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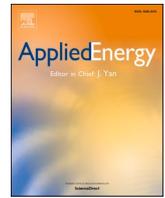
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Methanol based Solid Oxide Reversible energy storage system – Does it make sense thermodynamically?

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HIGHLIGHTS

- Thermodynamic modelling of rSOC system based on Methanol- Steam process chain.
- Maximum system roundtrip efficiency of 64.32%.
- Discussion of energy efficiency definitions and the correctness of each.
- Design maps for operation of rSOC system.

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ABSTRACT

Hydrogen is yet to be widely accepted as a fuel for everyday operation due to stringent safety regulations involved around it. In the meanwhile, methanol could be a potential fuel of the future. In this work, an extensive thermodynamic investigation on an energy storage system with a reversible solid oxide stack at its core is presented. The current investigated system can operate either as an electrolyzer or as a fuel cell. It uses steam for electrolysis (charging mode) and methanol for fuel cell operation (discharging mode). A process model of the entire system is formulated by using Aspen Plus™. Energy and exergy efficiency have been reported for both modes of operation, along with maximum roundtrip efficiency that can be achieved for the entire system operation. Results indicate that during electrolysis mode, a maximum energy and exergy efficiency of 67.94% and 72.30% can be achieved and for fuel cell mode operation, the numbers are 74.14% and 62.61% respectively. The maximum reported value of RT efficiency is 64.32% which is quite high considering the infancy of reversible solid oxide technology and the fact that methanol is used as the fuel.

1. Introduction & literature

1.1. Introduction

Europe is making a transition to a low carbon economy by harnessing and maximising the potential of renewable energy technologies and also by investing in energy storage technologies which are seen as key and supplementary to renewable energy sources. A broad framework of the policy is available in the Europe 2020 agenda [1]. In addition, the European Commission aims for 80–95% reduction in carbon dioxide (CO₂) generation by 2050 in comparison with CO₂ produced during 1990. The increase in CO₂ emissions has skyrocketed by 70% during the period

1970–2004. Approximately 32 billion tonnes of CO₂ were emitted in 2014. CO₂ annual emissions are expected to rise to 50 billion tonnes by 2050 [2].

The rapid expansion of renewable energy technologies along with the combination of fuel cell systems is envisaged as an attractive option to provide electricity as well as fuels in order to sustain the world's growing energy demands. CO₂ capture from power plants offers possibilities to recycle the carbon dioxide (CO₂) in synthesizing chemicals which in turn can be directly consumed or utilized for other purposes by means of chemical energy storage [2]. The main disadvantage of renewable energy technologies, such as solar and wind energy is their intermittent nature [3–6]. If solar energy is taken as an example, it is possible to store excess electricity generated by the solar panels as fuel

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Nomenclature*List of abbreviations*

BOP	Balance of Plant
CAES	Compressed Air Energy Storage
CCS	Carbon Capture and Storage
DME	Dimethyl Ether
LHV	Lower Heating Value
MS	Methanol Synthesis
MTBE	Methyl tertiary-butyl ether
NIST	National Institute of Standards and Technology
PEM	Polymer Electrolyte Membrane
PHS	Pump-Hydro Storage
rSOC	Reversible Solid Oxide Cell
RT	Roundtrip (Efficiency)
RWGS	Reverse Water-Gas Shift
SNG	Synthetic Natural Gas
SOC	Solid Oxide Cell
SOEC	Solid Oxide Electrolysis Cell
WGS	Water-Gas Shift

List of symbols

A	Active electrode area (m ²)
N	Number (-)
N _{tube}	Number of tubes of MS reactor (-)
Q _H	Hot Utility (kW)
U _{f,st}	Steam Utilization (-)
U _f	Fuel Utilization (-)
V	Voltage
V _N	Nernst or Reversible Voltage (V)
V _N ⁰	Nernst or Reversible Voltage at reference conditions (V)
\dot{m}	Mass flow rate (kg/s)
\dot{n}	Molar flow (mol/s)
P ₀	Reference pressure (bar)
D:F (-)	Distillate to Feed ratio (-)
D:R (-)	Distillate to Reflux ratio (-)
E	Energy produced/consumed (J)
L	Length of MS reactor (m)
LHV	Lower heating value (J/kg)
η	Efficiency (-)
P	Electrical + Thermal Power (W)
q	Charge (C)
T	Temperature (K)
t	Time of operation (s)

V	Voltage (V)
W	Electricity produced/consumed (W)
x	Mole fraction (-)
z	Number of electrons transferred per molecule oxidized/reduced (equals 2)
ϵ	Porosity (-)
ρ	Density (kg/m ³)
Ex	Thermomechanical and chemical exergy (W)
F	Faraday Constant (C/mol)
R	Universal gas constant (J/mol K)
i	Current Density (A/m ²)
p	Pressure (bar)

Greek symbols

ΔH	Change in enthalpy (J/mol)
ΔG	Change in Gibbs free energy (J/mol)

List of subscripts

aft	Afterburner
c	Cell
cat	Catalyst
CH ₃ OH	Methanol
CO ₂	Carbon Dioxide
Col,pump	Cooling pump
colwat	Cooling water
distl	Distillation
el	Electrolysis
exh	Exhaust
fc	Fuel cell
H ₂	Hydrogen
H ₂ O	Steam/Water
in	Inlet
is	Isentropic
mech	Mechanical
MS	Methanol synthesis
O ₂	Oxygen
out	Outlet
ox	Oxidant
ref	Reformer
SG	Sweep Gas
st	Stack
tc	Turbomachinery (including compressors and expanders)
tot	Total
wat	Water

by use of an electrolyzer (alkaline, polymer electrolyte membrane or solid oxide cell). Either steam electrolysis or co-electrolysis can be carried out and the resulting product is either hydrogen or a syngas

mixture, which can then be used for synthesis of complex molecules. On the contrary, during winter when low solar irradiation levels are low, the stored fuel can be utilized in a fuel cell to produce electricity. Thus a

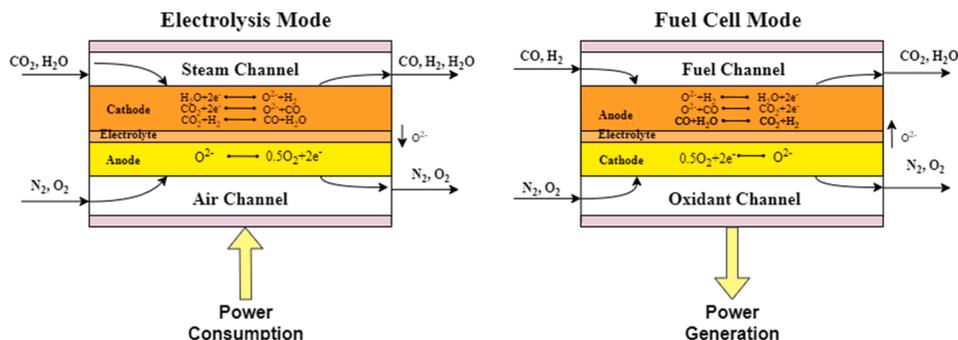


Fig. 1. Schematic representation of rSOC operation during steam electrolysis (or co-electrolysis) mode (left) and fuel cell operation (right).

circular approach is possible where excess electricity gets stored in the form of fuel and fuel is converted back to electricity when needed.

Estimates show that in the future, an energy amount equivalent to 15–20% of the annual energy demand has to be stored [4]. This amount of energy will be stored using long-term energy storage systems such as pumped-hydro storage (PHS) and compressed air energy storage (CAES). It is also stated that the storage duration should vary between one and eight hours by using 1 kW–10 MW electricity storage systems that could reach roundtrip (RT) efficiencies of 80% [5]. These solutions are offered by employing short-term energy storage systems such as batteries, flywheels or molten salts. Therefore, a mix of long-term and short-term energy storage systems will be necessary in the future.

Due to recent scientific advancements in SOCs where the focus has been on increased cycle life and lower degradation rates, systems based on reversible solid oxide cells (rSOC) seem to be very promising. rSOCs are an emerging technology and systems based on them, address the problem of long-term electricity storage. Their ability to work with carbon-containing fuels, their low overpotentials due to high operating temperature and the ability to catalyze desirable side reactions, such as methanation (electrolysis mode) and methane steam reforming (fuel cell mode), combined with high RT efficiency makes them a potential candidate for long-term energy storage [7]. Another advantage of rSOC systems is that they can store energy for several months by producing hydrogen *via* the steam electrolysis route or converting it to synthetic natural gas (SNG) and storing it using the existing infrastructure [7]. Reversible solid oxide cells have not yet been widely explored for their capabilities and therefore it is an active field of research.

Fig. 1 shows the schematic operation of a rSOC during both modes of operation.

1.2. Literature review

Steam electrolysis or co-electrolysis with the aim of producing methanol has been employed in the studies of Rivera-Tinoco, Farran, Bouallou, Aupretre, Valentin, Millet et al. [2], Hansen, Christiansen and Nielsen [8] and Leonard, Giulini and Villarreal-Singer [9]. The concept of electricity storage *via* high-temperature electrolysis-fuel cell operation in combination with intermediate methanol synthesis has only been realized by Al-Musleh, Mallapragada and Agrawal [11].

More specifically, Leonard, Giulini and Villarreal-Singer [9] presented an Aspen Plus™ model with co-electrolysis in an SOC stack and production of methanol. The stack operating conditions were 850 °C and 1 bar. The co-electrolysis model was validated by comparing data with experiments under similar conditions as carried out by Sun, Chen, Jensen, Ebbesen, Graves and Mogensen [10]. The process flowsheet contains a CO₂ capture plant, a co-electrolysis section and a syngas compression section which then leads to the methanol synthesis loop and the final purification step *via* distillation. Methanol synthesis has been modelled in a clever way, including in-situ methanol condensation. Pinch analysis was used to determine the effect of heat integration in power-to-methanol efficiency and a value of 53% was reported whereas an efficiency of 40.1% was reported when no heat integration is applied. The authors concur that when the CO₂ capture system is included in the heat integration calculations, further improvement of power to methanol efficiency can be achieved.

Rivera-Tinoco, Farran, Bouallou, Aupretre, Valentin, Millet et al. [2] performed a techno-economic analysis of an electrolysis plant for methanol production by using high temperature steam electrolysis (SOEC) and a low-temperature water electrolysis (PEM). The model was developed in Aspen Plus™. When performing low or high-temperature steam electrolysis, the reported efficiency values were 45.3% and 54.8% respectively. Despite higher efficiency of the SOC electrolysis system, compared to the proton exchange membrane (PEM) electrolysis system, investment costs of an SOC system is high due to higher temperatures involved and also there is the issue of reduced lifespan of SOEC modules. Methanol cost is deduced to be much higher when utilizing

SOC (5459 €/tonne) instead of PEM electrolysis (891 €/tonne) [2].

Hansen, Christiansen and Nielsen [8] analyzed a co-electrolysis system with possible coupling to methanol or methane production. In both cases, a pressurized stack was used and a lower heating value (LHV) efficiency of 74.8–78.1% was reported for SNG production, while 75.8–80.1% was achieved for methanol production. The LHV efficiency is simply the chemical energy of the produced fuel divided by the total electricity input. The authors cite that pressurized operation can boost energy efficiency by 3–4% due to the fact that the syngas compression section is relieved from excessive compression load. Pumping water and compressing CO₂ is beneficial in energy terms rather than compressing the effluent syngas. According to the authors, the syngas compressor is four times larger than the CO₂ compressor and that is the reason why pressurized stack operation led to increase of efficiencies. Efficiency numbers are very high but in their work it is unclear if the system hot utility comes from a free heat source. It is a very common phenomenon that authors report very high efficiencies.

Hauck, Herrmann and Spliethoff [11] performed rSOC simulations using Aspen Plus™ and they validated their model with existing experimental data from literature. Both steam electrolysis and co-electrolysis was investigated. They also stated that neglecting CO₂ electrolysis is a valid assumption as CO₂ is mostly converted due to reverse water-gas shift reaction (RWGS). CO₂ addition has a beneficial effect on cell performance due to the effect of RWGS compared with the case where CO₂ was substituted with an inert gas. In addition, cell performance can be increased by either increase of stack pressure or temperature, while varying inlet composition promotes the efficient operation of one mode and the inefficient operation of the other mode. For example, an increase in hydrogen content is beneficial for the performance of fuel cell mode while reducing the performance during electrolysis operation. The exact opposite behavior is observed when the steam content is enhanced.

Al-Musleh, Mallapragada and Agrawal [12] have proposed novel cycles for methane (CH₄) or methanol (CH₃OH) synthesis. The necessary hydrogen is produced through high temperature steam electrolysis while the synthesized molecules (i.e. methane or methanol) are reformed and electrochemically oxidized for electricity production. CO₂ is circulated in the system without using an external CO₂ source. It is obtained through liquefaction and the use of high-intensity refrigeration cycles is made. Afterwards, it is stored in a separate tank. In this work, although the concept of the reversible solid oxide fuel cell is not referred to *per se*, it is still relevant because they employ two different stacks, one for electrolysis and one for fuel cell operation. For methanol synthesis, storage efficiency was calculated to be 48.2% but it can be increased up to 54.3% when the distillation step is omitted and the mixture of water/methanol is stored at pressurized conditions. This storage efficiency definition is equivalent to the roundtrip (RT) efficiency definition used by Wendel, Kazemipoor and Braun [13]. It is simply the ratio of generated electricity during fuel cell mode divided by the consumed electricity during electrolysis mode.

1.3. Research objective

The objective of this research article is the formulation of an efficient process chain with the rSOC stack at its core and which employs methanol as fuel in the fuel cell mode and carries out steam electrolysis in the electrolysis mode. This is one of the attractive process chains that is envisaged for rSOC technology as described in the article by Venkataraman, Perez-Fortes, Wang, Hajimolana, Boigues-Munoz, Agostini et al. [14].

The authors will address the following key research questions in the current article:

1. In the event of a methanol based economy in the future, will an rSOC plant based on methanol as fuel be attractive enough from an energy and exergy efficiency point of view?

