation and
183 has been validated with experimental data on planar SOFCs. In the development of such
184 models, one must distinguish between electrochemical modelling (to obtain cell voltage and cell
185 efficiency), calculation of cell and stack power (via number of stacks and their connections) and
186 finally the species compositions at the cell outlet. Each of these is explained below in details.

187 **3.1.1 Electrochemical Modelling**

188 First, one needs to calculate the cell voltage of SOFC, which can theoretically be expressed
189 by Nernst equation. However, in reality there exist losses, which decreases the theoretical cell

190 voltage. These losses are mainly activation loss (cell voltage decreases as soon as current starts
 191 drawn from the cell), ohmic loss (cell voltage decreases when current is increased; linear
 192 dependency) and concentration loss (the current is so high that further increase in current causes
 193 drop in cell voltage significantly). These losses must be calculated in detail, which are
 194 expressed below. The SOFC model proposed in a previous study [26],[27] is adopted in this
 195 investigation. For electrochemical modelling, the operational voltage (E_{cell}) is represented by
 196 equation 1.

$$E_{cell} = E_{Nernst} - \Delta E_{act} - \Delta E_{ohm} - \Delta E_{conc} \quad (1)$$

197
 198
 199 where E_{Nernst} , ΔE_{act} , ΔE_{ohm} , and ΔE_{conc} are the Nernst ideal reversible voltage, activation
 200 polarization, ohmic polarization, and concentration polarization, respectively. Assuming that
 201 only H_2 is electrochemically converted the Nernst equation can be written as shown in
 202 equations 2 and 3.
 203

$$E_{Nernst} = \frac{-\Delta g_f^0}{n_e F} + \frac{RT}{n_e F} \ln \left(\frac{p_{H_2, tot} \sqrt{p_{O_2}}}{p_{H_2O}} \right) \quad (2)$$

$$p_{H_2, tot} = p_{H_2} + p_{CO} + 4p_{CH_4} \quad (3)$$

204
 205
 206 where Δg_f^0 is the Gibbs free energy (for H_2 reaction) at standard temperature and pressure. The
 207 water-gas shift reaction is very fast and therefore the assumption that H_2 is the only species to
 208 be electrochemically converted is justified [28], [29]. In the above equations, p_{H_2} and p_{H_2O} are
 209 the partial pressures for H_2 and H_2O , respectively. It should be noted that the steam reforming
 210 and the associated water gas shift reactions are efficiently modelled in the calculations.
 211

212 The activation polarization can be evaluated using the Butler–Volmer equation [30]. The
 213 activation polarization term is isolated from the other polarization terms, to determine the
 214 charge transfer coefficients and the exchange current density from the experiments by the curve
 215 fitting technique. The activation polarization is expressed by equation 4.

$$\Delta E_{act} = \frac{RT}{(0.001698T - 1.254)F} \sinh^{-1} \left[\frac{i_d}{2(13.087T - 1.096 \times 10^4)} \right], \quad (4)$$

216
 217 where R , T , F , and i_d are the universal gas constant, operating temperature, Faraday constant,
 218 and current density, respectively.
 219

220 The ohmic polarization [31] depends on the electrical conductivity of the electrodes as well
 221 as the ionic conductivity of the electrolyte. This is also validated with experimental data for a
 222 cell with a specified anode thickness (t_{an}), electrolyte thickness (t_{el}), and cathode thickness (t_{ca}).
 223 The ohmic polarization is given as follows.

$$\Delta E_{ohm} = \left(\frac{t_{an}}{\sigma_{an}} + \frac{t_{el}}{\sigma_{el}} + \frac{t_{ca}}{\sigma_{ca}} \right) i_d, \quad (5)$$

224
 225 where $t_{an} = 600 \mu m$, $t_{el} = 50 \mu m$, and $t_{ca} = 10 \mu m$. σ_{an} , σ_{el} , and σ_{ca} are the conductivities of the
 226 anode, electrolyte, and cathode, respectively, and may be expressed as follows.
 227

$$\sigma_{an} = 10^5, \quad \sigma_{ca} = \frac{5.760 \times 10^7}{T} \exp \left(-\frac{0.117}{8.617 \times 10^{-5} T} \right) \quad (6)$$

$$\sigma_{el} = 8.588 \times 10^{-8} T^3 - 1.101 \times 10^{-4} T^2 + 0.04679 T - 6.54 \quad (7)$$

230

231 The concentration polarization is dominant at high current densities for anode-supported
 232 SOFCs, wherein insufficient amounts of reactants are transported to the electrodes and
 233 consequently, the voltage is reduced significantly. As in the previous case, the concentration
 234 polarization was validated with experimental data by introducing the anode limiting current,
 235 [32], in which the anode porosity and tortuosity were considered among other parameters. The
 236 concentration polarization is modelled as shown in equation 8.

$$237 \quad \Delta E_{conc} = B \left(\ln \left(1 + \frac{P_{H_2} i_d}{P_{H_2O} i_{as}} \right) - \ln \left(1 - \frac{i_d}{i_{as}} \right) \right), \quad (8)$$

238 where B is the diffusion coefficient, which is determined using a calibration technique as
 239

$$240 \quad B = \left(0.008039 X_{H_2}^{-1} - 0.007272 \right) \frac{T}{T_{ref}} \quad (9)$$

241 T_{ref} is the reference temperature (1023 K), and the anode limiting current is defined as
 242

$$243 \quad i_{as} = \frac{2F p_{H_2} D_{bin} V_{an}}{RT t_{an} \tau_{an}}, \quad (10)$$

244 where V_{an} and τ_{an} are the porosity (30%) and tortuosity (2.5 μm) of the anode, respectively.
 245 The binary diffusion coefficient is given by
 246

$$247 \quad D_{bin} = \left(-4.107 \times 10^{-5} X_{H_2} + 8.704 \times 10^{-5} \right) \left(\frac{T}{T_{ref}} \right)^{1.75} \frac{P_{ref}}{P}, \quad (11)$$

248 which is also calibrated against the experimental data. p_{ref} is the reference pressure (1.013
 249 bar), and X_{H_2} is the mass reaction rate of H_2 . Lastly, the current density i_d is directly
 250 proportional to the amount of reacting H_2 according to Faraday's law (equation 12).
 251

$$252 \quad i_d = \frac{\dot{n}_{H_2} 2F}{A}, \quad (12)$$

253 where \dot{n}_{H_2} is the molar reaction rate of H_2 . The area A is a physical property of the cell and
 254 was 144 cm^2 in this study.

255 The SOFC model in this study aims at representing the performance of the second generation
 256 SOFC stacks developed by Topsoe Fuel Cell A/S (TOFC) and the Fuel Cells and Solid State
 257 Chemistry Division at Risø – DTU (Technical University of Denmark). This SOFC type is
 258 anode supported, with a Ni/YSZ¹ anode, a YSZ electrolyte, and an LSM²/YSZ cathode [33].

259 3.1.2 Stack Power and Related Calculations

260 Once the cell voltage is calculated then the stack power the power production from the
 261 SOFCs (P_{SOFC}) can be decided using the equation (13). As shown, it depends on the amount of
 262 chemical energy fed to the anode, the reversible efficiency (η_{rev}), the voltage efficiency (η_v),
 263 and the fuel utilization factor (U_F). It is defined in the mathematical form as.

$$265 \quad P_{SOFC} = \left(\text{LHV}_{H_2} \dot{n}_{H_2, in} + \text{LHV}_{CO} \dot{n}_{CO, in} + \text{LHV}_{CH_4} \dot{n}_{CH_4, in} \right) \eta_{rev} \eta_v U_F \quad (13)$$

266 where U_F is a constant and η_v is defined as follows.
 267

¹ Yttria-stabilized zirconia.

² Lanthanum strontium manganite.

$$\eta_v = \frac{\Delta E_{\text{cell}}}{E_{\text{Nernst}}}. \quad (14)$$

Note that the utilization factor in SOFCs can be defined as the amount of O₂ consumed, because O₂ ions are the carriers. The reversible efficiency is the maximum possible efficiency, which is defined as the relationship between the maximum electrical energy available (change in Gibbs free energy) and the LHV (lower heating value) of the fuels, as shown below [34].

$$\eta_{\text{rev}} = \frac{(\Delta \bar{g}_f)_{\text{fuel}}}{\text{LHV}_{\text{fuel}}} \quad (15)$$

$$\begin{aligned} (\Delta \bar{g}_f)_{\text{fuel}} = & \left[(\bar{g}_f)_{\text{H}_2\text{O}} - (\bar{g}_f)_{\text{H}_2} - \frac{1}{2}(\bar{g}_f)_{\text{O}_2} \right] y_{\text{H}_2,\text{in}} \\ & + \left[(\bar{g}_f)_{\text{CO}_2} - (\bar{g}_f)_{\text{CO}} - \frac{1}{2}(\bar{g}_f)_{\text{O}_2} \right] y_{\text{CO},\text{in}} \\ & + \left[(\bar{g}_f)_{\text{CO}_2} + 2(\bar{g}_f)_{\text{H}_2\text{O}} - (\bar{g}_f)_{\text{CH}_4} - 2(\bar{g}_f)_{\text{O}_2} \right] y_{\text{CH}_4,\text{in}} \end{aligned} \quad (16)$$

where $\Delta \bar{g}$ is the average Gibbs free energy from the inlet to the outlet and y is the mole fraction. The partial pressures are assumed to be the average pressures between the inlet and the outlet.