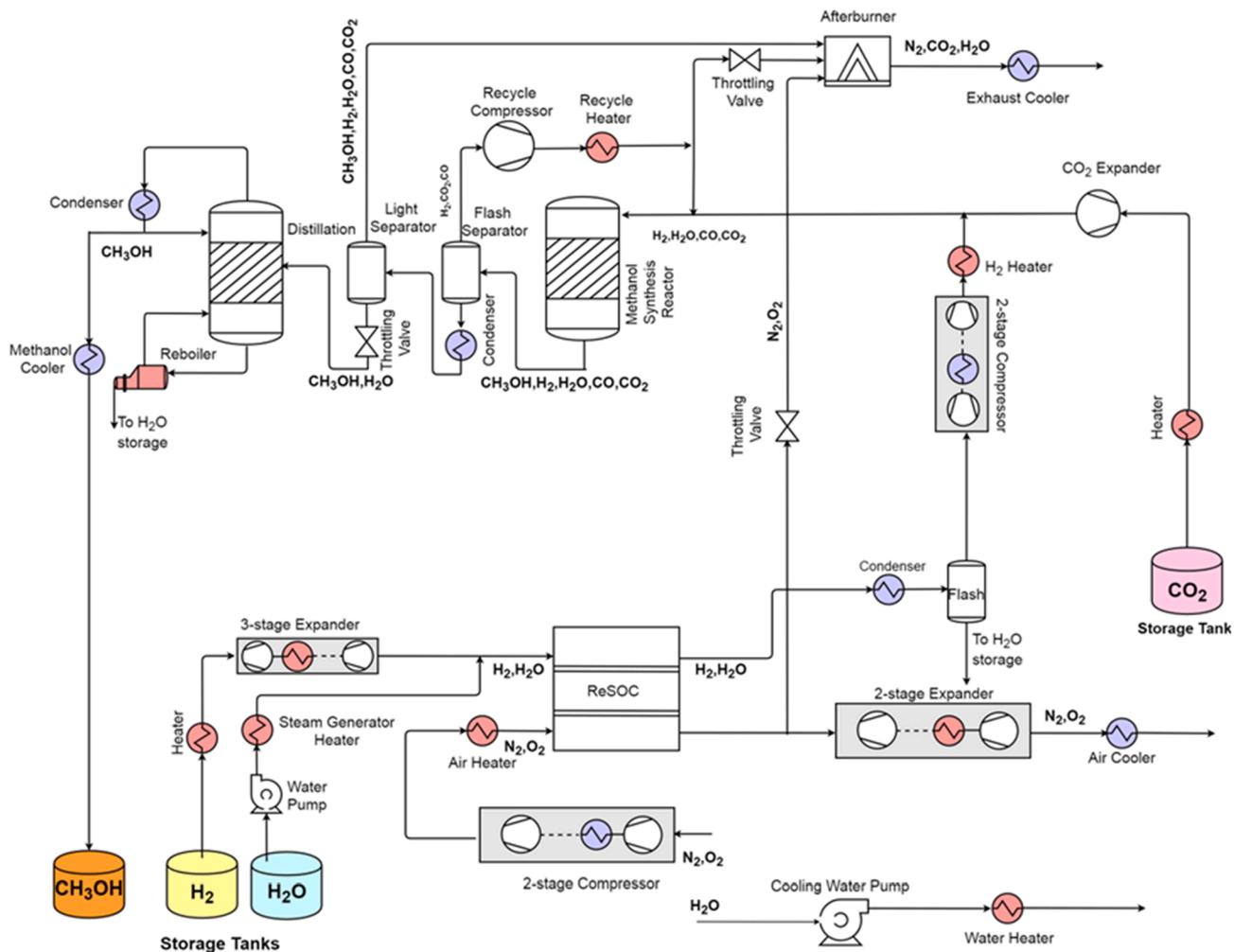


Fig. 2. Process Schematic for Electrolytic operation of rSOC system.

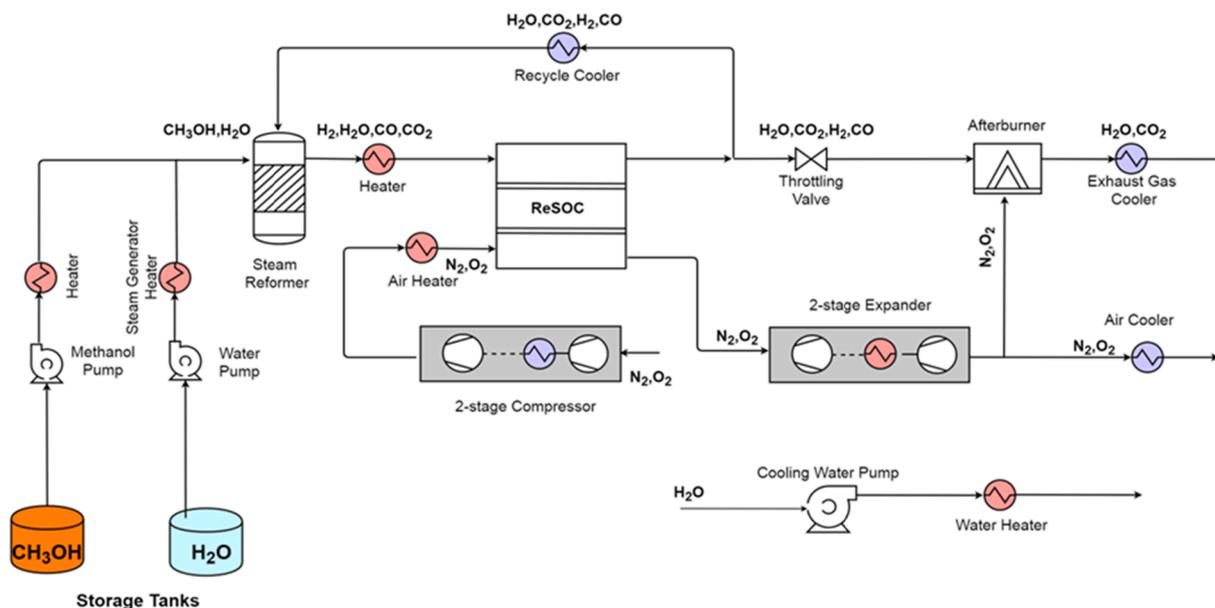


Fig. 3. Process Schematic for fuel cell operation of rSOC system.

2. What are the most thermodynamically favorable conditions for the rSOC plant operation from an energy and exergy point of view?
3. What process improvements can be done to improve the efficiency on a system level?
4. How the use of different efficiency definitions affects the values which in turn have an effect on how a particular technology is perceived.

In addition, there is only one paper on high-temperature electrolyzer-fuel cell operation with intermediate methanol synthesis as realized by Al-Musleh, Mallapragada and Agrawal [12]. Hence the current work adds to the research base of power-to-X concept using rSOCs. Consequently, there is a gap in knowledge in rSOC to methanol systems for electricity storage. Also there have been no studies concerning the energy and exergy efficiency of each mode of operation in rSOC to methanol systems. The current work aims to provide more information about the system performance towards that direction and partly fill the research gap. The main focus is laid on energy and exergy efficiency for each mode of operation. In short, a set of design maps for the complete rSOC plant is provided which helps in identifying the regions where the plant has the highest efficiency. RT efficiency is also evaluated and discussed.

2. Modelling approach

The entire rSOC plant has been modelled using Aspen Plus™, a process simulation software widely employed in the chemical industry.

2.1. Schematic of rSOC plant

The schematic of the rSOC plant during operation in electrolysis and fuel cell mode is shown in Fig. 2 and Fig. 3 respectively. A system cyclic operation, where the product streams from one mode is used as inlet streams for the other mode, is not considered in the present study. CO₂ and small quantities of hydrogen (H₂) are initially stored in separate tanks by assuming that they are readily available. This means that the authors do not consider any process design prior to CO₂ utilization, related to carbon capture and storage (CCS). For example, an amine-based or potassium carbonate solution CCS system could be employed in order to capture this CO₂ [15], however, in the current study, CO₂ is assumed to be readily available and a CCS system has not been included in the thermodynamic investigation.

Note: The rSOC plant can be designed in a number of ways with a number of components. The authors have chosen this configuration based on the current state of the art technology with regard to general SOC plant design and methanol synthesis process.

2.1.1. Electrolysis mode operation

Hydrogen (H₂) and water (H₂O) are drawn from their respective storage tanks. Initially, the H₂ which is stored in a highly pressurized storage tank is heated and then expanded to stack operating pressure in order to generate electricity. H₂O(l) is pumped up to stack operating pressure and then is evaporated at stack operating temperature before it is mixed with H₂. The resulting mixture enters the fuel electrode. After steam electrolysis, the outlet stream (from the fuel electrode) mainly consists of H₂ and small amounts of H₂O(g), depending on steam utilization. The H₂O(g) content is condensed and sent back to the H₂O storage tank, while the highly pure H₂ stream is sent for downstream processing. H₂ is then pressurized at methanol synthesis pressure. The CO₂(l) stream is drawn from its respective storage tank. In order to exploit its high pressure, the stream is heated up and expanded for electricity production before it mixes with H₂. The outlet pressure of CO₂ expansion corresponds to the methanol synthesis pressure. Afterwards, the mixture of H₂ and CO₂ enters the methanol synthesis reactor where effective conversion to methanol takes place. A recycle loop has also been employed in order to enhance the carbon conversion. The recycle loop

contains unreacted gases which recirculate and mix with the initial H₂/CO₂ mixture. A small purge stream is necessary in order to avoid excessive reactant accumulation in the reactor. The methanol and water content of the product stream is condensed and separated. Dissolved gases in the methanol-water mixture are further extracted in a separate flash column through pressure reduction. The resulting methanol-water mixture is finally separated in a conventional distillation column in order to obtain high purity (>99%) methanol. The bottom product, which is mainly water, returns to the water storage tank. The purge gas and the light gases separated from the methanol-water mixture are combusted in an afterburner in order to partly cover the system hot utility. The exhaust gases are cooled down in order to exploit the heat of combustion.

For stack thermal balancing, an air stream is provided (79% N₂, 21% O₂ molar basis). By fixing temperature difference at stack inlet and outlet and by employing the calculated absorbed/removed heat, the air flow rate can be determined. When operating in thermoneutral mode, the air flow is considered to be equal to zero. The air flow is compressed and heated prior to the rSOC stack and afterwards, a small portion is separated in order to provide the necessary oxidant in the afterburner where the combustion of the light gases and the purge stream is taking place. The remaining air flow is then expanded and cooled down before its exit to the environment.

In order to remove heat from the system, a cooling water circuit was employed. The pump in the cooling water circuit has to overcome the overall pressure drop of the system which has been assumed to be equal to 2 bar. This pressure drop is very large (deliberately assumed) and therefore the results will be a bit more conservative without losing their reliability since electricity consumption by the pump is small.

2.1.2. Fuel cell mode operation

Initially, during fuel cell operation, CH₃OH(l) and H₂O(l) are extracted from their respective storage tanks. Each stream is separately pumped up to stack pressure and thereafter heated up to methanol steam reforming temperature. The mixture enters the methanol steam reformer and the outlet stream contains mainly a mixture of H₂(g), CO₂(g), CO(g), and H₂O(g). This stream is fed to undergo electrochemical oxidation and power production in the rSOC stack. The fuel electrode off-gas stream is then split into two sub-streams. The first sub-stream is recycled back to the methanol steam reformer in order to simultaneously utilize methanol by reforming and minimize its content at the rSOC stack inlet and also to increase power production through hydrogen recycling. The second sub-stream of the fuel electrode off-gas is led to an afterburner. The split fraction is determined in such a way that the system hot utility will be entirely covered by using the afterburner. Therefore, the goal is to maximize the fuel electrode-off gas recycle sub-stream while the hot utility is totally satisfied internally. An air stream is also provided into the stack in order to supply the necessary oxidant for the electrochemical oxidation in the stack. This also removes the generated heat from the rSOC stack. The oxidant flow is compressed and heated prior to the rSOC stack and afterwards, the oxidant flow is expanded and cooled down for electricity and heat recovery while a small portion of the oxidant is led to the afterburner for fuel electrode off-gas combustion. In order to cool down the system, a cooling water pump has been employed. As previously reported, the total pressure drop assumed is 2 bar.

More details on the modeling of each subsystem can be found in Appendix D.

3. Exergy, energy and roundtrip efficiency definitions

For system evaluation, certain metrics have to be used in order to assess if the system is worth pursuing when taken to a practical level. In this study, energy, exergy and RT efficiency has been used as important metrics to evaluate the system. Special attention is given to the formulation of energy and exergy efficiency definitions since one has to

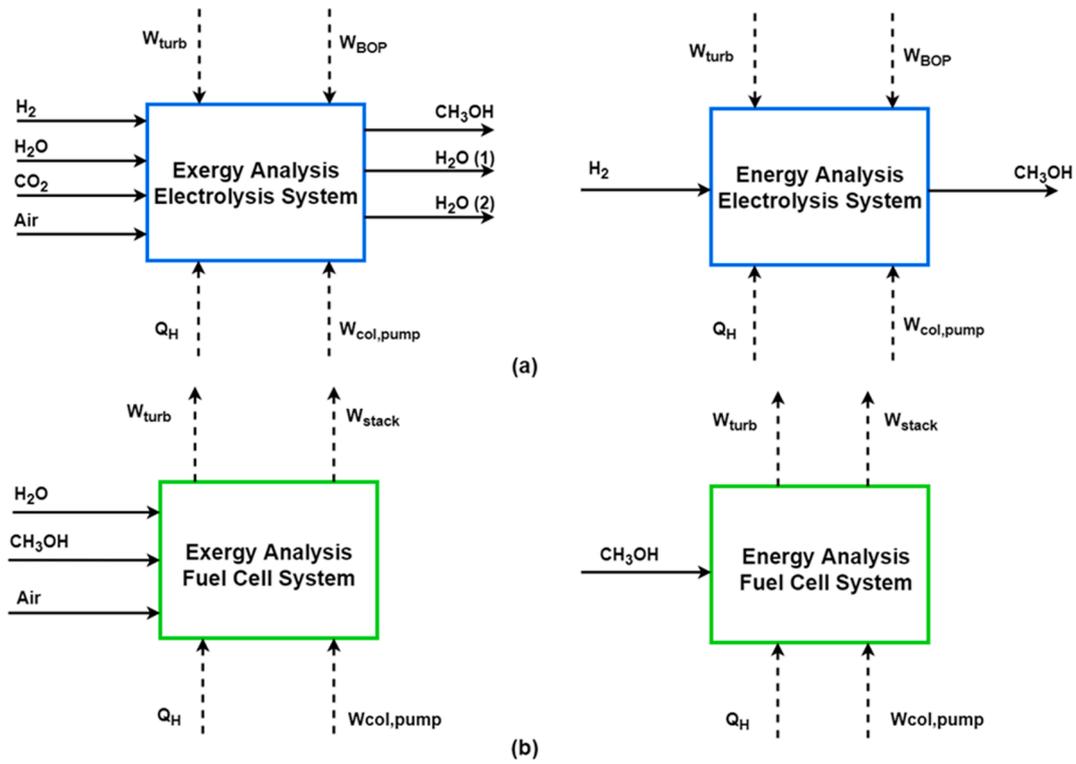


Fig. 4. Exergy and Energy Efficiency line diagram for (a) electrolysis mode (b) fuel cell mode.

distinguish between a functional or a universal type of definition. Many a time one comes across a certain study claiming very high efficiency for a system only to be realised later that the high numbers were obtained only if a particular definition was used. Hence, the choice of definition used for efficiency is very critical and important and one always has to look at the definition of efficiency (energy or other) before delving into the practicality of the concept.

The definitions used in this study resemble a functional-type definition for efficiency rather than a universal one. The distinction between the two definitions is that a universal exergy or energy efficiency definition would have every output from the system in the numerator, either thermomechanical or electrical. On the other hand, a functional efficiency definition focuses on the most useful “product” of each process. The exergy content of the useful “product” is placed in the numerator and will be either thermomechanical/chemical or electrical. Exergy streams of the same type are also placed in the numerator, while exergy terms of different types are placed in the denominator. For example, during the electrolysis mode of this system, the useful output refers to the stored methanol stream, while in the case of fuel cell operation, the useful output refers to the generated electricity (or electrical power) of the system. Because of that, thermomechanical and chemical exergy terms are placed on the numerator of the exergy and energy efficiency during electrolytic operation, while electricity terms are used at the numerator during fuel cell operation.

Another point to be stressed is that only the stored streams are included in the exergy efficiency definition. There are also streams which are vented out to the environment and these are not included. For example, during electrolysis mode, an exit stream is the exhaust gas from the afterburner, but since this stream is released to the environment, and not stored, it is not included in the definition.

Roundtrip (RT) efficiency is a metric which characterizes both modes of operation as a whole. According to the definition given by Wendel, Kazempoor and Braun [13], the system RT efficiency of an rSOC system is simply the total energy generated during fuel cell operation (including BOP components) divided by the total energy consumed during electrolytic operation (including BOP components).

Definition of evaluation metrics used for electrolytic operation:

Since one of the research objectives of this article is to chalk out different efficiency definitions and how they affect the numbers, it is vital to give correct definitions and also state when to use them.

The exergy efficiency of the system is given in Eq. (12)

$$n_{ex,el} = \frac{Ex_{out,el} - Ex_{in,el}}{W_{stack} + W_{tc} + Q_H + W_{Cooling,Pump}} \quad (12)$$

where $Ex_{in,el} = Ex_{H_2,in} + Ex_{H_2O,in} + Ex_{CO_2,in} + Ex_{SG,in}$, refers to the exergy of streams flowing into the system and $Ex_{out,el} = Ex_{CH_3OH,out} + Ex_{H_2O(1),out} + Ex_{H_2O(2),out}$, refers to the exergy of streams flowing out of the system.

The energy efficiency of the system is given in Eq. (13)

$$n_{en,el} = \frac{\dot{m}_{CH_3OH,out} \cdot LHV_{CH_3OH} - \dot{m}_{H_2,in} \cdot LHV_{H_2}}{W_{stack} + W_{tc} + Q_H + W_{Col,Pump}} \quad (13)$$

The term regarding the turbomachinery (which includes both compressors and turbines) has a positive sign because a positive W_{tc} is equivalent to an overall power consumption while a negative W_{tc} is equivalent to an overall power generation. For example, during electrolysis mode, when there is a net power consumption (i.e. positive W_{tc}), the denominator will increase and the overall efficiency will decrease and vice versa.

Definition of evaluation metrics used for fuel cell operation:

The exergy efficiency of the system is given in Eq. (14)

$$n_{ex,fc} = \frac{W_{stack} - W_{tc} - Q_H - W_{Col,Pump}}{Ex_{in,fc}} \quad (14)$$

where $Ex_{in,fc} = Ex_{CH_3OH,in} + Ex_{H_2O,in} + Ex_{SG,in}$ refers to the exergy of streams flowing into the system.

Energy efficiency of the system is given in Eq. (15)

$$n_{en,fc} = \frac{W_{stack} - W_{tc} - Q_H - W_{Col,Pump}}{\dot{m}_{CH_3OH,in} \cdot LHV_{CH_3OH}} \quad (15)$$

During fuel cell operation there are no stored outlet streams. Both air

Table 1
rSOC varying and constant parameters during electrolytic operation.

Sensitivity Analysis	p&T	T&j	p&j
p (bar)	1–10	1.01	1–10
T (°C)	650–800	650–800	800
$U_{f, st}$	0.7	0.7	0.7
j (A/m ²)	10,000	500–10,000	500–10,000
\dot{n}_{H_2} (mol/s)	0.01	0.01	0.01

flow and the afterburner exhaust gas stream are released to the environment and therefore, they are neglected. In the definitions during fuel cell mode, the term regarding the turbomachinery has a negative sign because a positive W_{ic} is equivalent to an overall power consumption while a negative W_{ic} is equivalent to an overall power generation. For example, during fuel cell mode, when there is a net power consumption (i.e. positive W_{ic}), the numerator will decrease and the overall efficiency will be reduced and vice versa. A better representation of incoming energy and exergy streams which are taken into account in Eq. (12) to Eq. (15) is shown in Fig. 4 for both modes.

In addition, RT efficiency for system and stack level are shown in Eq. (16) & Eq. (17).

Roundtrip efficiency (System) as defined by Wendel et al. [16]:

$$n_{RT, sys} = \frac{V_{cell, fc} q_{fc} - E_{BOP, fc}}{V_{cell, el} q_{el} + E_{BOP, el}} \quad (16)$$

Roundtrip efficiency (Stack) as defined by Wendel et al. [16]:

$$n_{RT, stack} = \frac{V_{fc} q_{fc}}{V_{el} q_{el}} \quad (17)$$

Finally, energy efficiency numbers for the stack will also be used herein. It has to be noted that during electrolysis not only electricity is needed, but also thermal energy to cover the total energy needs ($P_{st, tot}$) and therefore, in the denominator the term $P_{st, tot}$ is included instead of only the necessary electrical energy (Eq. (18)). The numerator contains the generation of chemical energy. On the contrary, the useful output from a stack during fuel cell operation is the electricity generation. Despite the fact that the stack also produces heat, the numerator contains only the term related to electricity generation. The denominator contains the chemical energy reduction of the fuel stream (Eq. (19)).

Energy efficiency (stack) – electrolysis:

$$n_{en, stack, el} = \frac{(\dot{m}_{H_2, out} - \dot{m}_{H_2, in}) LHV_{H_2}}{P_{stack, tot}} = \frac{(\dot{m}_{H_2, out} - \dot{m}_{H_2, in}) LHV_{H_2}}{U_{f, st} \dot{n}_{H_2, O} \Delta H} \quad (18)$$

Energy efficiency (stack) – fuel cell:

$$n_{en, stack, fc} = \frac{W_{stack}}{(\dot{m}_{H_2, in} - \dot{m}_{H_2, out}) LHV_{H_2} + (\dot{m}_{CO, in} - \dot{m}_{CO, out}) LHV_{CO}} \quad (19)$$

These definitions will provide a clear idea for the reader in understanding the system in a more comprehensive manner and will also clear out the fact that efficiency numbers are affected when employing different definitions.

4. Results & discussion

In this section, a sensitivity analysis is performed for some of the crucial rSOC parameters which are deemed to make the most impact on the system level. The following parameters were varied and its effects on system efficiency studied:

- Stack Pressure (p)
- Stack Temperature (T)
- Current density (j)

For all sensitivity analysis, certain parameters have been fixed. Then, two parameters out the three aforementioned are varied and then

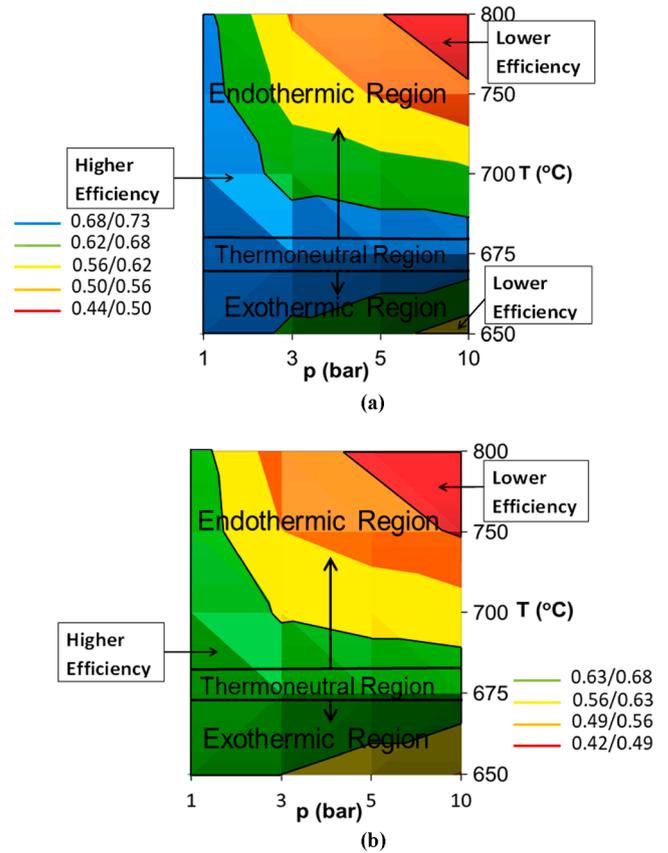


Fig. 5. (a) Exergy, (b) Energy efficiency during Electrolysis mode as a function of rSOC stack pressure and temperature (p-T Sensitivity Analysis).

efficiency maps are made. Out of all these sensitivity analyses, the maximum obtained values of efficiencies are reported. The list of fixed parameters is given in Appendix B for each mode.

4.1. Electrolysis mode

Table 1 summarizes all the parameters that were varied during the sensitivity analysis related to the steam electrolysis mode. A small amount of H_2 is necessary for electrolysis operation to avoid nickel oxidation and the percentage of H_2 in steam is around 10% [17].

These ranges for p, T and j were chosen as they represent typical operation range for rSOC units. In reality, operation at higher temperatures will sacrifice mechanical integrity of the system as excessive thermal stresses will be induced. For higher pressures, it is more difficult to keep the system tight and leak-proof. Finally, current densities were limited to 10,000 A/m² because at higher current densities concentration losses will kick in, while typical operation of such systems is restricted to the ohmic region of the j-V curve. The rSOC j-V curves used in this study is provided in Appendix C. Cold and hot composite curves for the optimum run in electrolysis mode are presented in Appendix E.

Table 2
Maximum Efficiencies at 700 °C - Results.

Pressure (bar)	Temperature (°C)	Cell Voltage (V)	Thermoneutral Voltage (V)	Ex. Eff. (%)	En. Eff. (%)
1	700	1.2469	1,2826	72.30	67.97
3	700	1.2670		71.57	67.22
5	700	1.2770		72.17	67.76
10	700	1.2909		72.07	67.67

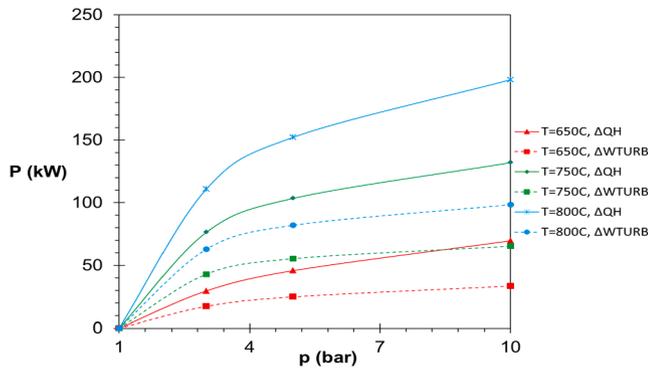


Fig. 6. Change in Hot Utility and Work from turbomachinery for different temperatures compared to pressure of 1 bar (during p-T sensitivity analysis).

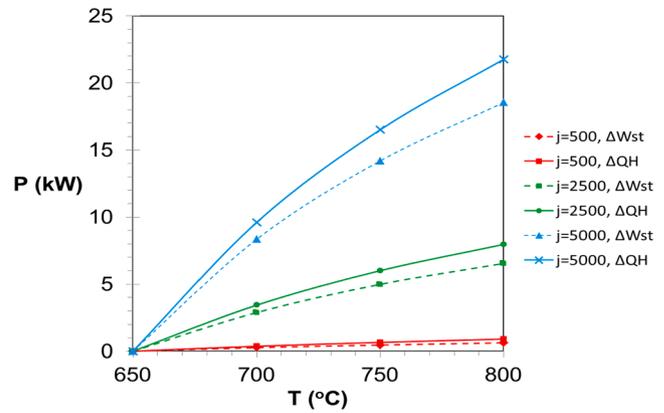


Fig. 8. Change in Hot Utility and Electrical Energy Consumption for various values of current density compared to T = 650 °C (during j-T sensitivity analysis).

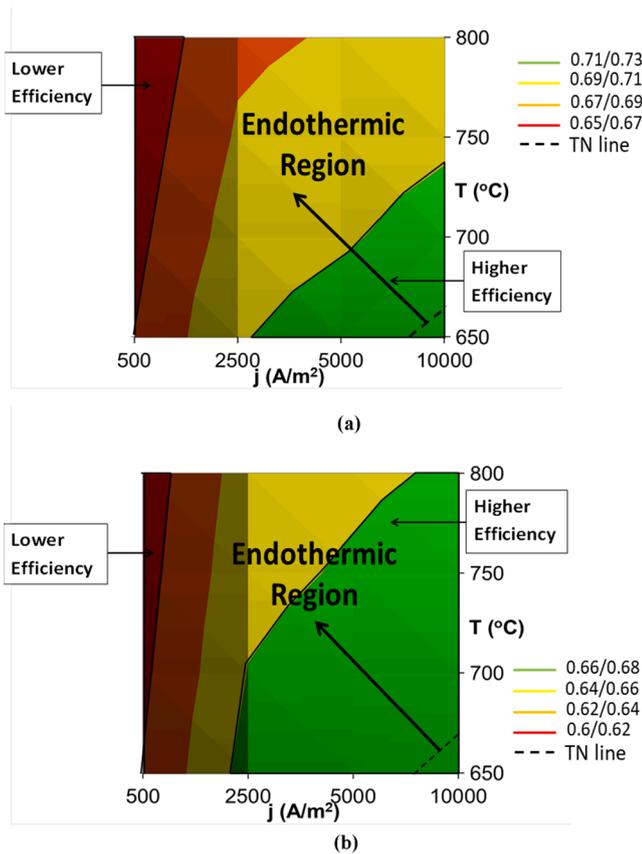


Fig. 7. (a) Exergy, (b) Energy efficiency during Electrolysis mode as a function of rSOC stack pressure and temperature (j-T Sensitivity Analysis) (TN = Thermoneutral).

4.1.1. p-T sensitivity analysis

In Fig. 5, the respective exergy and energy efficiency maps have been drawn for variations in rSOC stack operating pressure (1–10 bar) and temperature (650–800 °C).

The main trends observed by the results are the following:

- It can be observed that a temperature around 675 °C, as indicated by the light blue (a) and green portion (b) of the design maps, energy and exergy efficiency is maximised. According to the results, this is the region where cell voltage is close to the thermoneutral voltage. This is also the point where the sweep gas flow rate was minimal. These results are also documented in Table 2 for the ease of the reader.

- Additionally, operating the system at a pressure of 1 bar, maximizes both efficiencies irrespective of temperature. According to thermodynamics, the efficiency of a recuperative gas turbine increases when the pressure ratio (ratio of outlet and inlet pressure) decreases. It is true that by increasing the stack pressure, the electricity generated by the system turbomachinery also increases, but the increase in hot utility of the entire system overshadows this beneficial effect, leading to reduced efficiencies (as shown in Fig. 6). As an example, when observing green and the dashed green curve which refer to a temperature of 750 °C, it can be seen that hot utility (shown with green curve) increases at a higher rate compared to the increase of generated electricity from turbomachinery (shown with the dashed green curve). The same can be observed for the rest of the temperatures as well.
- As the stack pressure increases, the area of maximum efficiency is narrowed down to around the thermoneutral operation. At high pressures and highly endothermic or exothermic mode (i.e. very high or very low temperature), the efficiency rapidly decreases not only because of high pressure ratios but also due to large flow rates of sweep gas needed for stack thermal management which further increases the hot and cold utility.