$$\begin{aligned} \bar{p}_j &= \left(\frac{y_{j,\text{out}} + y_{j,\text{in}}}{2} \right) \bar{p} \quad j = \{\text{H}_2, \text{CO}, \text{CH}_4, \text{CO}_2, \text{H}_2\text{O}, \text{N}_2\} \\ \bar{p}_{\text{O}_2} &= \left(\frac{y_{\text{O}_2,\text{out}} + y_{\text{O}_2,\text{in}}}{2} \right) \bar{p}_c \end{aligned} \quad (17)$$

3.1.3 Fuel Composition

Finally, one needs to calculate the fuel composition at outlet of the cells. The compositions at outlets is calculated using the Gibbs minimization method [35]. First the unreacted fuels at outlet is decided by fuel cell utilization factor, then equilibrium at the anode outlet temperature and pressure is assumed for H₂, CO, CO₂, H₂O, CH₄, and N₂. Finally, the Gibbs minimization method is used to calculate the compositions of these species at the outlet by minimizing their Gibbs energy. Gibbs minimization method facilitates calculating of the composition without taking into account the chemical reaction paths. The reason is that all the chemical reactions tends to undergo in a way that the Gibbs energy will be minimum, as explained in [35]. Similar calculations can also be carried out for the cathode side.

3.1.4 Validation

A comparison between the SOFC model developed here and the experimental data is shown in Fig. 3, in terms of current density and cell voltage (IV curve). As seen from the figure, the model captures the experimental data very well at different fuel compositions with a standard error of less than 0.01 unless for 10% H₂ which was 0.05. Different stack operating temperatures were used when developing the model. However, only the data for 750C is shown here. 97% H₂ with 3% water vapour is shown in Fig. 3. four different cell operating temperatures from 650 °C to 800 °C

Figure 3. Cell voltage versus current density and a comparison between the modelling results and experimental data at 750 °C with different fuel compositions.

3.1.5 Additional Considerations

Additionally, equations for conservation of mass (with molar flows), conservation of energy, and conservation of momentum were also included in the model. Table 1 displays the main

305 parameters for the SOFC stacks used in this study. Operating temperature of the fuel cell is
 306 based on the experimental data presented in [33]. A temperature difference of 130 °C to 180 °C
 307 is applied to avoid thermal stresses in the cells, see e.g. [26]. The assumption of pressure drops
 308 is based on a simple calculation for heat exchangers via friction factor and Reynold number
 309 (see, e.g. [36]). Number of cells in one stack is assumed so that each stack generates about 1.2
 310 kW. The assumption of DC/AC convertor efficiency is somewhat low due to small size of the
 311 plant. Note that stack power is set to 10.2 kW which is achieved by varying fuel inlet mass
 312 flow. Thus plant can generate about 10 kW net powers after auxiliary power consumption. The
 313 sensitivity analysis of these values have already been widely discussed in previous publications,
 314 such as in [13], [26] and [37] and therefore there is no need to repeat them here.

315
 316 *Table 1. The main SOFC parameters used in this study [13], [8].*
 317

318 3.2 Modelling of Methanator

319 A simple Gibbs reactor, where the total Gibbs free energy is minimized upon reaching
 320 chemical equilibrium, is implemented to calculate the gas composition at a specified
 321 temperature and pressure without considering the reaction pathways [35]. The Gibbs free
 322 energy of a gas (which is assumed to be a mixture of k perfect gases) can be written as
 323

$$324 \quad \dot{G} = \sum_{i=1}^k \dot{n}_i [g_i^0 + RT \ln(n_i p)] \quad (18)$$

325 where g^0 , R , and T are the specific Gibbs free energy, universal gas constant, and gas
 326 temperature respectively. Each element in the inlet gas is in balance with the outlet gas
 327 composition, implying that the flow of each constituent has to be conserved. For N elements,
 328 this balance is expressed by equation 19.
 329
 330

$$331 \quad \sum_{i=1}^k \dot{n}_{i,in} \mathbf{A}_{ij} = \sum_{m=1}^w \dot{n}_{m,out} \mathbf{A}_{mj} \quad \text{for } j = 1, N \quad (19)$$

332 The N elements correspond to H₂, O₂, N₂, CO, NO, CO₂, steam, NH₃, CH₄, C, NO₂, HCN
 333 (hydrogen cyanide) and Ar, and in the methanation process. \mathbf{A}_{mj} is the number of atoms of
 334 element j (H, C, O, and N) in each molecule of the entering compound i (H₂, CH₄, CO, CO₂,
 335 H₂O, O₂, N₂, and Ar), whereas \mathbf{A}_{ij} is the number of atoms of element j in each molecule of the
 336 leaving compound m (H₂, O₂, N₂, CO, NO, CO₂, steam, NH₃, CH₄, C, NO₂, HCN and Ar). The
 337 minimization of the Gibbs free energy can be mathematically formulated by introducing a
 338 Lagrange multiplier (μ) for each of the N constraints. After adding the constraints, the
 339 expression to be minimized is given by
 340
 341

$$342 \quad \phi = \dot{G}_{tot,out} + \sum_{j=1}^N \mu_j \left(\sum_{i=1}^k \dot{n}_{i,out} A_{ij} - \sum_{m=1}^w \dot{n}_{m,in} A_{mj} \right) \quad (20)$$

343
 344 By setting the partial derivative of this equation with respect to $\dot{n}_{i,out}$ to zero, the function ϕ
 345 can be minimized as
 346

$$347 \quad \frac{\partial \phi}{\partial \dot{n}_{i,out}} = \frac{\partial \dot{G}_{tot,out}}{\partial \dot{n}_{i,out}} + \sum_{j=1}^N \mu_j \mathbf{A}_{ij} = 0 \quad \text{for } i = 1, k \quad (21a)$$

$$348 \quad \Rightarrow \quad g_{i,out}^0 + RT \ln(n_{i,out} p_{out}) + \sum_{j=1}^N \mu_j \mathbf{A}_{ij} = 0 \quad \text{for } i = 1, k \quad (21b)$$

349 Thus, a set of k equations are defined for each chemical compound leaving the system. Solving
350 these equations gives the composition leaving the methanator.

351 3.3 Modelling of Other Components

352 The power consumption of the pumps was calculated as in equation 22.

353

$$354 \quad W_{pump} = \left[\frac{\dot{m} \nu_{in} (p_{out} - p_{in})}{\eta} \right]_{pump} \quad (22)$$

355 where \dot{m} , p , ν and η are the mass flow, pressure, specific volume (m^3/kg) and efficiency of
356 the pump, respectively. The pump efficiency is defined as shown below.

357 The power consumption of the compressors was modeled based on the definitions of
358 isentropic and mechanical efficiencies (given values) in equations 23 and 24.

359

$$360 \quad \eta_{is} = \left[\frac{h_{out,Sin} - h_{in}}{h_{out} - h_{in}} \right]_{compressor} \quad (23)$$

$$361 \quad \eta_m = \left[\frac{\dot{m}(h_{out} - h_{in})}{W} \right]_{compressor} \quad (24)$$

362 where h is the enthalpy. h_s is the enthalpy when the entropy is constant. The subscripts in and
363 out refer to the inlet and outlet of the component.

364 In modeling the heat exchanger, it was assumed that all energy from one side is transferred
365 to the other side by neglecting the heat losses. Depending on the type of heat exchanger used,
366 both the LMTD (logarithmic mean temperature difference) and ε -NTU (effectiveness-number
367 of transferred unit) methods were used (see [36]).

368

369 *Table 2. The main parameters for the accessory components [13], [26].*

370

371 The desulfurizer unit is a simple model in which the sulfur content is removed. The
372 compositions are re-calculated after sulfur removal. The main parameters for the accessory
373 components are presented in Table 2. The pressure drops for all heat exchangers are assumed
374 to be 0.001 bar at the fuel side and 0.005 bar at the air side. Because the system is designed
375 for low-scale power, the fuel and air mass flows tend to be small, resulting in lower
376 efficiencies of the turbomachines. Therefore, the compressor isentropic efficiency and
377 mechanical efficiency are assumed to be 0.6 and 0.95, respectively.

378 4. RESULTS AND CONCLUSIONS

379 Different alternative fuels will be used in this investigation and the results of plant design
380 as well as anode recirculation (fuel recirculation) will be discussed for each fuel. Fuels under
381 attention are ammonia, pure hydrogen, ethanol, methanol, DME and natural gas. Depending
382 on the fuel the plant design will be altered as discussed below. If needed a methanator is

383 included into the plant design to enhance plant performance. It shall be noted that the
384 performance of a methanator is different from a pre-reformer and therefore the carbon
385 decomposition will not be severe in as in the case with natural gas. As mentioned above,
386 studies on anode off-fuel recycling on plant efficiency are very limited and which makes the
387 basis of this study. Different types of fuels are used to investigate the effect of anode
388 recycling on plant efficiency, which may provide an in-depth understanding of why anode
389 recycle shall be used and how it effect on plant efficiency.