4.1.2. j-T sensitivity analysis

A sensitivity analysis for stack temperature (650–800 °C) and current density (500–10,000 A/m²) has been conducted. The results are depicted in Fig. 7.

The main trends observed by the results are the following:

- For sufficiently high current densities (i.e. $j \geq 3000$ A/m²), both efficiencies are entering the higher efficiency area (as shown in the green area). As rSOC stack temperature increases, the higher efficiency area is restricted to high current densities. The reason for this can be explained by the fact that at lower rSOC operating temperature, overpotential losses are very high and operation at low current density is enough to achieve thermoneutral operation. On the other hand, at higher temperatures, overpotential losses are very low and high current densities are required to reach the thermoneutral region.
- When operating current density is kept constant and temperature is increased, the stack electrical power consumption decreases. However, the hot utility increases at a higher rate causing the reduction of both efficiencies (as shown in Fig. 8). As an example, when observing the green and the dashed green curve which refer to a current density of 2500 A/m², it can be seen that hot utility (shown with green curve) increases at a higher rate compared to the decrease of stack

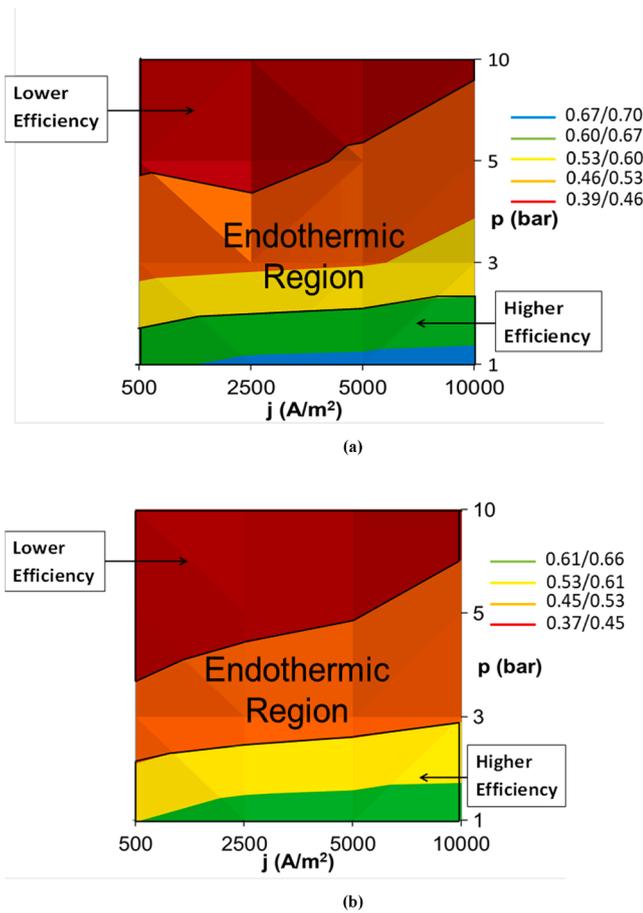


Fig. 9. (a) Exergy, (b) Energy efficiency during Electrolysis mode as a function of rSOC stack pressure and temperature (p-j Sensitivity Analysis).

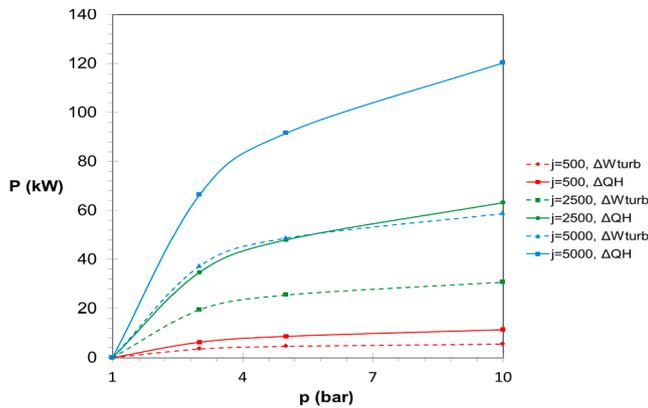


Fig. 10. Change in Hot Utility and Work from Turbomachinery for different current densities compared to pressure of 1 bar (during p-j sensitivity analysis).

power consumption (shown with the dashed green curve). The same can be observed for the rest of current densities.

4.1.3. p-j sensitivity analysis

A sensitivity analysis for stack pressure (1–10 bar) and current density (500–10,000 A/m²) has been conducted. The results are depicted in Fig. 9.

The main trends observed by the results are the following:

- During the whole sensitivity analysis, the stack is in highly endothermic region. By increasing the stack pressure, the pressure ratio of

Table 3
rSOC varying and constant parameters during fuel cell operation.

Sensitivity Analysis	p&T	T&j	p&j
p (bar)	1–10	1.01	1–10
T (°C)	650–800	650–800	800
U_f	0.8	0.8	0.8
J (A/m ²)	10,000	500–10,000	500–10,000
\dot{n}_{H_2O} (mol/s)	0.125	0.0125–0.25	0.0125–0.25

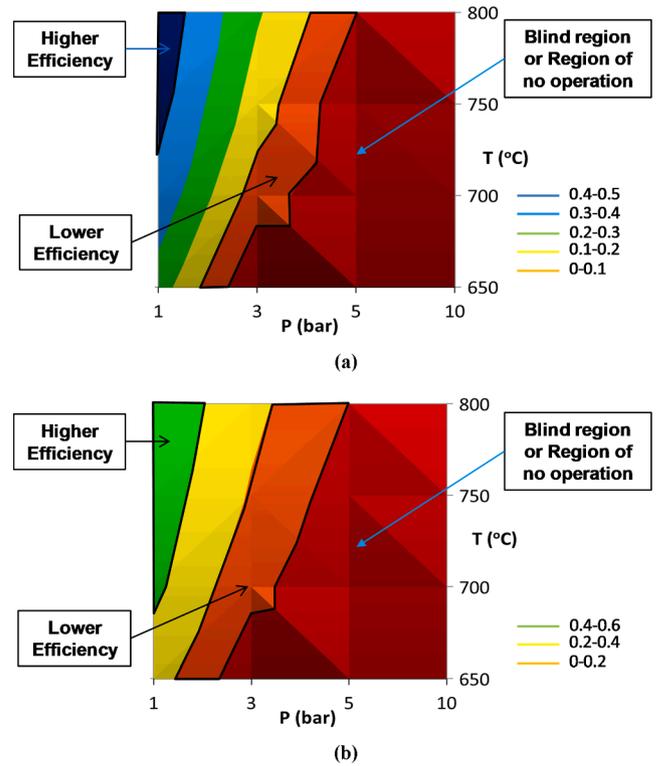


Fig. 11. (a) Exergy, (b) Energy efficiency during Fuel Cell mode as a function of rSOC stack pressure and temperature (p-T Sensitivity Analysis). Note: The RED area in Fig. 11 is a ‘no-operation’ zone or a ‘blind region’ as the system efficiencies are negative.

the recuperated gas turbine is increased and consequently, both exergy and energy efficiency decrease. Despite the higher electricity generation by the turbomachinery at higher stack pressure, increased hot utility overshadows this beneficial effect (as shown in Fig. 10). As an example, when observing the green and the dashed green blue curve which refer to a current density of 2500 A/m², it can be seen that the increase in hot utility (shown with the green curve) increases at a higher rate compared to the increase of generated power by the turbomachinery (shown with the dashed green curve). The same can be observed for the rest of current densities.

- Both efficiencies increase when stack pressure is the lowest which is equivalent to minimum system hot utility and very high current densities, approaching thermoneutral operation as much as possible.
- Finally, as the stack pressure increases and the current density remains constant, electrical power consumption by the stack is also enhanced due to increase of cell voltage. This also has a slightly negative effect in both efficiencies.

4.2. Fuel cell mode

Table 3 summarizes the parameters that were varied during all sensitivity analysis related to the fuel cell operation. The other system parameters were kept constant as given in Appendix B. It must be noted

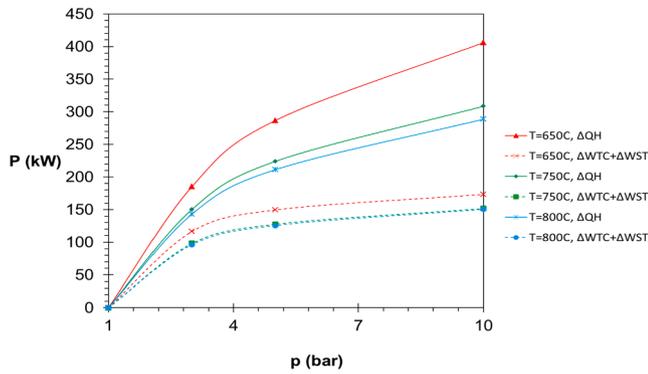


Fig. 12. Change in Work from Turbomachinery and rSOC stack for different temperatures compared to pressure of 1 bar (during p-T sensitivity analysis).

that the methanol (molar) flow rate is equal to the water (molar) flow rate due to stoichiometry of methanol Cold and hot composite curves for the optimum run in electrolysis mode are presented in Appendix E.

4.2.1. p-T sensitivity analysis

In Fig. 11, exergy and energy efficiency maps are drawn for variations in stack operating pressure (1–10 bar) and temperature (650–800 °C).

The main trends observed by the results are the following:

- The lower the pressure, the higher the efficiencies for the whole temperature range. This result is mainly explained due to heightened hot utility at high stack pressures. Hot utility increases due to decreased performance of recuperative gas turbines at high pressure ratios, and therefore, high stack operating pressures. The same phenomenon was observed during electrolytic operation when operating the stack under high pressure and away from thermo-neutral condition. Despite the fact that at higher pressure, more electricity is produced both by the stack and the system turbomachinery, the hot utility increase increases more severely leading to decreased efficiencies and thus although beneficial on a stack level it is detrimental on a system level (see Fig. 12). For example, when looking at 650 °C (red curve and dashed red curve), it is observed that the hot utility (depicted with the red² curve), increases more steeply, compared to the increase in generated electricity from the rSOC stack and system turbomachinery (depicted by the dashed red curve).
- As observed from electrolytic operation of the rSOC stack, the higher the air flow rate, the lower the efficiencies. The same happens during the fuel cell operation. In this case, only exothermic operation takes place and the higher the overpotential losses, the higher is the oxidant flow rate needed to cool the rSOC stack and hence lower the efficiencies. In order to reduce the overpotential losses, higher operating temperatures are required. Higher operating temperature also leads to maximum power production from the rSOC stack.
- For high operating pressures and low temperatures, efficiencies tend to go into the negative zone. This means that the power required for the system BOP is greater than the power produced by the stack and system turbomachinery. The excessive hot utility required for system operation overshadows any power produced by the system, leading to power consumption and thus negative values. It makes no sense to operate the system in these regions and thus should be avoided.

When running a fuel cell at high overpotential losses (i.e. low temperature), excessive air flow is required in order to remove the excess

² For interpretation of color in Fig. 12, the reader is referred to the web version of this article.

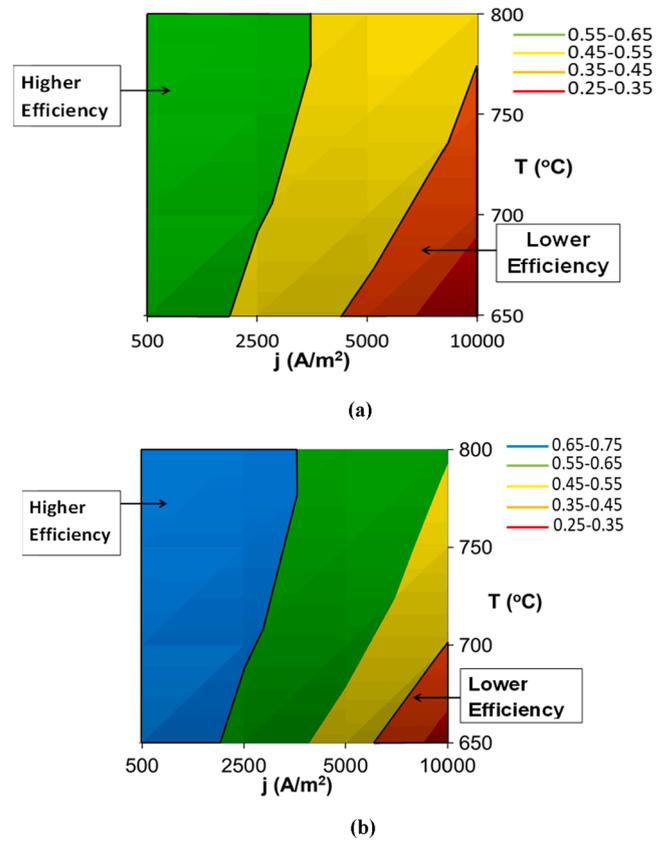


Fig. 13. (a) Exergy, (b) Energy efficiency during fuel cell mode as a function of rSOC stack pressure and temperature (j-T Sensitivity Analysis).

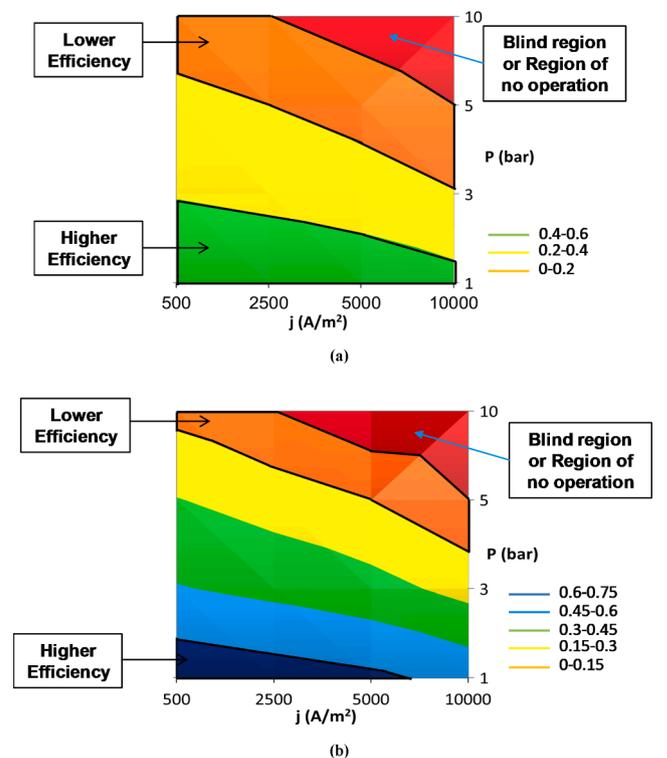


Fig. 14. (a) Exergy, (b) Energy efficiency during fuel cell mode as a function of rSOC stack pressure and temperature (p-j Sensitivity Analysis). Note: The RED area in Fig. 14 is a 'no-operation' zone or a 'blind region' as the system efficiencies are negative.

thermal energy generated and for stack thermal management. At higher pressure, a recuperative gas turbine reduces the heat exchange between hot and cold air stream and the hot utility becomes excessively large. On the contrary, higher pressures are beneficial for fuel cell operation per se since more electricity is produced from the stack, mainly due to increase of reversible voltage (Eq.(2)). The problem at high pressures is the excessive external heat, which in turn leads to negative efficiencies. This could be overcome in situations where heat (of sufficiently high temperature i.e. 1000 °C) is freely available, for example near power plant chimneys, leading to positive and high efficiencies.

4.2.2. *j-T sensitivity analysis*

In Fig. 13 a sensitivity analysis for current density (500–10,000 A/m²) and temperature (650–800 °C) has been conducted.

The main trends observed by the results are the following:

- Operation at high current densities is detrimental for the stack. During this sensitivity analysis, the hot utility remained zero because a large enough portion of the fuel electrode off-gas was sent to the afterburner (18% in molar basis). Despite the fact that at higher current densities both electricity generated by the stack and the system turbomachinery is higher, overall efficiencies drop because the initial flow rates of methanol and water (exergy and energy inlet terms) are higher.
- Additionally, operating the stack at higher temperatures will lead to reduced overpotential losses and therefore reduced air flow rate and higher efficiency. It can be seen that at higher temperature the allowable current density range is larger in order to stay at the higher efficiency area (i.e. 500–3500 A/m²).

4.2.3. *p-j sensitivity analysis*

In Fig. 14, a sensitivity analysis for stack pressure (1–10 bar) and current density (500–10,000 A/m²) has been conducted.

The main trends observed by the results are the following:

- In this case, only exothermic operation takes place and the higher the overpotential losses, the higher the air flow rate needed to cool the rSOC stack and hence, lower efficiencies. Consequently, to lessen the amount of air flow rate, lower current densities will lead to maximum efficiencies
- The lower the pressure, the higher the efficiencies for the whole temperature range. This result is mainly explained due to increased hot utility at high stack pressures. Hot utility increases due to decreased performance of recuperative gas turbines at high pressure ratios, and therefore, high stack pressure. The same trend took place during electrolytic operation when operating under high stack pressure and away from thermoneutral condition

4.3. Roundtrip efficiency

RT efficiency of an rSOC system as been defined by Wendel, Kazempoor and Braun [13] in energy terms is mentioned in Section 3. In order to calculate the energy terms defined in Eq. (13), a relation between the duration of operation in each mode is necessary. Wendel, Gao, Barnett and Braun [18] who modelled rSOC operation with intermediate syngas and methane production assumed a cyclic operation for his system incorporating the equal charge transfer rule. Cyclic operation here refers to the usage of exhaust streams from one mode as input streams for the other mode. In other words, if a certain amount of H₂O molecules were reduced, then the same amount of H₂ molecules were oxidized. This translates into the following equation relating the time of operation in electrolysis mode (*t_{el}*) and in fuel cell mode (*t_{fc}*) respectively (Eq. (20)):

$$q_{fc} = q_{el} \leftrightarrow j_{fc} A_{tot} t_{fc} = j_{el} A_{tot} t_{el} \leftrightarrow j_{fc} t_{fc} = j_{el} t_{el} \quad (20)$$

In the current study, there is no cyclic operation. CO₂, H₂ and H₂O

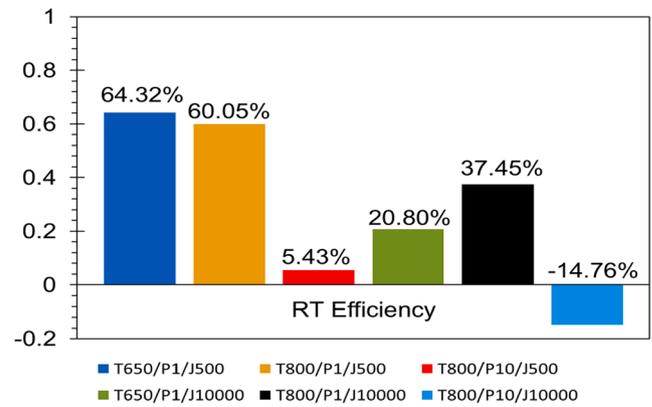


Fig. 15. System RT Efficiency for various conditions (same conditions for both modes).

are provided externally in electrolysis mode while the afterburner exhaust is disposed to the environment. Therefore, the only way to relate the duration of operation between the two modes is to take into account that the amount of methanol produced and stored is equal to the methanol consumed for power generation (Eq. (21)). In other words,

$$\dot{m}_{CH_3OH,el} t_{el} = \dot{m}_{CH_3OH,fc} t_{fc} \leftrightarrow \frac{\dot{m}_{CH_3OH,el}}{\dot{m}_{CH_3OH,fc}} = \frac{t_{fc}}{t_{el}} \quad (21)$$

Therefore in this study, the system RT efficiency will be calculated as follows (Eq. (22)):

$$n_{RT,sys} = \left(\frac{W_{st,fc} - W_{BOP,fc}}{W_{st,el} + W_{BOP,el}} \right) \frac{t_{fc}}{t_{el}} = \left(\frac{W_{st,fc} - W_{BOP,fc}}{W_{st,el} + W_{BOP,el}} \right) \frac{\dot{m}_{CH_3OH,el}}{\dot{m}_{CH_3OH,fc}} \quad (22)$$

Cyclic operation was not taken into consideration for this study, because this would require the use of intense refrigeration systems for the liquefaction and reuse of produced CO₂ after electrochemical oxidation. The authors concurred that this would induce severe exergy losses which would drastically reduce all efficiencies.

RT Efficiency has also been defined for a rSOC stack by Wendel as in Eq. (17). By employing the following modifications, Eq. (23) is obtained.

$$n_{RT,stack} = \frac{V_{fc} q_{fc}}{V_{el} q_{el}} = \frac{V_{fc} j_{fc} A_{tot} t_{fc}}{V_{el} j_{el} A_{tot} t_{el}} = \frac{V_{fc} j_{fc} \dot{m}_{CH_3OH,el}}{V_{el} j_{el} \dot{m}_{CH_3OH,fc}} \quad (23)$$

To limit our study, only system RT efficiencies (Eq. (22)) will be shown when the rSOC stack operates with the same operating conditions for both modes. For example, to obtain the RT eff. of 60.05% (as indicated by the yellow bar), a temperature of 800 °C, a pressure of 1 bar and a current density of 500 A/m² is used for both modes. Fig. 15 shows RT efficiency for various combinations of parameters during operation and the maximum obtained value for RT efficiency is 64.32% which is obtained for a temperature of 650 °C, a pressure of 1 bar and a current density of 500 A/m². An important point to note is that RT efficiency of 64.32% is still the maximum even for dissimilar stack operating conditions between the two modes.

Other observations that can be made from Fig. 15 are the following:

- Operation of both modes at low current density and low pressure will lead to high RT efficiency. Once again, the detrimental role of high pressure is also shown here, but also the beneficial role of low current density which minimizes the air flow during the fuel cell mode (even if electrolytic operation is not thermoneutral).
- It can be seen that for *j* = 500 A/m² (dark blue and yellow bars), lower temperature of operation leads to higher RT efficiency while for *j* = 10,000 A/m² (green and black bars), higher temperatures will lead to higher RT efficiency. This is reasonable since in order to reach closer to thermoneutral operation during electrolysis, lower

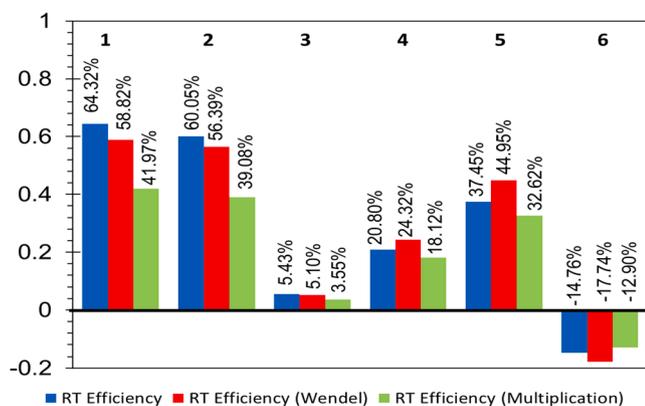


Fig. 16. Comparison of System RT Efficiency (blue) with RT Efficiency definition used by Wendel et al. (red) and RT Efficiency which is equal with the multiplication of exergy efficiency (green) for each mode.

Table 4
Stack operating conditions – Supplementary Information for Fig. 16 and Fig. 17.

Conditions	1	2	3	4	5	6
T (°C)	650	800	800	650	800	800
P (bar)	1	1	10	1	1	10
J (A/m ²)	500	500	500	10,000	10,000	10,000

temperatures will be needed for very low current densities and higher temperatures are necessary for higher current densities.

- By comparing the red and light blue bars the following observations can be made: For the red bar, low current density and high temperature is beneficial for the fuel cell operation, but the detrimental role of high pressure kicks in, limiting RT efficiency to 5.43%. On the contrary for the light blue bar, the higher current density value of 10,000 A/m² combined with high pressure deteriorates system RT efficiency, leading to negative values (-14.76%). Negative RT efficiency means that fuel cell operation leads to a net energy consumption and cannot sustain operation unless an external source of energy is supplied to the system. Operation at negative efficiencies region should always be avoided.

Next, in Fig. 16, a comparison for different efficiency definitions is shown. The blue bars use the definitions of RT efficiency as shown in Eq. (22), the red bars show the RT efficiency for the same process conditions for the definition used by Wendel coupled with the equal charge transfer rule (Eq. (20)) [19] and finally the green column uses a definition of RT efficiency as the multiplication of exergy efficiencies for both modes. It is reasonable that different results occur with each different definition, but all definitions follow the same trend. For example, the highest efficiencies are all clustered in Group 1, while the lowest efficiencies are

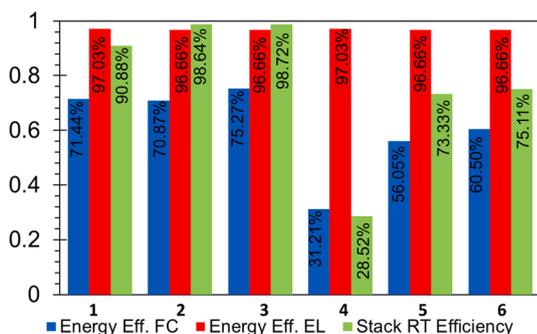


Fig. 17. Stack Energy Efficiency during fuel cell/electrolytic operation and stack RT Efficiency.

clustered in Group 6. The stack operating conditions for each group are summarized in Table 4.

Fig. 17 shows the energy efficiency of only the rSOC stack when operating in the fuel cell mode and electrolysis mode and also the RT energy efficiency of the stack. As one can observe, the RT efficiency of the stack is very high, reaching over 90% for low current densities (500 Am⁻²) and over 70% for high current densities (10,000 Am⁻²). These high RT efficiency numbers pertain to the stack alone and the SOC technology is able to perform very well, reaching the desired targets of 80% RT efficiency set by EES (European Energy Storage) and US DOE (United States Department of Energy).

Answers to research questions

With all the results presented above, the research questions posed at the beginning of the paper can be answered with much more clarity.

- In the event of a methanol based economy in the future, will an rSOC plant based on methanol as fuel be attractive enough from an energy and exergy efficiency point of view?

Methanol is an attractive fuel which can readily be used in the fuel cell operation mode of SOCs. Besides that, 70% of the total methanol produced worldwide is consumed by the chemical industry. So it is also an important industrial chemical. Methanol-to-X results in production of gasoline, olefin, propene and other aromatics which in turn have numerous applications. Methanol and its derivatives such as MTBE, DME and bio-diesel can be blended with gasoline and this in turn serves as a fuel for transportation. Methanol can also be converted to ethanol and then blended with gasoline. Thus, the possibilities are numerous.

For practical reasons, the energy storage plant needs to be analysed from a system point of view and not from a stack point of view. The SOC stack in itself is a wonderful piece of technology and the RT efficiencies are above 70% even when operating at 10,000 A/m². With further developments on the fundamental science aspects of SOCs this number is projected to get higher. When analysing the system as a whole, the energy and exergy efficiency of the plant takes a hit. Let's take a closer look at some of the practical operating conditions at which SOCs need to operate in order to supply enough power in the FC mode and absorb enough power in the EL mode. Temperatures need to be between 750 and 800 °C, operating pressures between 1 and 3 bar and current densities around 7000 A/m² (operating at 10,000 A/m² will be pushing the SOCs to the limit currently). At these conditions, the rSOC plant designed, when operating in electrolysis mode, is able to attain a maximum efficiency (both energy and exergy) of around 73% and an average efficiency of ~65%. When operating in the fuel cell mode, the numbers are 55% maximum efficiency and an average of around 45%. From the point of view of the authors, these numbers seem reasonable when considering the entire plant because BOP and other fuel processing equipment, both upstream and downstream, will have a significant influence on efficiency numbers. These numbers can be taken even higher if some of the recommendations mentioned in points 2 and 3 given below are implemented.

The rSOC system based on methanol as fuel in the fuel cell mode and steam in electrolysis mode attains a RT efficiency of just around 40% and this is way below the RT efficiency target of 80% set by both EES and USDOE but the number set by both these organisations pertain only to the technology itself and not to the whole system. However, one has to bear in mind that in order to attain a RT energy efficiency of 80% on a system level, each mode needs to attain 90% energy efficiency and this can be extremely challenging because the more complex the system is, the higher are the losses at each stage/component. From an investor point of view, building such a plant is attractive enough when the following factors are considered:

- Availability of excess renewable energy which is then used for Power-to-methanol and that in turn is used for methanol-to-X.