390 **4.1 Ammonia**

391 The first fuel to be studied is ammonia for which the plant design is shown in Fig. 4a. Air
392 is preheated in a cathode preheater (CP) before entering the cathode side of the fuel cell. On
393 the other side, fuel is preheated in an anode preheater (AP) prior to the anode side of the fuel
394 cell. The plant efficiency and power are calculated to be about 51.0% and 10.2 kW
395 respectively, with 8 stacks of 74 cells per stack and pressure drops defined above. The fuel
396 after the anode contains mainly of 60% steam, 25% N₂ and 15% H₂ (molar fraction). Some
397 traces of CO, CO₂ and NH₃ can also be found as, 8.84×10^{-5} , 4.12×10^{-4} and 1.26×10^{-3}
398 respectively. Since the fuel amount after the anode (off-fuel) is extremely low then having
399 anode recycle will not be necessary at all in such system, see Fig. 4b. Any anode off-fuel
400 recycling decreases pant performance as shown in Fig. 4b.

401
402 *Figure 4. a) SOFC plant design fed by ammonia and b) effect of recycle ratio.*

403
404 Decreasing SOFC utilization factor allows more fuel to be available in the off-fuel and
405 therefore it might be of interest to investigate if it has any impact on plant performance. Fig. 5
406 shows that regardless of utilization factor, no anode recycling is necessarily.

407
408 *Figure 5. Effect SOFC fuel utilization factor on plant efficiency, fed by ammonia.*

410 **4.2 Pure Hydrogen**

411 The second fuel to be studied is hydrogen for which the plant design will be the same in
412 Fig. 4. Plant power and efficiency are calculated as 10.0 and 45.5% respectively. The off-fuel
413 after the anode-exit contains mainly of 20% H₂ and 80% steam (again molar basis). Traces of
414 CO, CO₂ and CH₄ can also be found which are very small to be discussed. Since the off-fuel
415 contains of about 20% hydrogen then it would be necessarily to discuss an alternative plant
416 design including anode recirculation as shown in Fig. 6. Fuel is preheated in a two steps heat
417 exchangers; fuel preheater (FP) and anode preheater (AP) and in between these heat
418 exchangers an ejector is placed (see. e.g. [38]). Note that inserting a pump instead of an
419 ejector is very crucial due to high temperature of the off-fuel (780 °C). A pump running on
420 such high temperature must be costume made and thus extremely expensive.

421
422 *Figure 6. Plant design fed by hydrogen, alternative design.*

423
424 The recycling ratio of an ejector cannot be regulated and depends entire on the pressure
425 difference between the ejector mail flow (fuel) and secondary flow (off-fuel to be recycled).
426 Neglecting this issue the effect of off-fuel recirculation on plant efficiency is shown in Fig.
427 7a. As can be seen increasing recycling decreases plant efficiency (LHV) even though it can
428 be found that there exist a certain amount of recycling for which the plant efficiency is
429 maximum (about 12% recycle). Below this value the efficiency does not change significantly.
430 The reason is the interplay between fuel fraction (hydrogen molar fraction into the anode),

431 fuel mass flow (to keep stack power constant at 10.2 kW) and compressor excess power
432 consumption (to keep stack temperature at 780 °C in addition to the oxygen needed).

433

435 *Figure 7. Effect of recycling on a SOFC plant fed by hydrogen, a) $U_f = 0.8$ and b) $U_f = 0.7$.*

436

437 Decreasing the fuel utilization changes the picture completely as demonstrated in Fig. 7b. For
438 the case of $U_f = 0.7$, plant efficiency increases by increasing anode recycle. The reason is that
439 more fuel will be available in the anode off-fuel when utilization factor is decreased resulting in
440 favour for plant efficiency by recycling. Thus the general conclusion is that at high utilization
441 factors (more than about 0.8) increasing anode recycle decreases plant efficiency while at low
442 utilization factors (less than about 0.8) increasing SOFC fuel utilization will in favour for plant
443 efficiency. This is also revealed in Fig. 8.

444 For example plant efficiency increases significantly sharper for the case with 0.6 utilization
445 factor when anode recycle is applied, while the increase in plant efficiency is less pronounced for
446 the case with 0.7 utilization factor with increasing anode recycle. For the case with $U_f = 0.7$ the
447 anode recycle needs to be about 40% to reach same efficiency as the case with $U_f = 0.8$ and 20%
448 off-fuel recycle. The anode recycle must be much more than 50% for the case with $U_f = 0.6$ to
449 reach the same efficiency as in the case with $U_f = 0.8$ and 20% off-fuel recycle.

450

451 *Figure 8. Effect SOFC fuel utilization factor on plant efficiency, fed by hydrogen.*

452

453 An alternative plant design for pure hydrogen may be designed as shown in Fig. 4a, in which
454 fuel preheater is removed and instead the anode preheater may also work as fuel preheater. Thus,
455 plant design is similar as in the case with pure ammonia. The duty of the anode preheater (or fuel
456 preheater) is increased and some saving in investment cost can be achieved. The disadvantage of
457 such design is that pressure drop along the off-fuel will be higher than the previous case and
458 therefore less pressure drop for the ejector between main flow and secondary flow, which in turn
459 makes the ejector not be able to recycle the off-fuel as efficient as the previous case. On the other
460 hand, in such design, the temperature of the fuel entering the anode side of the fuel cell increases
461 with increasing recycle ratio and at some point fuel temperature will reach to the limit and
462 therefore additional recycling will not be feasible.

463 Plant performance of such design is presented in Fig. 9. As shown, similar conclusion as the
464 original design can also be drawn here. Plant performance increases with increasing recycle ratio
465 at low utilization factors while at high utilization factor (e.g. $U_f = 0.8$) this is not true. In fact, at
466 $U_f = 0.8$ plant performance remains almost constant although a maxima can be found which is
467 around 12% recirculation.

468

469 *Figure 9. Effect of anode recycle for alternative plant design for hydrogen.*

470 **4.3 Methanol, Ethanol and DME**

471 The next fuels to be considered are methanol, ethanol and DME for which the plant design
472 will be the same in Fig. 10. A methanator is included to reform the fuel into methane,
473 hydrogen and carbon monoxide which in turn are considered to be fuel for solid oxide fuels.
474 Then an ejector is placed prior to the methanator to mix the fuel with off-fuel out of the anode
475 side of the fuel cell. Two plant configurations are considered here; one with anode preheater
476 and one without anode preheater. In the case of anode preheater the fuel is preheated to a
477 lower temperature such as 280 °C which is well above the minimum temperature (250 °C) for
478 complete reforming of the fuel in the presence of a catalyst (see e.g. [11]). In fact any values
479 between 250 °C and 400 °C can be used without altering the plant performances. Due to

480 endothermic nature of the reforming process the outlet temperature of the methanator will be
481 much higher than its inlet.

482
483 *Figure 10. Plant design fed by methanol, ethanol and DME.*

484
485 The reforming process within the methanator need steam which is available after the anode
486 side of the fuel cell, the so called off-fuel. Plant performance depends on how much off-fuel can
487 be recycled through the ejector, which in turn depends on the pressure difference from the main
488 flow to the secondary flow (injection). Both steam and unreacted fuel in the off-fuel can thus be
489 recycled back into the anode side of the fuel cell, see Fig. 10.

490 As mentioned above, steam is needed for operating the methanator and therefore some off-
491 fuel shall be recycled. With respect to the plant efficiency, recycling 20% of the anode off-fuel
492 would be suitable when $U_f = 0.8$. With 20% anode recycling then enough steam is available in
493 the fuel for fuel decomposition and water gas shift reaction (in the presence of a catalyst such as
494 copper supported on zinc oxide) which are the essential reactions associated with a methanator.
495 Increasing the recycling ratio decreases plant efficiency and the reason is that for such high
496 utilization factor the amount of steam is much more than the fuel in the off-fuel. Therefore, by
497 increasing the recycling ratio more steam will be recycled which would have negative impact on
498 the plant performance. Cell voltage decreases and current density increases to keep the output
499 power at 10.2 kW, see Fig. 11a through Fig. 13a.

500 However, for the case with lower utilization factor (for example $U_f = 0.7$) then the situation is
501 changed. Increasing anode recycle increases plant efficiency to a certain point as shown in Fig.
502 11b though 13b. The reason is that now more fuel will be available in the off-fuel, which would
503 be in favour of cell performance up to a certain amount. Further increase in recycling ratio
504 changes the ratio between the fuel and steam in the off-fuel and therefore it will decrease cell
505 performance. Plant efficiency is maximized when anode recycle is about 43%, 41% and 43% for
506 ethanol, methanol and DME, respectively.

507 As demonstrated, at high utilization factors (about 0.8) anode recycle should be kept as low
508 as possible so that the amount of steam is enough for the methanator while at low utilization
509 factors higher anode recycle is recommended.

510
511 *Figure 11. Effect of recycling on a SOFC plant fed by ethanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.*

512
513 *Figure 12. Effect of recycling on a SOFC plant fed by methanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.*

514
515 *Figure 13. Effect of recycling on a SOFC plant fed by DME, a) $U_f = 0.8$ and b) $U_f = 0.7$.*

516
517 Again, similar conclusion as in the case with pure hydrogen can be drawn here, low anode
518 recirculation for high utilization factors (about 0.8) and high anode recycle for low utilization
519 factors, see also Fig. 14 for better comparison. Note that anode recycle is essential for fuels with
520 methanator, which is due to available steam in the off-fuel required for methanation process.
521 Thus, approximately 20% of anode recycle for high utilization factors (such as 80%) and about
522 40% anode recycle for low utilization factors (about 70%). Further decrease in utilization,
523 requires higher anode recycling to compensate plant efficiency drop caused by low utilization
524 factors.

525 As it is displayed in Fig.14a, for the case with $U_f = 0.8$, plant efficiency (LHV) decreases as
526 anode recycle is increased, this is more distinct when anode off-fuel recycling is more than about
527 25%. Lowering utilization factor to 0.7, then there is exist an optimum for which plant efficiency
528 maximizes, see Fig. 14b.

529

530 *Figure 14. Effect of recycling on a SOFC plant fed by methanol, ethanol and DME, a) $U_f = 0.8$*
531 *and b) $U_f = 0.7$*

532 **4.4 Biogas**

533 Biogas investigated in this study has its origin from the biomass gasification considered in
534 [37]. The composition of the biogas (syngas) is assumed to be

535 $H_2 = 0.2532,$
536 $N_2 = 0.2877,$
537 $CO = 0.1718,$
538 $CO_2 = 0.1159,$
539 H_2O (steam) $= 0.1578,$
540 $CH_4 = 0.0102$ and
541 $Ar = 0.0034,$

542 which is based on the study of [37]. Since the quality of the fuel is substantially lower
543 compared to the other fuels, the number of stacks is increased to 20 to compensate the plant
544 performance, which otherwise this case cannot be studied throughout and in line with other
545 fuels. Plant design is the same as the case for methanol, ethanol and DME, meaning that the
546 fuel side includes a fuel preheater (FP), methanator and anode preheater (AP) while the
547 cathode side includes a cathode preheater (CP) prior to the stack. Both off-fuel and off-air are
548 sent to a burner to combust the remaining fuel. Again, the recycle device is placed as far
549 away as from the fuel to allow more pressure drop, which facilitates the use of an ejector.

550 As revealed in Fig. 15a, increasing off-fuel recycling decreases stack voltage and therefore
551 current density must be increased to reach the imposed stack power at 10.2 kW. At such high
552 utilization factor ($U_f = 0.8$) the off-fuel after the anode side of the stack contains mostly of water
553 and recycling the off-fuel results in mostly water recirculation which has a negative impact on
554 the cell voltage. Decreasing utilization factor to $U_f = 0.6$, results in higher amount of fuel
555 available in the off-fuel after the anode side and therefore anode fuel recirculation will be in
556 favour and plant efficiency increases as a consequent, (see Fig. 15c). When utilization factor is
557 0.7 ($U_f = 0.7$), then plant performance does not change significantly (because of composition of
558 the fuel after mixing) and therefore off-fuel recycling would not be necessary (see Fig. 15b).

559
560 *Figure 15. Effect of recycling on a SOFC plant fed by biogas from biomass gasification, a) $U_f =$*
561 *0.8, b) $U_f = 0.7$ and c) $U_f = 0.6$.*
562

563 Again, at high utilization factor fuel recycling is not necessarily while at low utilization it is
564 recommended, which is also demonstrated in Fig. 16. For the case with $U_f = 0.8$ plant efficiency
565 decreases sharply from 36.2% to 29.4% when anode off-fuel recycling is increased from 0 to
566 20%.

567
568 *Figure 16. Effect of recycling on a SOFC plant fed by biogas from biomass gasification, a) $U_f =$*
569 *0.8 and b) $U_f = 0.6$.*
570

571 If utilization factor is decreased to 0.7, then there would be more fuel available in the off-fuel
572 and therefore plant efficiency increases slightly when anode recycling is increased. Such increase
573 is small, from 37.4% to 37.9% when anode recycling reaches to 20%. Further decrease in
574 utilization factor results in sharper increase in plant performance. For the case with $U_f = 0.6$,
575 plant efficiency increases from 34.3% to 36.1%, as off-fuel recycling is increases from 0 to 20%.

576 As mentioned above, the number of stacks was increased to compensate fuel quality of the
577 biogas and have a throughout comparison with other fuels. However, it is also possible to
578 decrease the number of stacks to 8 as it was the case for the other fuels mentioned above.

579 Consequently, plant performance will decrease from about 36% to about 33% if fuel cell
580 utilization factor is decreased significantly (not more than about 0.6), as seen in Fig. 17. Here
581 again, at high utilization factor (comparably when $U_f = 0.7$), then there is no need for off-fuel
582 recirculation while at lower utilization factors there exist a point for which plant efficiency is
583 maximizes. The optimum recirculation is 65%, 45% and 20% when utilization factor is 0.4, 0.5
584 and 0.6 respectively. Note also that when $U_f = 0.7$ then plant performance decreases suddenly
585 with any fuel recirculation; see the line in the bottom left corner.

586 Another important point is that the optimum recirculation increases when utilization factor
587 decreases, allowing more off-fuel to be recycled to compensate fuel utilization in the stacks. The
588 sudden decrease in plant performance after the optimum point is that the mixed fuel and off-fuel
589 consists of too much amount of nitrogen and steam (more than 50%), which have negative effect
590 on stack voltage. It should also be mentioned that practically an ejector cannot recycle more than
591 50% of its incoming fuel (main flow).

592
593 *Figure 17. Effect of recycling on a SOFC plant fed by biogas from biomass gasification when*
594 *number of stacks is 8.*
595

596 5. CONCLUSION

597 A new study on anode recirculation in SOFC plants with alternative fuels is presented. Fuels
598 under study are ammonia, pure hydrogen, methanol, ethanol, DME and biogas from biomass.
599 Some of the founding are;

- 600 - No anode recycling is needed when the plant is fed by ammonia.
- 601 - When the system is fed by pure hydrogen and utilization factor is 80%, then the anode
602 recirculation should be about 20%. Further, plant fed by pure hydrogen has the lowest plant
603 efficiency, which is due to endothermic nature of reactions inside the cells and therefore
604 excessive air is needed to cool down the stacks and keep their temperature at the desired level.
- 605 - Anode recycle has a significant effect on plant efficiency when the SOFC plant is fed by
606 hydrogen, ethanol, methanol and DME. At low SOFC fuel utilization factors, it is desirable to
607 increase anode recycle to compensate for low utilization factors. However, at high SOFC fuel
608 utilization factors less anode recycle is needed which otherwise decreases plant efficiency with
609 increasing anode recycle.
- 610 - If the plant is fed by biogas from biomass then for each utilization factor, there exist an
611 optimum anode recirculation, which maximizes plant efficiency. For example, the optimum
612 recirculation is 65%, 45% and 20% when utilization factor is 0.4, 0.5 and 0.6 respectively.
- 613 - Plant efficiency of about 45% can be achieved if it is fed by pure hydrogen.
- 614 - Fed by Methanol and DME, the plant efficiency is about 51%.
- 615 - Plant fed by Ethanol has the highest efficiency, which is about 55%.
- 616 - Due to low quality fuel of biogas, plant efficiency will not be more than about 33%.

617 In addition, plant designs for different fuels than natural gas is presented/analysed such as
618 ammonia, pure hydrogen, methanol, ethanol and DME and biogas. The simplest plant design is
619 associated with ammonia while in the plants fed by ethanol, methanol, DME and biogas (from
620 biomass) a methanator is included to enhance plant performance.

622 6. REFERENCES

- 623 1. Calise F, Dentice d'Accadia M, Palombo A, Vanoli L. Simulation and exergy analysis of a
624 hybrid solid oxide fuel cell (SOFC)–Gas turbine system. *Energy* 2006;31:3278–99.