- (b) There is a complete ban on use of fossil fuels for reasons of climate change and global warming and transportation still needs liquid hydrocarbon fuels. This way the methanol and its derivatives can be synthesized in a clean way.
2. What are the most thermodynamically favorable conditions for the rSOC plant operation from an energy and exergy point of view?
- In the models presented, where all excess heat removed/added was accomplished through air flow rate regulation, energy and exergy efficiency is maximized when sweep gas/oxidant flow rate is kept at a minimum. In electrolysis mode, the optimum point of operation was the thermoneutral one which almost eliminates sweep gas flow rate. This comes in agreement with the statement from Hansen et al. [8] “the best operating strategy for the SOEC is the thermoneutral mode”. During fuel cell operation, there is no thermoneutral point of operation and therefore lower current density resulted in lower thermal energy generated within the stack which enabled lower oxidant flow.
 - Lower stack pressures increase efficiencies in both modes. The sweep gas/oxidant flow train has been modelled by a recuperative gas turbine model and according to thermodynamics of recuperative gas turbines, the higher their pressure ratio the lower the efficiency due to inefficient heat transfer between the final cooler after the expansion section and the heater before the stack inlet.
 - The air flow rate in fuel cell mode is highly dependent on operating current density and temperature. These two operating parameters regulate overpotential losses and therefore the oxidant flow rate. During sensitivity analyses in fuel cell mode, it was observed that high current densities and low temperatures are detrimental for both efficiencies
 - The air flow rate in electrolysis mode depends on careful selection of the rest of parameters (temperature, pressure, steam flow rate, hydrogen flow rate, current density). When selection of these parameters result in close to thermoneutral operation, it is beneficial for both energy and exergy efficiencies. On the contrary, when a parameter selection results to operation away from thermoneutral (i.e. exothermic or endothermic), both energy and exergy efficiencies decrease
 - In fuel cell mode, inappropriate selection of operating parameters (i.e. low temperature, high pressure and high current density) can lead to negative efficiencies. In this case, the electricity required by the BOP components is higher than the power generation by the stack and the system is no longer able to accomplish its basic function of power generation. These regions of operation should be avoided.
 - The highest energy and exergy efficiency values achieved were 67.94% and 72.30% respectively, for electrolysis mode ($T = 675\text{ }^{\circ}\text{C}$, $j = 10,000\text{ Am}^{-2}$, $p = 1\text{ bar}$)
 - The highest energy and exergy values achieved were 74.14% and 62.61% respectively, for fuel cell mode ($T = 800\text{ }^{\circ}\text{C}$, $j = 500\text{ Am}^{-2}$, $p = 1\text{ bar}$)
 - The maximum RT efficiency achieved for the system is 64.32% when considering operation of both modes at similar operating conditions of temperature, pressure and current density ($T = 650\text{ }^{\circ}\text{C}$, $j = 500\text{ Am}^{-2}$, $p = 1\text{ bar}$).
- It is true that by employing the pinch analysis, the maximum efficiencies will be obtained, but in reality, incorporating a detailed heat exchanger system which will achieve the minimum hot and cold utility in the system might result in a very large heat exchanger network and thus might not be practically feasible. Therefore, in reality, only a certain number of heat exchangers will be placed and the minimum hot and cold utility will not be achieved. This in turn, will impact all efficiencies negatively.
 - It has also been assumed that CO_2 is “free” in the storage tank but in reality, a CO_2 capture system induces an energy and exergy penalty due to reboiler and compression duties. If someone incorporates the CCS system in the thermodynamic study, further efficiency reduction can be expected. However, since CO_2 desorption temperature is kept at low levels (i.e. $120\text{--}140\text{ }^{\circ}\text{C}$), the reboiler duty can be partly covered through internal heat integration. The CO_2 capture system can also be installed after the combusted fuel electrode off-gas in order to sequester and store CO_2 . With this way, the system operation could be carbon neutral since no stream of CO_2 would be disposed to the environment
 - The system RT efficiency has been calculated by using pinch analysis which minimizes hot and cold utility. In reality, a stand-alone system will have higher hot and cold utilities than the minimum values and therefore reduced RT efficiencies. Installing a system near a heat source of sufficiently high temperature (i.e. 1200 K or more) will increase efficiencies even more and will simplify the heat exchanger design. In such a case, the studied system would be viable from a thermodynamic point of view.
 - Finally, in order to achieve a very high RT efficiency, operation at very low current densities for both modes of operation is warranted. This means that this rSOC stack which has a nominal power output of approximately 100 kW , will operate at approximately 6 kW output. What this means is that although operation at lower current densities is beneficial from an efficiency point of view, the stack remains under utilised. The power producing capability (in FC mode) and the power absorbing capability (in EL mode) of the stack is reduced. In order to utilize the stack to its full capability, operation at current densities greater than 5000 Am^{-2} are required but this will have a negative impact in RT efficiency as shown in Fig. 15.
3. What process improvements can be done to improve the efficiency on a system level?
- A way to increase the roundtrip efficiency is to install a latent heat storage system (PCM or any other new technology). In such a scenario, the thermal energy generated during the exothermic operation of the rSOC stack working in fuel cell mode can be stored and later be consumed during operation of the stack in electrolysis mode. With this modification, operation at reduced cell voltages can be accomplished during electrolytic operation without providing tremendous amounts of thermal energy through increased sweep gas flow rates. In other words, the stack electrical energy consumption along with hot and cold utilities can be minimised during steam electrolysis. The challenge here would be the long-term operation of latent heat energy storage device. Despite the fact that latent heat storage is accompanied with high volumetric energy density compared to sensible heat storage, there

Table B1
Constant Parameters along all simulations for both modes.

Electrolysis mode	
N_{cells} (-)	1300
A_{cell} (m ²)	0.01
$p_{SG,in}$ (bar)	1
$T_{SG,in}$ (K)	298.15
$p_{wat,in}$ (bar)	1
$T_{wat,in}$ (K)	298.15
$\dot{n}_{H_2,in}$ (mol/s)	0.01
$p_{H_2,in}$ (bar)	300
$T_{H_2,in}$ (K)	298.15
$p_{CO_2,in}$ (bar)	120
$T_{CO_2,in}$ (K)	298.15
MS reactor	
L (m)	5
N_{tube} (-)	1000
d_{tube} (m)	0.02
ϵ_{cat} (-)	0.5
ρ_{cat} (kg/m ³)	1775
p_{MS} (bar)	100
T_{MS} (K)	520
p_{distil} (bar)	1
Distillation column	
D:R (-)	1.2
D:F (-)	0.485
N_{stage} (-)	30
$T_{aft,out}$ (°C)	1500
$n_{is,C}$ (-)	0.85
$n_{is,T}$ (-)	0.85
n_{mech} (-)	0.98
$x_{H_2O,in}$ (-)	1
$x_{CO_2,in}$ (-)	1
$x_{H_2,in}$ (-)	1
$T_{exh,out}$ (°C)	400
$x_{N_2,in}$ (-)	0.79
$x_{O_2,in}$ (-)	0.21
Purge Fraction (-)	0.01
$p_{out,colwat}$ (bar)	3
$T_{in,colwat}$ (°C)	20
$T_{out,colwat}$ (°C)	22
Fuel cell mode	
N_{cells} (-)	1300
A_{cell} (m ²)	0.01
$p_{Ox,in}$ (bar)	1
$T_{Ox,in}$ (K)	298.15
$p_{meth,in}$ (bar)	1
$T_{meth,in}$ (K)	298.15
$T_{wat,in}$ (K)	298.15
$T_{ref,in}$ (K)	523.15
x_{aft} (-)	0.18
p_{aft} (bar)	1
$T_{exh,out}$ (°C)	400
$p_{out,colwat}$ (bar)	3
$T_{in,colwat}$ (°C)	20
$T_{out,colwat}$ (°C)	22

is limited data on the cyclic performance of such materials [20]. Thermal cycling diminishes system performance after a certain number of cycles. Another difficulty is the heat storage at such high temperature, as well as the availability of heat when needed. Latent heat storage is accompanied with low thermal conductivity

Table A1
Arrhenius Parameters of kinetic constants for methanol synthesis.

$\sqrt{K_{H_2}}$	A	0.499
	B	17.197
K_{H_2O}	A	$6.62 \cdot 10^{-11}$
	B	124.119
$\frac{K_{H_2O}}{K_8 K_9 K_{H_2}}$	A	3453.38
	B	-
$k_{5a} K_2 K_3 K_4 K_{H_2}$	A	1.07
	B	36.696
k_1	A	$1.22 \cdot 10^{10}$
	B	-94.765

and generally it is a slow process and may induce difficulties when switching between the modes where fast responses are required. If a latent heat storage system was installed, then the application of such a system would reduce only to short-term operation with increased RT efficiency.

- Finally, the system can successfully operate at high pressures but only in the case where a heat source of sufficiently high temperature is freely available. The main heat requirement at higher stack pressure is heating of the air stream. Therefore, if the stack operates at 800 °C in endothermic mode where ambient air needs to be heated at 900 °C, then an external heat source of approximately 1000 °C would be necessary. At higher pressures the electrical work from turbomachinery increases while the stack power generation during the fuel cell mode also increases.

- How the use of different efficiency definitions affects the values which in turn has an effect on how a particular technology is perceived.

In a lot of technology presentations, business pitch-ups, research proposals etc. people claim very high efficiencies for a certain technology in order to gain an outcome that is favourable. These high efficiency numbers are then locked into people's mind and the way they perceive a particular technology. Any deviations from these high numbers is immediately met with criticism and might result in either reduced funding or being crossed of the list as a potential solution or stated a simply not good enough. This in turn has ramifications that that particular technology is not able to cross the 'valley of death' and dies out only to be renewed decades later when someone realizes that the definition used was not entirely correct and thus did not present a holistic picture.

In light of the above, the authors have made a conscious effort to put forward different definitions of energy efficiency, as seen in Figs. 16 and 17. The trend followed by using different definitions is the same but the absolute numbers are not. So, in this paper if one were to use the RT efficiency definition of the system as given in Eq. (22) one would get a very high number as opposed to multiplying the efficiency numbers in each mode. The different definitions given are all correct in their own way and thus one has to be really clear in stating the energy efficiency definition when they make a certain claim to their design or prototype. Blindly stating efficiency numbers without actually providing a supporting definition leads to information being misinterpreted in the wrong way and in turn affects the technology and its further development.

The rSOC stack when considered on its own (decoupled from the system) has very high RT energy efficiency and thus presents itself as wonderful energy conversion device. These high numbers when presented to potential investors will make them want to invest in SOC/rSOC technology but this does not present a complete picture as given by the statements presented earlier.

5. Conclusions

This article presented how an energy storage system with the

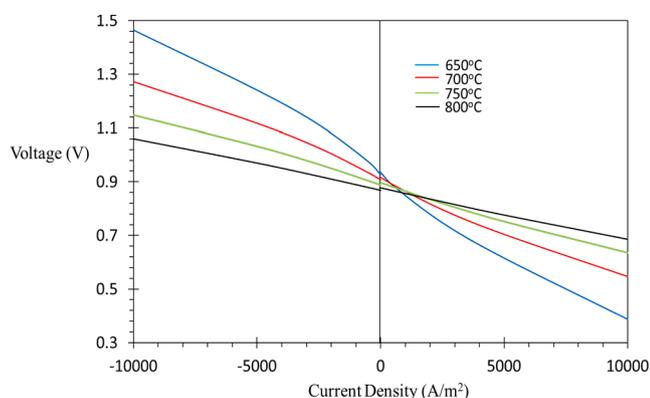


Fig. C1. j-V Curves for rSOC stack for different temperatures ($p = 1$ bar).

reversible solid oxide stack at its core can be realised when methanol is the choice of fuel in the fuel cell mode and steam is electrolysed in the electrolysis mode. It is indeed thermodynamically feasible and practical to realise such a system and it does make sense from both an energy and exergy efficiency point of view to build such systems because the numbers are greater than 50% for many of the operating points. Since the performance of the system greatly depends on the operating parameters/conditions, the authors have provided comprehensive design maps for system energy and exergy efficiencies. These maps are developed with variations in parameters that have the most effect on system efficiency – viz *temperature, pressure and operating current density* and are a collection of a large number of operating parameter set. These maps

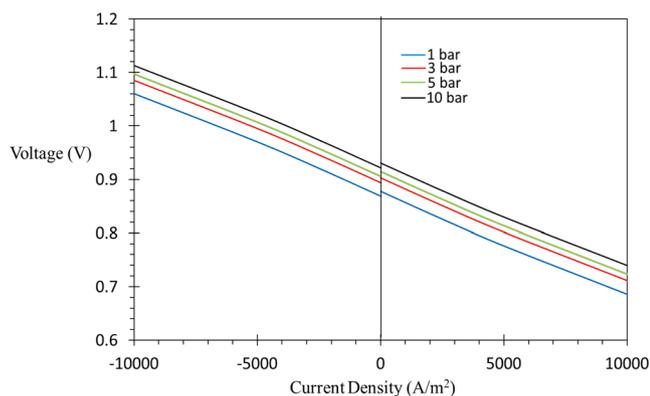


Fig. C2. j-V Curves for rSOC stack for different pressures ($T = 800$ °C). Note: The above polarization curves are based on the model made in Aspen Plus by the authors. The corresponding parameters for the rSOC stack for making the model have been taken from Hauck, Herrmann and Spliethoff [11].

facilitate in providing the reader a quick insight into the high and low efficiency regions of operation.

The highest energy and exergy system efficiency achieved when the system is operating in the *fuel cell* mode is 74.14% and 62.61%. But these are for a specific set of operating parameters with a temperature of 800 °C, an operating current density of 500 A m⁻² and an operating pressure of 1 bar. Operation at higher pressures is beneficial from a stack point of view but not from a system point of view. This is because the hot utility (of the system) increases and outweighs the advantages incurred from pressurized stack operation. Operating the system at current densities over 5000 A m⁻² is preferred so that reasonable amount of power can be gleaned from the stack. For temperature and pressure, a range between 750 and 800 °C and between 1 and 3 bar is preferred. With these set of ranges for T , p and j , the system is able to achieve an energy and exergy efficiency anywhere between 50 and 65% which is still considered very high when compared to conventional fossil-based electricity production systems.

During electrolysis mode, the system is able to achieve a highest energy efficiency of 67.94% and a highest exergy efficiency of 72.3%. Once again this is for a specific operating parameter set of $T = 675$ °C, $j = 10,000$ A m⁻² and $p = 1$ bar. In general, if the temperature of the rSOC (Reversible Solid Oxide stack) stack is kept constant, high efficiencies (both energy and exergy) can be achieved for the entire range of current density from 500 A m⁻² to 10,000 A m⁻² provided system pressures are limited between 1 and 3 bars, as seen from Fig. 9. For electrolysis mode, the preferred operating temperature, to maximise efficiency, lies between 650 and 750 °C and operating pressures higher than 3 bars are to be avoided for the same reasons as given for fuel cell mode operation.

The roundtrip efficiency numbers are very crucial when evaluating a technology. In this paper, a conscious effort has been made to distinguish the stack roundtrip efficiency from the system roundtrip efficiency. At the stack level, roundtrip efficiency of even 98% is achievable when the operating current density is as low as 500 A m⁻² and roundtrip efficiency greater than 75% can be achieved for high current densities of 10,000 A m⁻². At the system level, these numbers drop down to 60% and 37% respectively. Hence, the rSOC technology per se is very efficient. Integration of upstream and downstream processes with the rSOC technology brings down the total system efficiency and thus the roundtrip efficiency.