- 625 2. Rokni M, Introduction of a fuel cell into combined cycle: a competitive choice for future
626 cogeneration, *ASME Cogen – Turbo IGTI* 1993; 8: 255–261.
- 627 3. Komatsu Y, Kimijima S and Szymid JS. Performance analysis for the part-load operation of a
628 solid oxide fuel cell–micro gas turbine hybrid system. *Energy* 2010; 35: 982–988.
- 629 4. Jia J, Abudula A, Wei L, Sun B, Shi Y. Thermodynamic modeling of an integrated biomass
630 gasification and solid oxide fuel cell system. *Renewable Energy* 2015;81:400–410.
- 631 5. Farhad S, Hamdullahpur F, Yoo Y. Performance evaluation of different configurations of
632 biogas-fuelled SOFC micro-CHP systems for residential applications. *Hydrogen Energy*
633 2010;35:3758–3768.
- 634 6. Papurello D, Lanzini A, Tognana L, Silvestri S, Santarelli M. Waste to energy: Exploitation
635 of biogas from organic waste in a 500 W_{el} solid oxide fuel cell (SOFC) stack. *Energy*
636 2015;85:145–158.
- 637 7. Gandiglio M, Lanzini A, Santarelli M, Leone P. Design and balance-of-plant of a
638 demonstration plant with a solid oxide fuel cell fed by biogas from waste-water and exhaust
639 carbon recycling for algae growth. *Fuel Cell Science and Technology* 2014;11:31003.
- 640 8. Bellomare F, Rokni M. Integration of a municipal solid waste gasification plant with solid
641 oxide fuel cell and gas turbine. *Renewable Energy* 2013;55:490–500.
- 642 9. Leone P, Lanzini A, Ortigoza-Villalba GA and Borchiellini R. Operation of a solid oxide fuel
643 cell under direct internal reforming of liquid fuels. *Chemical Engineering* 2012;191:349-355.
- 644 10. Cocco D and Tola V. Externally reformed solid oxide fuel cell–micro-gas turbine (SOFC–
645 MGT) hybrid systems fueled by methanol and di-methyl-ether (DME). *Energy* 2009;34:
646 2124-2130.
- 647 11. Jamsak W, Assabumrungrat S, Douglas PL, Croiset E, Laosiripojana N, Suwanwarangkul R
648 and Charojrochkul S. Performance. Assessment of Bioethanol-Fed Solid Oxide Fuel Cell
649 System Integrated with Distillation Column. *ECS Transactions* 2007; 7(1): 1475-1482.
- 650 12. Baniyasi E and Dincer I. Energy and exergy analyses of a combined ammonia-fed solid
651 oxide fuel cell system for vehicular applications. *Hydrogen Energy* 2011; 36: 11128-11136.
- 652 13. Rokni M. Thermodynamic analysis of SOFC (solid oxide fuel cell) – Stirling hybrid plants
653 using alternative fuels. *Energy* 2013;61:87–97.
- 654 14. Kihlman J, Sucipto J, Kaisalo N, Simell P, Lehtonen J. Carbon formation in catalytic steam
655 reforming of natural gas with SOFC anode off-gas. *Hydrogen Energy* 2015;40:1548–1558.
- 656 15. Shekhawat D, Berry DA, Gardner TH, Haynes DJ, Spivey JJ. Effects of fuel cell anode
657 recycle on catalytic fuel reforming. *Power Sources* 2007;168:477–483.
- 658 16. Eveloy V. Anode fuel and steam recycling for internal methane reforming SOFCs: analysis of
659 carbon deposition. *Fuel Cell Science and Technology* 2011;8: 0110061–0110068.
- 660 17. Watanabe K, Yokoo M, Hayashi K, Arai H. Demonstration of principle of electrical power
661 generation at high fuel utilization efficiency by an SOFC system with an anode recycle line.
662 *ECS Transactions* 2011;30 (1):151–155.
- 663 18. Tanaka Y, Momma A, Sato K, Kato T. Improvement of electrical efficiency of solid oxide
664 fuel cells by anode gas recycle. *ECS Transactions* 2011;30 (1):145–150.
- 665 19. Noponen M, Halinen M, Saarinen J, Kiviaho J. Experimental Study of Anode Gas Recycling
666 on Efficiency of SOFC. *ECS Transactions* 2007;5(1):545–551.
- 667 20. Braun RJ, Klein SA, Reindl DT. Evaluation of system configurations for solid oxide fuel
668 cell-based micro-combined heat and power generators in residential applications. *Power*
669 *Sources* 2006;158:1290–1305.
- 670 21. Schluckner C, Subotic V, Lawlor V, Hochenauer C. Carbon Deposition Simulation in Porous
671 SOFC Anodes: A Detailed Numerical Analysis of Major Carbon Precursors, *ASME Fuel Cell*
672 *Science and Technology* 2015;12:051007:1–12.
- 673 22. Girona K, Laurencin J, Fouletier J, F. Lefebvre-Joud F. Carbon deposition in CH₄/CO₂
674 operated SOFC: Simulation and experimentation studies. *Power Sources* 2012;210:381–391.

- 675 23. Yashiro K, Takase M, Sato K, Kawada T. Carbon deposition and electrochemical reaction of
676 anode for SOFC in methane containing atmosphere. *ECS Transactions* 2009;16(51):213–218.
677 24. Hofmann PH, Schweiger A, Fryda L, Panopoulos KD, Hohenwarter U, Bentzen JD,
678 Ouweltjes JP, Ahrenfeldt J, Henriksen U, Kakaras E High temperature electrolyte supported
679 Ni-GDC/YSZ/LSM SOFC operation on two-stage Viking gasifier product gas. *Power*
680 *Sources* 2007;173:357–366.
681 25. Elmegaard B, Houbak N. DNA—a general energy system simulation tool. Proceeding of
682 SIMS, Trondheim, Norway; 2005.
683 26. Rokni M. Thermodynamic investigation of an integrated gasification plant with solid oxide
684 fuel cell and steam cycles. *Green* 2012;2:71–86.
685 27. Rokni M. Thermodynamic analyses of municipal solid waste gasification plant integrated
686 with solid oxide fuel cell and Stirling hybrid system. *Hydrogen Energy* 2015;40:7855–7869.
687 28. Holtappels P, DeHaart LGJ, Stimming U, Vinke IC, Mogensen M. Reaction of CO/CO₂ gas
688 mixtures on Ni-YSZ cermet electrode. *Applied Electrochemistry* 1999;29:561–68.
689 29. Matsuzaki Y Yasuda I. Electrochemical oxidation of H₂ and CO in a H₂-H₂O-CO-CO₂
690 system at the interface of a Ni-YSZ cermet electrode and YSZ electrolyte. *Electrochemical*
691 *Society* 2000;147(5):1630–35.
692 30. Keegan KM, Khaleel M, Chick LA, Recknagle K, Simner SP, Diebler J. Analysis of a planar
693 solid oxide fuel cell based automotive auxiliary power unit. *SAE Technical Paper Series*
694 2002;No. 2002-01-0413.
695 31. Zhu H, Kee RJ. A general mathematical model for analyzing the performance of fuel-cell
696 membrane-electrode assemblies. *Power Sources* 2003;117:61–74.
697 32. Costamagna P, Selimovic A, Del Borghi M, Agnew G. Electrochemical model of the
698 integrated planar solid oxide fuel cell (IP-SOFC). *Chemical Engineering* 2004;102(1):61–69.
699 33. Christiansen N, Hansen JB, Holm-Larsen H, Linderoth S, Larsen PH, Hendriksen PV, Hagen
700 A. Solid oxide fuel cell development at Topsøe fuel cell and Risø. *Electrochemical Society*
701 2007;7(1):31–38.
702 34. Winnick J. 1997. *Chemical engineering thermodynamics*. John Wiley & Sons, New Yourk.
703 35. Smith JM, Van Ness HC, Abbott MM. *Introduction to Chemical Engineering*
704 *Thermodynamics*, 7th edition, Boston: McGraw-Hill, 2005.
705 36. Incropera FP, DeWitt DP, Bergman TL and Lavine AS. *Introduction to Heat Transfer*, 5th
706 edition, Wiley 2006, ISBN 978-0471457275.
707 37. Rokni, M. Biomass Gasification Integrated with a Solid Oxide Fuel Cell and Stirling Engine.
708 *Energy* 2014;77:6–18.
709 38. Baba S, Kobayashi N, Takahashi S. Development of anode gas recycle system using ejector
710 for 1 kW solid oxide fuel cell. *Engineering for Gas Turbines and Power* 2015;137:021504-1.
711

713 Nomenclature

- 714 A Area, m²
715 \mathbf{A}_{ij} Matrix
716 B Diffusion coefficient
717 D_{bin} Binary diffusion coefficient
718 D_{cell} Cell diameter, m
719 \dot{E} Exergy flow rate, kW
720 E_{FC} Electricity from fuel cell, V
721 E_{Nernst} Nernst ideal reversible voltage, V
722 F Faradays constant, C/mol
723 g^0 Standard Gibbs free energy, J/mol

724	g_f	Gibbs free energy, J/mol
725	h	Enthalpy, J/kg
726	h_f	Enthalpy of formation, J/mol
727	I_{comp}	Purchase cost of component k
728	i_{as}	Anode limiting current, mA/cm ²
729	i_d	Current density, mA/cm ²
730	L_{cell}	Cell length, m
731	\dot{n}_{H_2}	Molar reaction rate of H ₂ , mol/s
732	P	Power, W
733	p	Pressure, bar
734	p_{H_2}	Partial pressure for H ₂ , bar
735	p_{H_2O}	Partial pressure for H ₂ O, bar
736	Q	Heat, J/s
737	T	Operating temperature, K
738	t	Thickness, m
739	R	Universal gas constant, J/mol K
740	U_F	Fuel utilization factor
741	V	Volume, m ³
742	V_{an}	Anode porosity
743	W	Work, W
744	X_{H_2}	Mass reaction rate of H ₂
745	Y	Molar fraction
746		
747		Greek symbols
748	ΔE_{act}	Activation polarization, V
749	ΔE_{conc}	Concentration polarization, V
750	ΔE_{offset}	Offset polarization, V
751	ΔE_{ohm}	Ohmic polarization, V
752	ΔT_{ml}	Logarithmic mean temperature difference, K
753	ε	Effectiveness
754	η_{rev}	Reversible efficiency
755	η_v	Voltage efficiency
756	η_{mec}	Mechanical efficiency
757	η_{pump}	Efficiency of pump
758	σ	Conductivity, S/cm
759	τ_{an}	Anode tortuosity, m
760	v	specific volume, m ³ /kg
761		
762		Subscript
763	an	Anode
764	ca	Cathode
765	el	Electrolyte
766	ref	Reference
767		
768		Abbreviations
769	AP	Anode pre-heater
770	CP	Cathode air pre-heater
771	DME	Di-Methyl Ether
772	DNA	Dynamic network analysis

773 FP Fuel Preheater
774 LHV Lower heating value
775 NG Natural Gas
776 O/C Oxygen-Carbon ratio
777 S/C Steam-Carbon ratio
778 SOFC Solid oxide fuel cell
779
780

List of Figure Captions

- 781
782
783 *Figure 1. General fuel cell plant with anode off-fuel recirculation. CP: Cathode Preheater, AP:*
784 *Anode Preheater.*
785 *Figure 2. Calculation procedure.*
786 *Figure 3. Cell voltage versus current density and a comparison between the modelling results*
787 *and experimental data at 750 °C with different fuel compositions.*
788 *Figure 4. a) SOFC plant design fed by ammonia and b) effect of recycle ratio.*
789 *Figure 5. Effect SOFC fuel utilization factor on plant efficiency, fed by ammonia.*
790 *Figure 6. Plant design fed by hydrogen, alternative design.*
791 *Figure 7. Effect of recycling on a SOFC plant fed by hydrogen, a) $U_f = 0.8$ and b) $U_f = 0.7$.*
792 *Figure 8. Effect SOFC fuel utilization factor on plant efficiency, fed by hydrogen.*
793 *Figure 9. Effect of anode recycle for alternative plant design for hydrogen.*
794 *Figure 10. Plant design fed by methanol, ethanol and DME.*
795 *Figure 11. Effect of recycling on a SOFC plant fed by ethanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.*
796 *Figure 12. Effect of recycling on a SOFC plant fed by methanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.*
797 *Figure 13. Effect of recycling on a SOFC plant fed by DME, a) $U_f = 0.8$ and b) $U_f = 0.7$.*
798 *Figure 14. Effect of recycling on a SOFC plant fed by methanol, ethanol and DME, a) $U_f = 0.8$*
799 *and b) $U_f = 0.7$*
800 *Figure 15. Effect of recycling on a SOFC plant fed by biogas from biomass gasification , a) $U_f =$*
801 *0.8, b) $U_f = 0.7$ and c) $U_f = 0.6$.*
802 *Figure 16. Effect of recycling on a SOFC plant fed by biogas from biomass gasification, a) $U_f =$*
803 *0.8 and b) $U_f = 0.6$.*
804 *Figure 17. Effect of recycling on a SOFC plant fed by biogas from biomass gasification when*
805 *number of stacks is 8.*
806
807

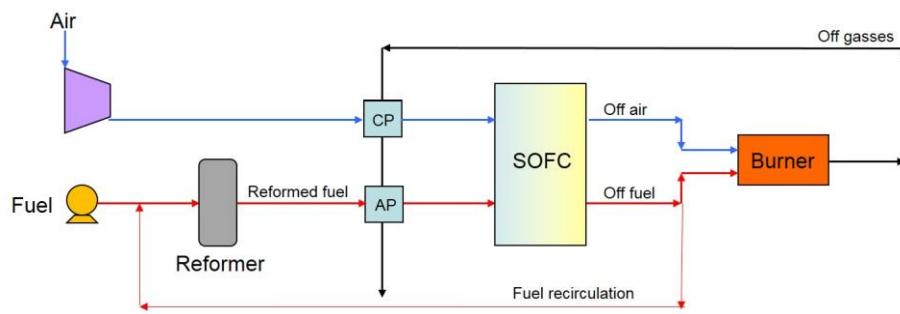
808
809
810
811
812
813

Table Captions

Table 1. The main SOFC parameters used in this study [13], [8].

Table 2. The main parameters for the accessory components [13], [26].

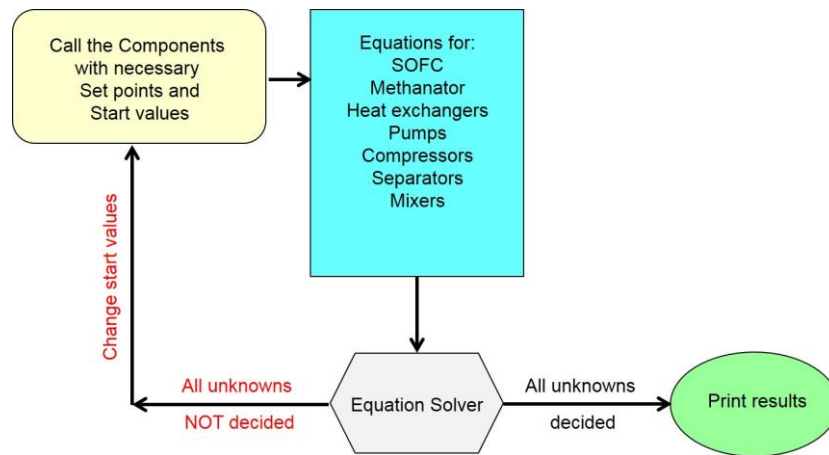
814



815
816
817
818
819
820
821
822
823
824

Figure 1. General fuel cell plant with anode off-fuel recirculation. CP: Cathode Preheater, AP: Anode Preheater.

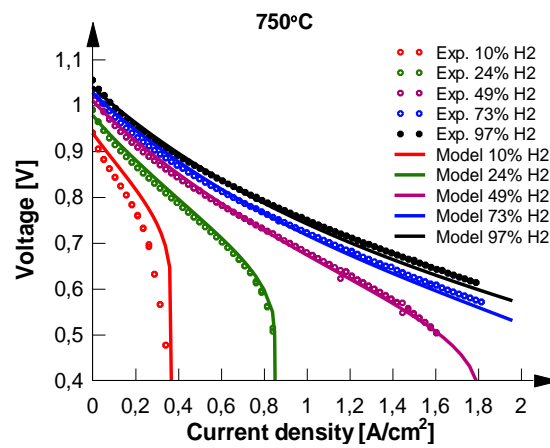
825



826
827
828
829
830
831
832
833
834

Figure 2. Calculation procedure.

835



836

837

838

839

840

841

842

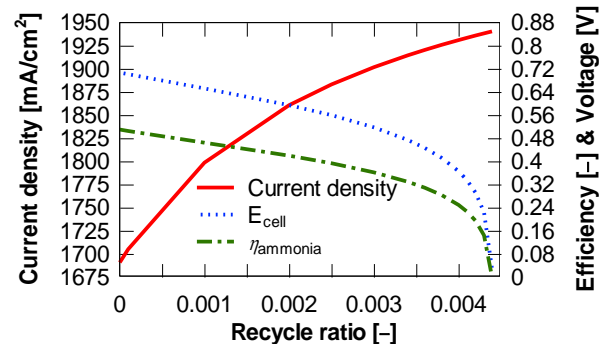
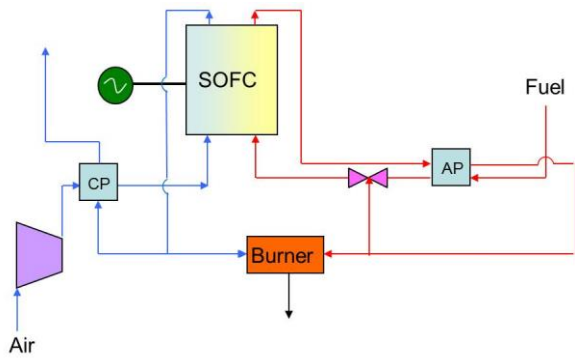
Figure 3. Cell voltage versus current density and a comparison between the modelling results and experimental data at 750°C with different fuel compositions.

843

844

845

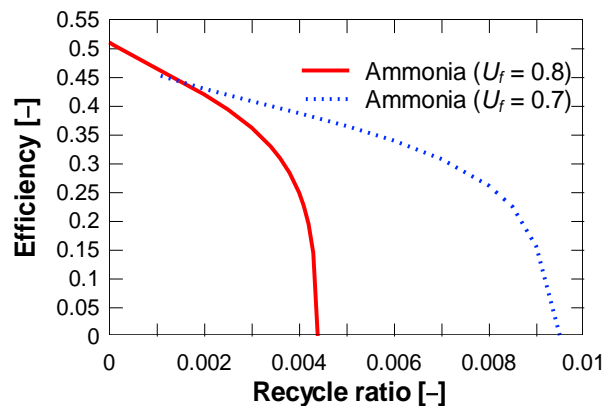
846



847
848
849
850
851
852
853
854
855
856
857
858
859

a) SOFC plant design fed by ammonia and b) effect of recycle ratio.