There is an urgent need for the world to shift its operations from fossil fuels to alternate sources. A hydrogen-based economy where all operations are free from fossil fuels seems to be far-fetched although doable. In order to get there, the world has to go through intermediate steps or a transition stage and a methanol-based economy could potentially be a solution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

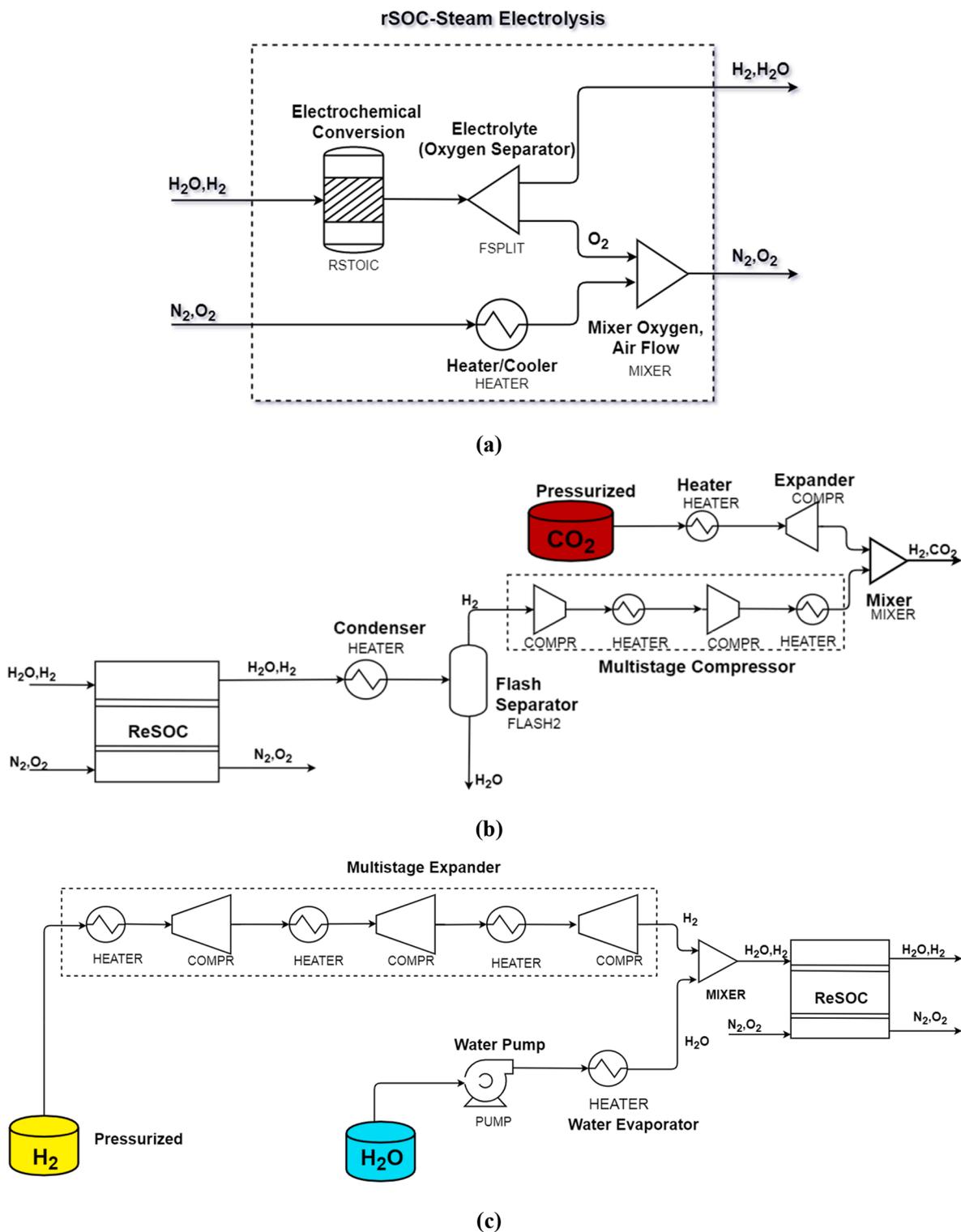


Fig. D1. (a) rSOC stack - Electrolysis, (b) Preparation for Methanol Synthesis, (c) Feed Preparation to rSOC stack, (d) Methanol Synthesis Loop, (e) Methanol Synthesis loop and final separation steps, (f) Air flow train.

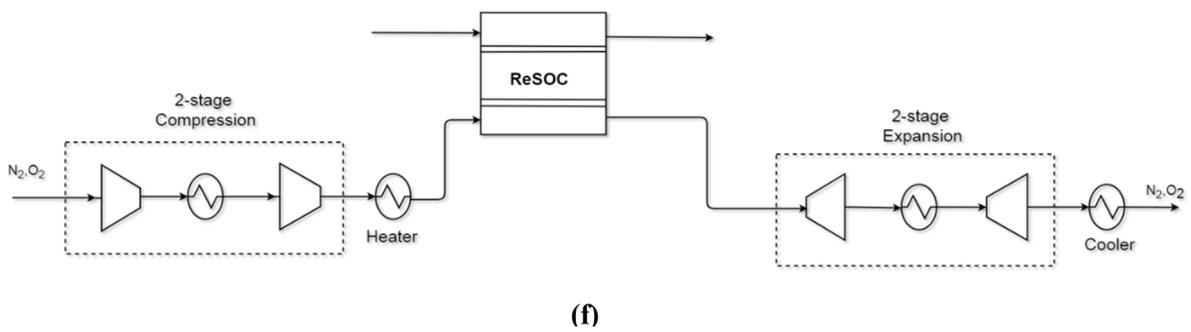
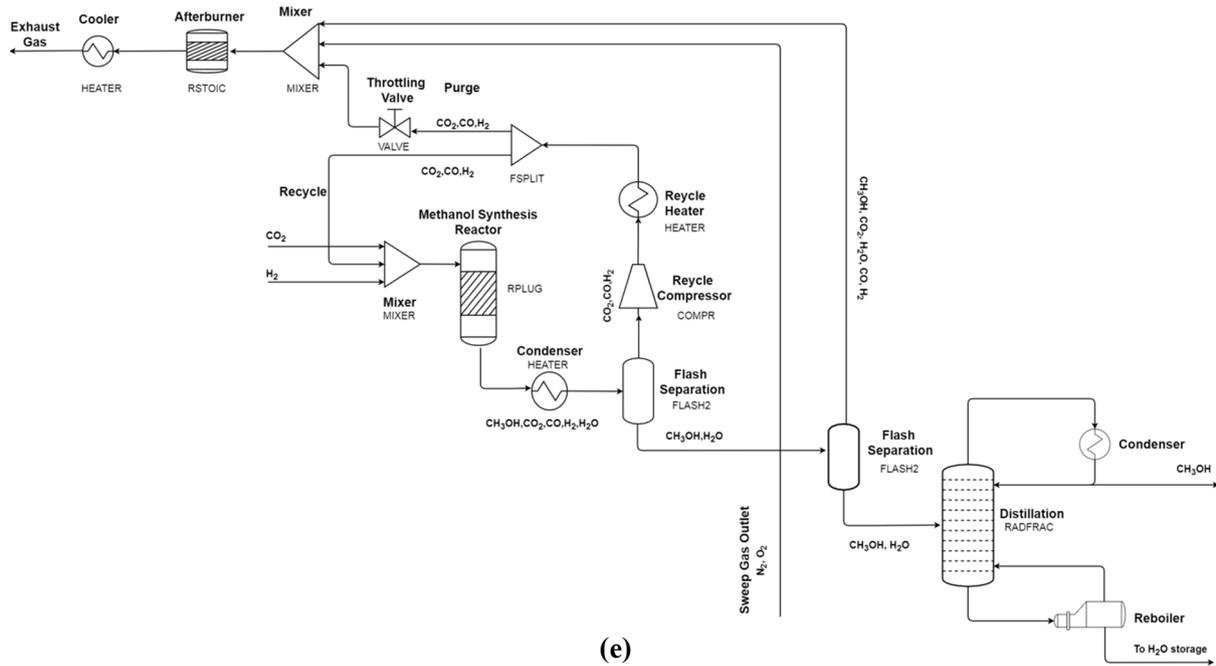
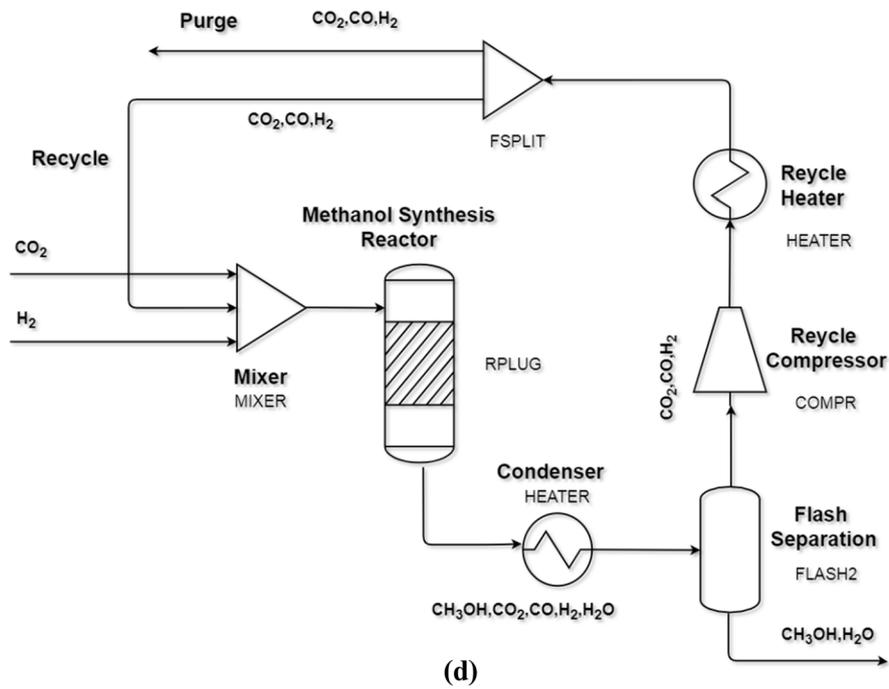
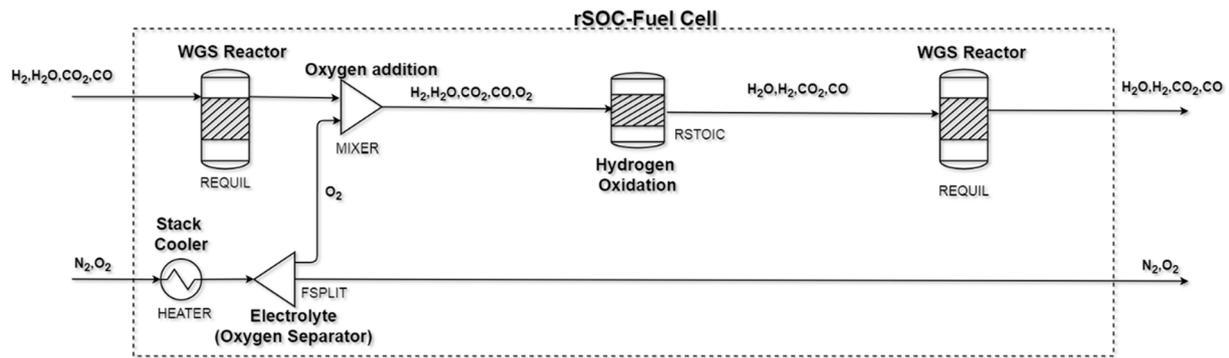
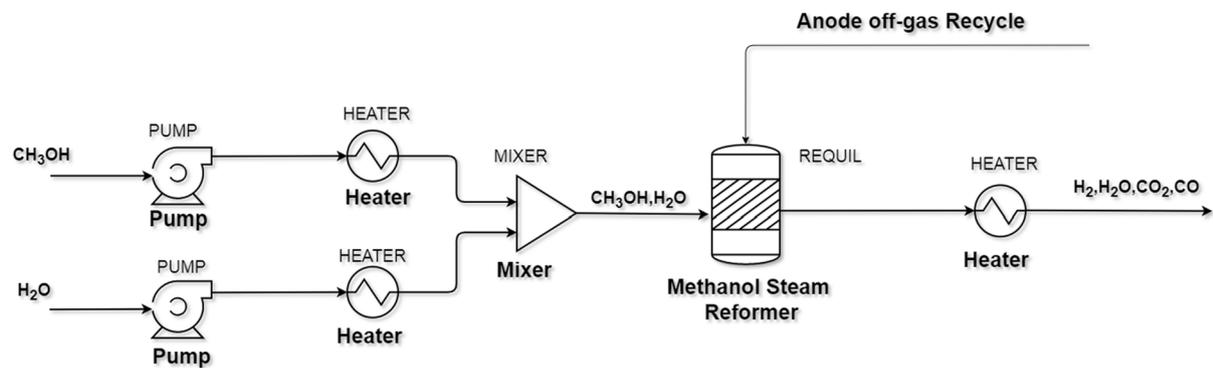


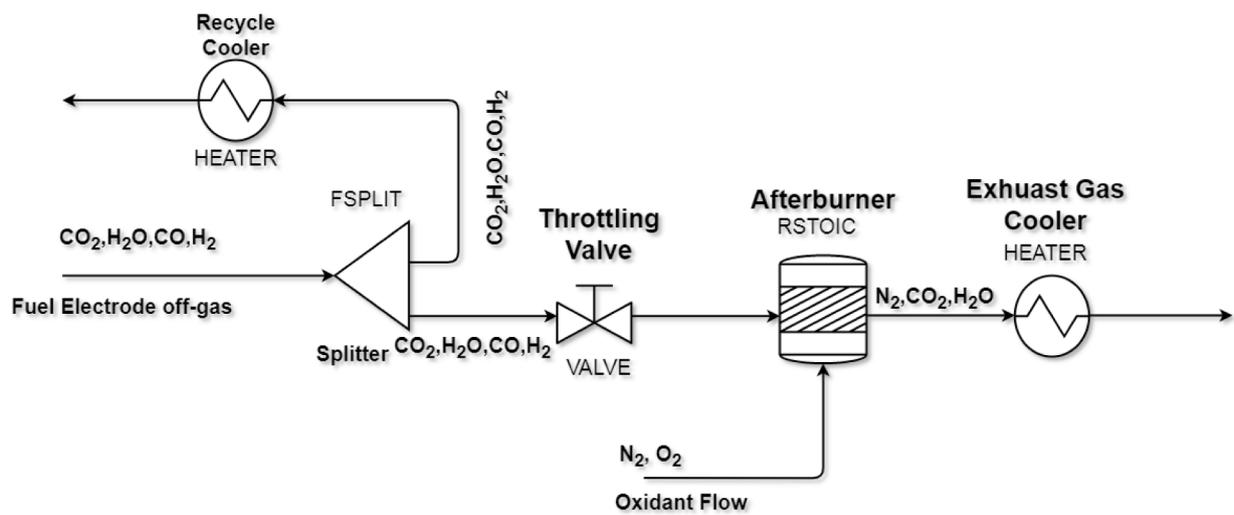
Fig. D1. (continued).