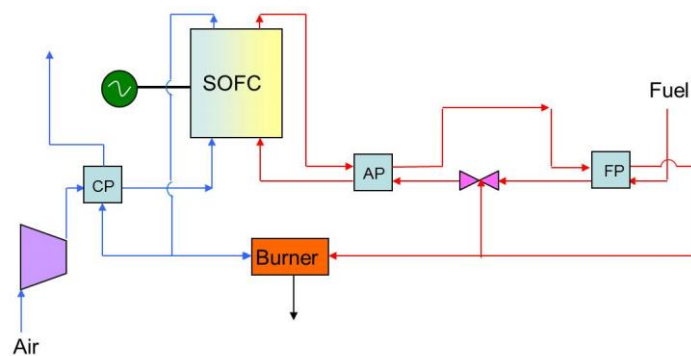
860



861
862
863
864
865
866
867
868
869

Figure 5. Effect SOFC fuel utilization factor on plant efficiency, fed by ammonia.

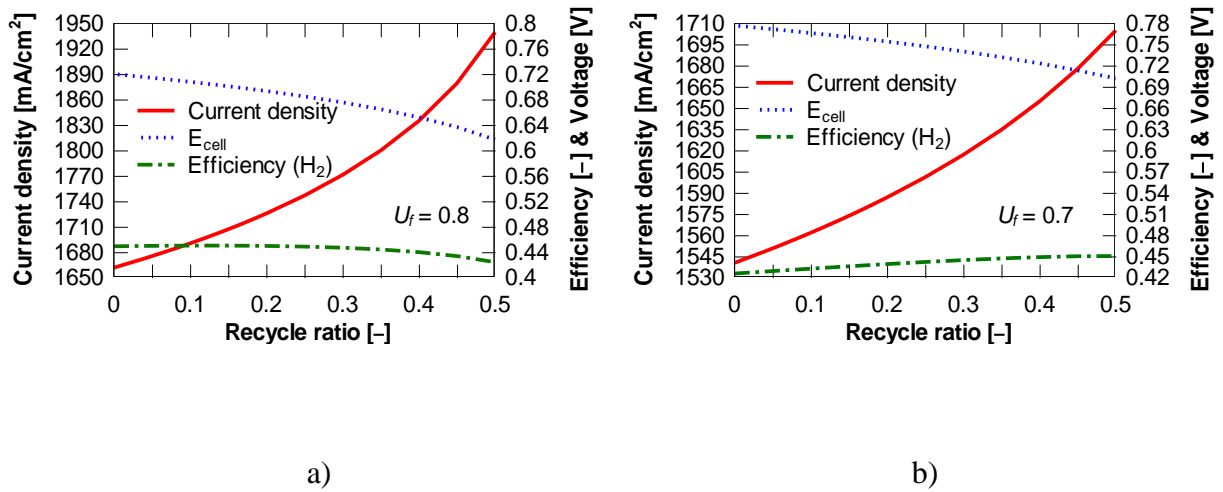
870



871
872
873
874
875
876
877
878
879

Figure 6. Plant design fed by hydrogen, alternative design.

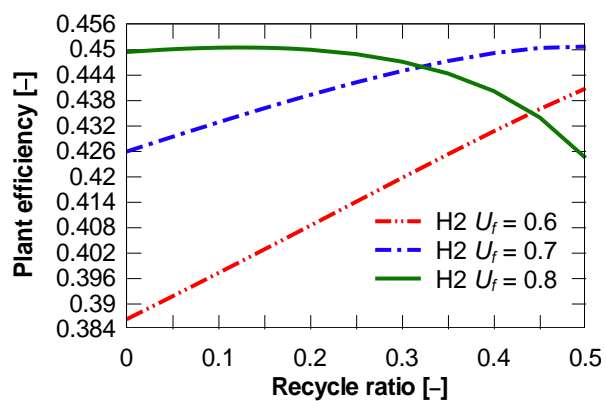
880



881
882
883
884
885
886
887
888
889
890
891
892
893

Figure 7. Effect of recycling on a SOFC plant fed by hydrogen, a) $U_f = 0.8$ and b) $U_f = 0.7$.

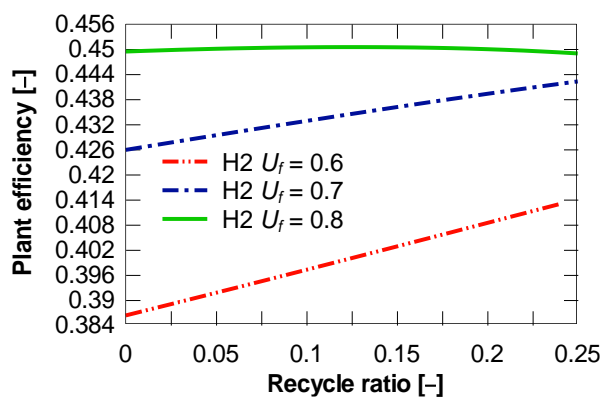
894



895
896
897
898
899
900
901
902
903

Figure 8. Effect SOFC fuel utilization factor on plant efficiency, fed by hydrogen.

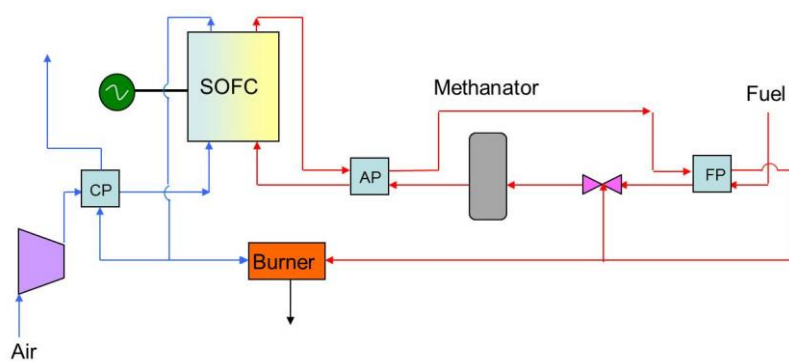
904



905
906
907
908
909
910
911
912
913

Figure 9. Effect of anode recycle for alternative plant design for hydrogen.

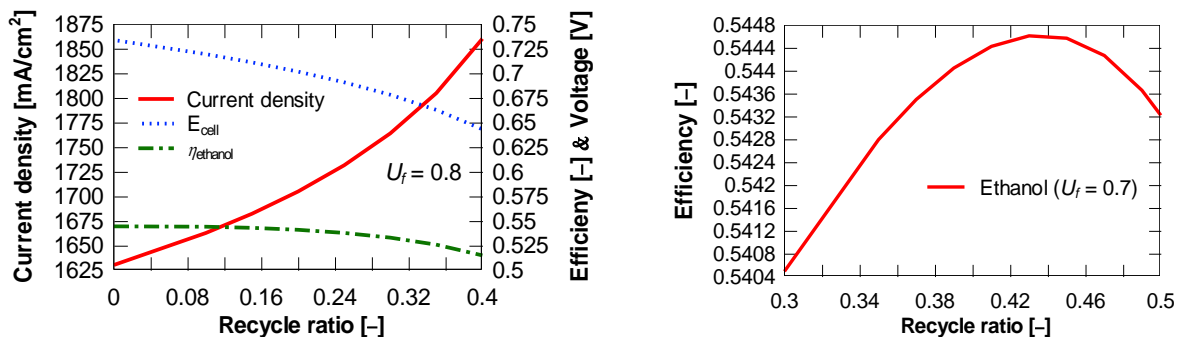
914



915
916
917
918
919
920
921
922
923

Figure 10. Plant design fed by methanol, ethanol and DME.

924



925

926

927

928

929

930

931

932

933

934

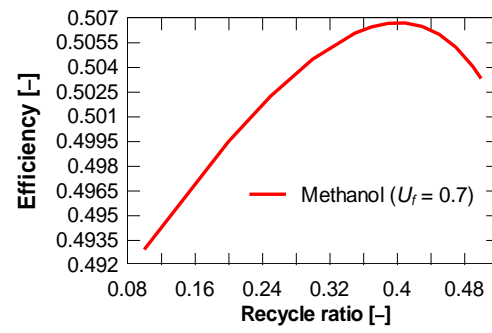
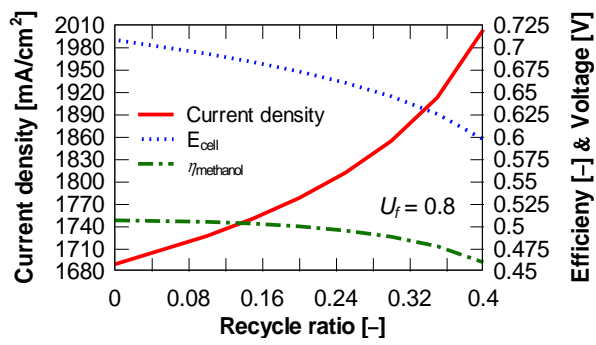
935

936

937

Figure 11. Effect of recycling on a SOFC plant fed by ethanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.

938
939



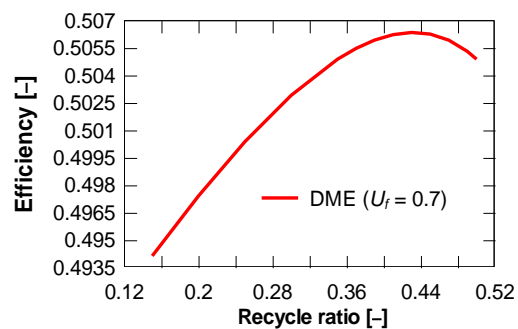
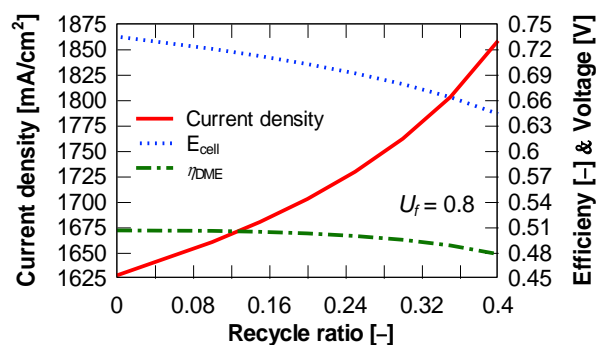
a)

b)

940
941
942
943
944
945
946
947
948
949
950
951
952

Figure 12. Effect of recycling on a SOFC plant fed by methanol, a) $U_f = 0.8$ and b) $U_f = 0.7$.

953
954



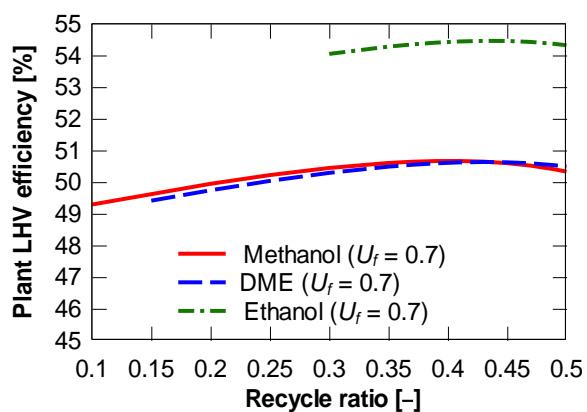
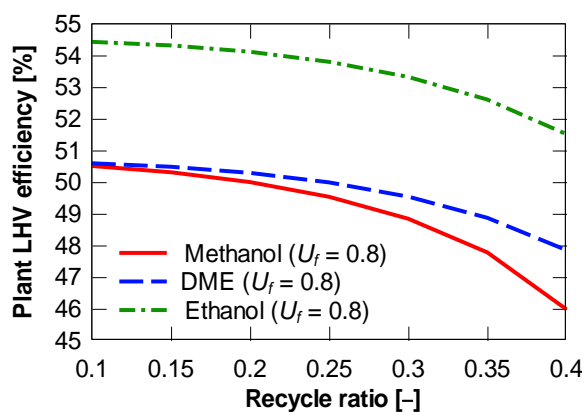
955
956
957
958
959
960
961
962
963
964
965
966
967

a)

b)

Figure 13. Effect of recycling on a SOFC plant fed by DME, a) $U_f = 0.8$ and b) $U_f = 0.7$.

968



a)

b)

969

970

971

972

973

974

975

976

977

978

979

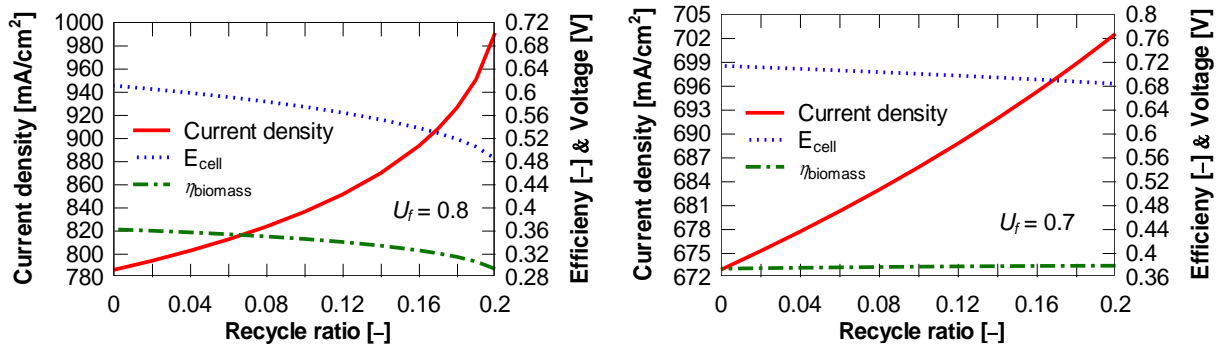
980

981

982

Figure 14. Effect of recycling on a SOFC plant fed by methanol, ethanol and DME, a) $U_f = 0.8$ and b) $U_f = 0.7$

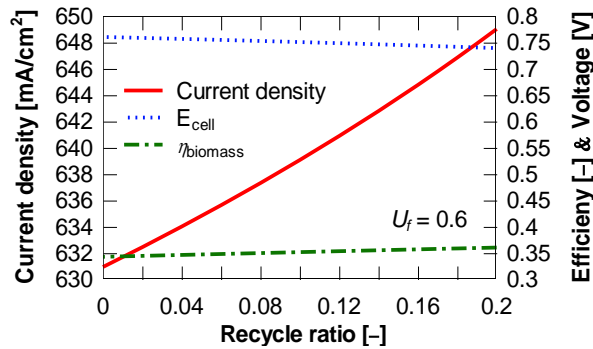
983



a)

b)

984
985
986
987
988
989
990
991

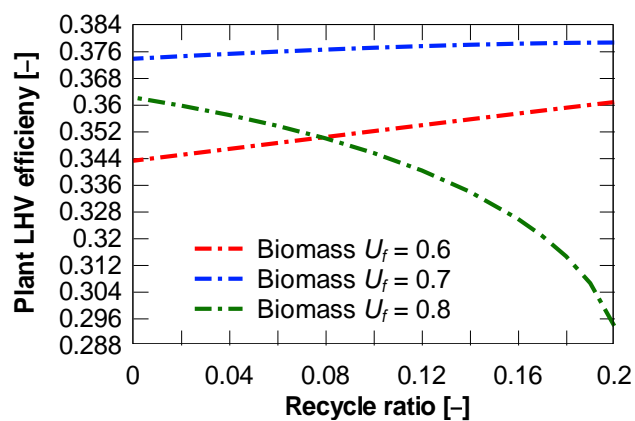


c)

992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005

Figure 15. Effect of recycling on a SOFC plant fed by biogas from biomass gasification , a) $U_f = 0.8$, b) $U_f = 0.7$ and c) $U_f = 0.6$.

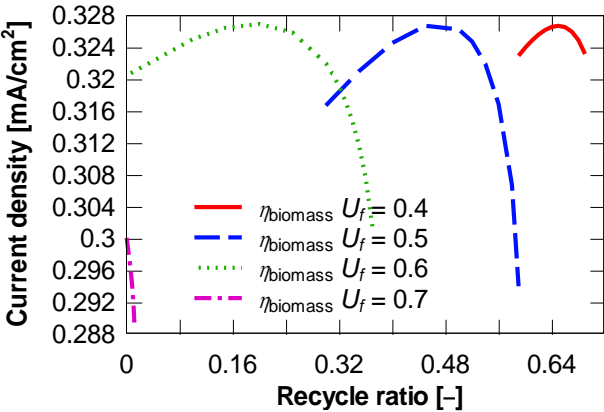
1006



1007
1008
1009
1010
1011
1012
1013
1014
1015
1016

Figure 16. Effect of recycling on a SOFC plant fed by biogas from biomass gasification, a) $U_f = 0.8$ and b) $U_f = 0.6$.

1017



1018
1019
1020
1021
1022
1023
1024
1025
1026
1027

Figure 17. Effect of recycling on a SOFC plant fed by biogas from biomass gasification when number of stacks is 8.

1028
1029
1030
1031
1032
1033
1034

Table 1. The main SOFC parameters used in this study [13], [8].

Parameter	Value
Fuel utilization factor	0.8
Number of cells in stack	74
Number of stacks	8
Stack electricity production (kW)	10.2
Cathode pressure drop ratio (bar)	0.005
Anode pressure drop ratio (bar)	0.001
Cathode inlet temperature (°C)	600
Anode inlet temperature (°C)	650
Outlet temperatures (°C)	780
DC/AC convertor efficiency	0.95

1035
1036
1037

1038
1039
1040
1041
1042
1043
1044

Table 2. The main parameters for the accessory components [13], [26].

Parameter	Value
Compressor isentropic efficiency	0.6
Compressor mechanical efficiency	0.95
Fuel side heat exchangers Δp (bar)	0.001
Air/Gas side heat exchangers Δp (bar)	0.005
Desulfurizer temperature ($^{\circ}\text{C}$)	200
Fuel inlet temperature ($^{\circ}\text{C}$)	25
Burner efficiency	0.97
Depleted air temperature ($^{\circ}\text{C}$)	40

1045
1046