(a)

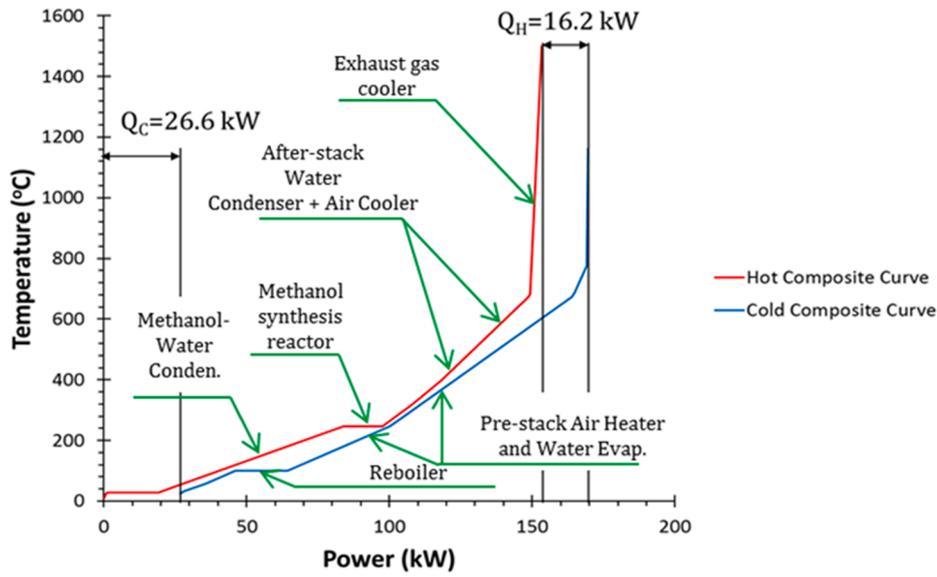


(b)

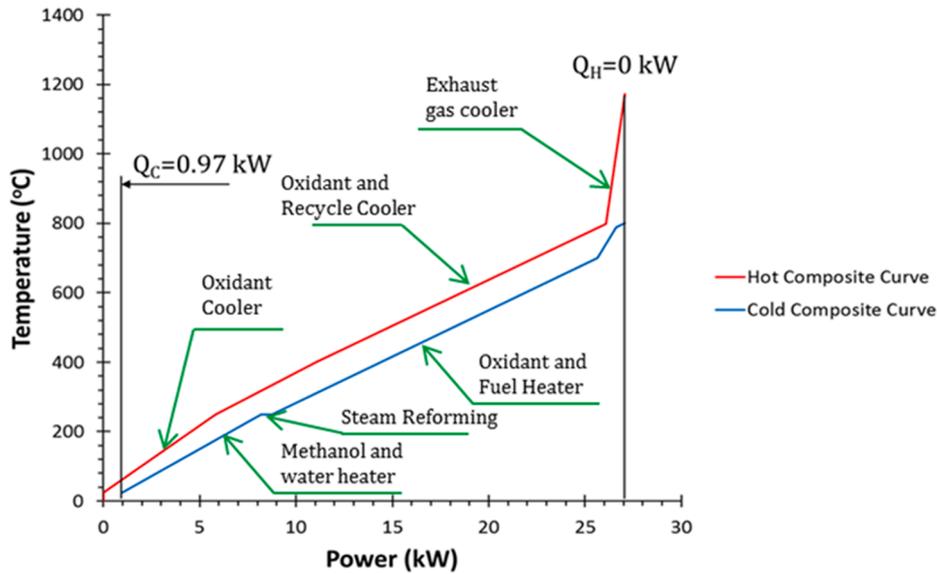


(c)

Fig. D2. (a) rSOC stack - Fuel Cell modelling, (b) Feed preparation and methanol reforming step, (c) Fuel electrode off-gas treatment.



(a)



(b)

Fig. E1. Hot and Cold Composite Curves for the optimum run (a) Electrolysis mode, (b) Fuel Cell mode.

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Appendix A. Methanol synthesis kinetic model

The model is summarized in Eq. (B1) and Eq. (B2):

$$r_{MeOH} = \frac{k'_5 K'_2 K'_3 K_4 K_{H_2} P_{CO_2} P_{H_2} \left[1 - \left(\frac{1}{K} \right) \frac{P_{H_2O} P_{CH_3OH}}{P_{H_2}^3 P_{CO_2}} \right]}{\left(1 + \frac{K_{H_2O}}{K_8 K_9 K_{H_2}} \frac{P_{H_2O}}{P_{H_2}} + \sqrt{K_{H_2}} P_{H_2} + K_{H_2O} P_{H_2O} \right)^3} \tag{B1}$$

$$\Gamma_{RWGS} = \frac{k_1 P_{CO_2} \left[1 - K_3 \frac{P_{H_2O} P_{CO}}{P_{CO_2} P_{H_2}} \right]}{1 + \frac{K_8 K_9 P_{H_2O}}{K_8 K_9 K_{H_2}} \frac{P_{H_2O}}{P_{H_2}} + \sqrt{K_{H_2} P_{H_2}} + K_{H_2O} P_{H_2O}} \quad (B2)$$

where the values depicted in Table A1 are used. Those values correspond to the preexponential factor and the activation energy of the Arrhenius equation (Eq (B3)):

$$k(i) = A(i) e^{\frac{B(i)}{RT}} \quad (B3)$$

Appendix B. Fixed parameters

In the current Appendix all parameters which remained fixed during each mode of operation are shown along with their values in Table B1.

Appendix C. j-V curves

Fig. C1 and Fig. C2 show j-V curves for rSOC stack when varying temperature ($P = 1.01 \text{ bar} = \text{constant}$) and pressure ($T = 800 \text{ }^\circ\text{C} = \text{constant}$).

Appendix D. Modeling approach

D.1. Equations for modelling rSOC in electrolysis mode

In the case of steam electrolysis, the overall reaction taking place is the following (Eq. (D1)) [21]:



Regarding the stack model, the change in enthalpy (ΔH) and the change in Gibbs free energy (ΔG) are calculated according to National Institute of Standards and Technology (NIST) [22]. At first, the reversible voltage (V_N) is estimated according to the Nernst equation (Eq. (D2)), by using the stack inlet composition for both streams.

$$V_N = \frac{\Delta G}{zF} + \frac{RT}{zF} \ln \left[\left(\frac{x_{H_2} x_{O_2}^{1/2}}{x_{H_2O}} \right) \left(\frac{P}{P_0} \right)^{1/2} \right] \quad (D2)$$

For the estimation of each type of losses, the model provided by Hauck, Herrmann and Spliethoff [11] was used and thereafter, the cell voltage (V_c) was calculated. Finally, the electrical power consumption (W_{st}) and the total power requirement for electrolysis ($P_{st,tot}$) during electrolysis mode were estimated as shown (Eqs. (D3) and (D4)):

$$W_{st} = N_c V_c i A_c \quad (D3)$$

$$P_{st,tot} = U_{f,st} \dot{n}_{H_2O} \Delta H \quad (D4)$$

where $P_{st,tot}$ is the total energy input to the rSOC stack during electrolysis, W_{st} is the electrical energy that is provided to the rSOC stack and the remaining energy to be supplied or removed depends on the operating region. Three different cases can be discerned.

- **Endothermic Operation** ($W_{st} < P_{st,tot}$): In this case, the extra energy needed for electrolysis needs to be provided by means of heat or electricity.
- **Exothermic Operation** ($W_{st} > P_{st,tot}$): In this case, excess electrical energy is dissipated as heat which needs to be removed from the rSOC stack.
- **Thermoneutral Operation** ($W_{st} = P_{st,tot}$): In this case, the electrical energy provided matches the total energy requirements for electrolysis and no energy needs to be provided or removed.

In all cases, during electrolysis, the necessary heat addition or removal is provided by the air stream. This is so far the only means of thermal management in an SOC stack. According to Wendel et al. [16], during fuel cell operation, the air stream enters the stack at 60–200 °C below the stack temperature. In the current study, if the mode of operation is endothermic, heat needs to be supplied and the air stream enters the stack at a temperature which is 100 °C above the stack temperature. The exact opposite happens for the exothermic mode of operation (i.e. 100 °C lower than stack temperature).

For stack modelling, during electrolysis, the stack model used by Rivera-Tinoco, Farran, Bouallou, Aupretre, Valentin, Millet et al. [2] was employed. The main components of the model are:

- **Stoichiometric reactor**: In this reactor, the reaction at the fuel electrode takes place with a user-defined steam utilization.
- **Splitter block**: The splitter block is responsible for the separation of oxygen. It substitutes the role of the electrolyte which represents the transport of oxide ions from the fuel electrode to the oxygen electrode. It is assumed that oxygen is completely separated and transported to the oxygen electrode. The other stream from the splitter consists of a H_2O - H_2 gaseous mixture.
- A mixer is used to simulate the mixing of generated oxygen with the air stream for oxygen removal.

D.2. Methanol synthesis

Isothermal reactors usually ensure higher methanol productivity, longer catalyst lifetime, lower byproducts and more economic operation since it

includes a less intense recycle loop. The most commonly used type of isothermal reactor is the *Lurgi* reactor, which is similar to a shell and tube reactor [23]. The catalyst is placed in the tubes and water-steam acts as the cooling medium, which is placed in the shell. The methanol synthesis reactor has been modelled with the built-in model of a plug flow reactor in Aspen Plus™ since methanol synthesis takes place on multi-tubular reactors (i.e. isothermal). Methanol synthesis is a reaction which usually takes place at pressures of 50–100 bar and temperatures of 220–290 °C, while the most commercial catalyst used is Cu/ZnO/Al₂O₃ [24]. The main reactions taking place are the following (Eqs. (D5)–(D7)) [25]:



Again, there is an ambiguity on whether the methanol synthesis is initiated by CO or CO₂ hydrogenation and a number of studies for the kinetic equations have been proposed not only with regard to the substance which is hydrogenated but also the type of catalyst. In this study, the kinetic equations proposed by Vanden Bussche and Froment [26] are utilized. These equations are based on Cu/ZnO/Al₂O₃ catalyst and on the assumption that CO₂ hydrogenation is dominant during methanol synthesis. These reactions are elaborated in Appendix A.

D.3. Methanol steam reforming

Methanol is advantageous in terms of reforming temperature. Compared to other fuels, such as methane, which are reformed at high temperatures (i.e. 700 °C), methanol is reformed at a temperature range of 200–300 °C [27], which translates into lesser heating of the feed stream and thus lower hot utility. Of course, methanol can be also reformed at higher temperatures. This will translate in lesser carbon deposition rates and faster reaction kinetics, but more heat needs to be supplied to the feed stream. It is also possible to internally reform methanol in the fuel electrode during fuel cell operation. However, according to Laosiripojana and Assabumrungrat [28], methanol cannot be reformed internally (i.e. in the fuel electrode) without carbon deposition unless operating temperatures are above 900 °C. Since rSOC temperature range of 650–850 °C is investigated in this study, as this is the operating window for most stacks, an external low-temperature reformer was utilized. Water-gas shift (WGS) reaction also takes place during methanol steam reforming and low temperatures lead to increased CO₂ content at the outlet. Methanol steam reforming has been modelled by the use of the following reactions (Eq. (D8)–(D10)) [27]:



D.4. Equations used for modelling rSOC in fuel cell mode

In the case of hydrogen oxidation, the overall reaction taking place is shown below (Eq. (D11)) [13]:



Fuel cell operation is always exothermic. The model provided from Hauck et al. [11] is also utilized in this study for the estimation of overpotential losses and the estimation of V_{cell} . Again, the thermal power to be removed is calculated by a subtraction of the electrical power generated by the stack from the total energy liberated from electrochemical oxidation of hydrogen while also taking into account the heat duties related to water-gas shift/reverse water-gas shift (WGS/RWGS) reactions. This heat is removed by means of an air flow rate which enters the stack at 100 °C lower than stack temperature.

In this specific study, since the input to the fuel cell operation is carbonaceous, there is oxidation of two species, namely, hydrogen (H₂) and carbon monoxide (CO). Additionally, nickel is known to be an active catalyst for the WGS/RWGS and therefore this reaction must also be taken into account. In the scientific community there is an ambiguity on the effect of CO oxidation due to the “slowness” or “sluggishness” of the reaction and therefore, in this study, it has been neglected [11,29,30].

Regarding the fuel cell operation, the stack has been modified accordingly in order to incorporate the WGS/RWGS reaction. Since WGS/RWGS dominates, the fuel electrode stream has been modelled with two equilibrium reactors and a stoichiometric reactor in between, accounting only for H₂ oxidation and power production according to the model of Barelli, Bidini and Ottaviano [31]. CO oxidation has been neglected in this study and its conversion to CO₂ occurs only via the WGS route. In the model, a calculator block is used to calculate the stoichiometric quantity of oxygen needed to be transferred from the oxidant stream to the fuel stream.

The fuel composition at stack inlet is rich in CO₂. Finally, the fuel utilization is defined as hydrogen utilization since it is the only chemical component which is electrochemically oxidized.

D.5. Sweep gas & oxidant flow rate

An air flow is used for thermal balancing of the rSOC stack during both modes. Apart from thermal balancing, the air flow is necessary in order to supply the necessary oxidant during fuel cell operation. In both cases, the flow is compressed and heated prior to the stack, while it is expanded and cooled down after the stack. During the expansion train, only the necessary air flow is driven to the afterburner, as shown in Fig. 2 & Fig. 3. A calculator block is used for the estimation of the stoichiometric oxidant flow, which is drawn from the air stream.

D.6. Construction of the rSOC plant in Aspen Plus

The reactors and the unit operations used for modelling the rSOC plant in Aspen Plus™ are as follows:

D.6.1. Electrolysis mode

- The rSOC stack during electrolytic operation has been modelled with a 'RStoic' block which represents the electrochemical conversion of high-temperature steam to hydrogen. The oxygen which needs to be removed is separated from the stream with a 'FSplit' block while it is mixed with the sweep gas stream by using a 'Mixer' block.
- The methanol synthesis reactor has been modelled with a 'RPlug' block.

D.6.2. Fuel cell mode

- The rSOC stack during fuel cell mode has been modelled as follows. First, the modelling of fuel electrode is initiated with an 'REquil' block where WGS/RWGS reactions take place. Afterwards, the required stoichiometric quantity of oxygen is mixed with the resultant stream and led to the 'RStoic' block where electrochemical oxidation of hydrogen takes place. The resultant stream has no oxygen and passes through another 'REquil' reactor where WGS/RWGS takes place. The air flow has been modelled with a 'Heater' block and a 'Sep' block which separates the stoichiometric quantity of oxygen required for the reaction.
- The methanol steam reforming reactor has been modelled with an 'REquil' block.

D.6.3. Miscellaneous balance of plant components

- All heaters and coolers have been simulated with 'Heater' blocks. For the internal heat integration of the system, pinch analysis has been employed to estimate the lowest value of hot and cold utility. Pinch analysis is performed by utilizing Aspen Plus™ in tandem with Aspen Energy Analyzer™.
- Afterburners have been simulated by using the 'RStoic' block with combustion reactions.
- For pressure reduction, 'Valve' blocks have been utilized.
- Compressors and turbines have been simulated by using the 'Compr' block and specifying the isentropic and mechanical efficiency.
- For vapour-liquid separation, the 'Flash2' block from Aspen library has been used.
- For the distillation column, a first estimation of the number of stages, reflux ratio and distillate to feed ratio was obtained by using a shortcut distillation column ('DSTWU' block). Thereafter, these parameters were refined using the rigorous distillation model ('RadFrac' block) in order to attain methanol purities greater than 99% at all times.

Process modeling schematics for both modes of operation are given in Fig. D1 for electrolysis mode and Fig. D2 for fuel cell operation.

Appendix E. Hot and cold composite curves for both modes (optimum run)

See Fig. E1.

Appendix F. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apenergy.2020.115623>.

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