

# INTEGRATED ENERGY SYSTEM FOR THE PRODUCTION AND USE OF RENEWABLE METHANOL VIA ALKALINE ELECTROLYSIS AND SOLID OXIDE FUEL CELLS

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## ABSTRACT

The conversion of renewable hydrogen and recycled CO<sub>2</sub> to valuable fuels in power-to-liquids (PtL) systems could help mitigate the negative effects of CO<sub>2</sub> emissions. Within this context, methanol is a promising candidate, both as an energy carrier and a chemical feedstock.

This paper is focused on renewable methanol production and its use in a PtL integrated system based on alkaline water electrolysis, high temperature solid oxide fuel cells, a thermal energy storage system and an organic Rankine cycle (ORC) engine. Detailed models of the main subsystems were developed and implemented by using Aspen Plus software. A comprehensive analysis via mass and energy balances was carried out to evaluate performance indexes of each section and of the overall plant for two different configurations: with and without the ORC engine.

**Keywords:** alkaline electrolysis, methanol, CO<sub>2</sub> hydrogenation, energy storage, power-to-liquids, decarbonisation

## NOMENCLATURE

### *Abbreviations*

AEL	Alkaline electrolyser/electrolysis
BOP	Balance of plant
MSS	Methanol synthesis section
ORC	Organic Rankine cycle
PtL; PtX	Power-to-liquids; power-to-X
RES	Renewable energy sources
RSOC	Reversible solid oxide cell
SOFC	Solid oxide fuel cell
TES	Thermal energy storage

## 1. INTRODUCTION

Given the growing concerns relating to CO<sub>2</sub> emissions, research on new systems aimed at the decarbonisation of society is assumed to be of fundamental importance. Power-to-X (PtX) technologies represent a way to reduce the impact of CO<sub>2</sub> emissions in many different sectors (transportation, power generation, residential, industry and chemicals), while boosting renewable energy sources (RES) penetration and reliability. This work is focused on the conceptual design and analysis of an integrated energy storage system to produce and use renewable methanol. In such a system, renewable hydrogen from water electrolysis is converted to chemicals characterised by higher energy density via a conversion reaction with recycled CO<sub>2</sub>.

Methanol is a well-known fuel with many different uses as a chemical and energy feedstock [1–3]. It is a liquid at ambient conditions and is characterised by high energy density, by both weight and volume, resulting in a good energy storage medium, being unaffected by long-term decomposition or energy loss. Moreover, it can be used as a chemical feedstock to produce a wide variety of chemicals typically derived from fossil fuels, such as formaldehyde, acetic acid, dimethyl ether, gasoline, diesel and others [4]. Numerous studies regarding various PtX and power-to-liquids (PtL) systems based on different technologies and approaches can be found in the literature (e.g. [5–10]).

In this study, methanol is produced by an excess of electricity generated from RES (“charge phase”), stored at ambient conditions and reused by producing electricity to level out peak demand. Excess renewable energy (e.g. solar and wind) feeds an alkaline electrolyser (AEL) to produce hydrogen. Hydrogen and

CO<sub>2</sub> react in a methanol synthesis reactor to produce methanol for feeding a solid oxide fuel cell (SOFC). Heat recovery and thermal integration of the overall system are necessary to obtain optimal operating conditions and energy savings in each section. The proposed integrated energy system, based on commercially relevant AEL technology, was developed from a previous system studied by the same authors, in which methanol is produced and reused through innovative high temperature and reversible solid oxide cells (RSOC) [11]. Mass and energy balances were carried out to evaluate the performance indexes of each subsystem and of the entire plant. Functional schemes and simulation models were developed and implemented using the Aspen Plus software and its features. Two different configurations were studied: an AEL system coupled to a SOFC system and AEL coupled to an integrated SOFC-ORC (organic Rankine cycle) system, where residual heat released by the SOFC exhaust gases is exploited to boost electricity generation during the methanol utilisation phase (“discharge phase”). A comparison of the results with those from the previous work was carried out.

## 2. SYSTEM CONFIGURATION AND MODELS

### 2.1 Overall system configuration

The overall system is composed of the following sections and subsystems: an AEL, a methanol synthesis section (MSS), an SOFC, an ORC engine, a thermal energy storage (TES) system and a heat integration section comprising heaters to boot the system. Figure 1 shows a simplified functional scheme for the overall system. Water and renewables feed the AEL to produce hydrogen. Hydrogen and CO<sub>2</sub> are compressed at the operating pressure of the methanol synthesis reactor in two intercooled compressor trains. Methanol is produced in the MSS through CO<sub>2</sub> hydrogenation over a commercial catalyst (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) and purified in a distillation column. During the discharge phase, methanol is reformed and oxidised in the SOFC to produce electricity, while exhaust gases, rich in H<sub>2</sub> and CO, are burnt in a post combustor. Heat released by the SOFC is either stored in a TES device or supplied to an ORC engine and then stored. The heat stored during the discharge phase is mainly used to provide thermal energy for the reboiling process in the methanol distillation column during the charge phase.

The system and its sections were designed to produce about 600 kg/h of methanol (based on the George Olah Plant located in Iceland as it is the only

existing commercial renewable methanol plant [12,13]. Such methanol production results in power absorption of about 5.3 MW (charge phase) and power production of about 1.5 MW (discharge phase).

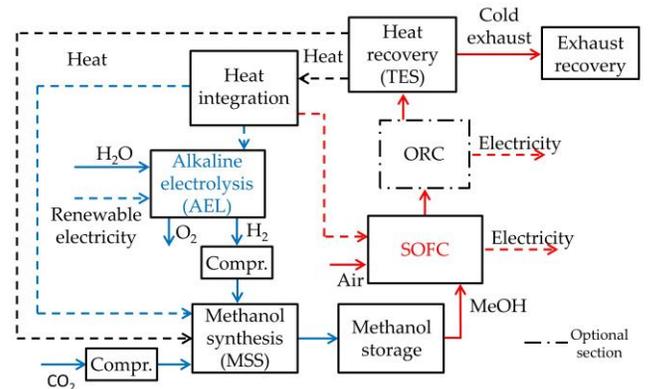


Fig 1 Simplified functional scheme of the overall system

### 2.2 Main sections, operating parameters, and models

#### Alkaline electrolysis

Alkaline electrolysis is performed at ambient pressure and 65 °C, since under these conditions efficiency reaches the highest value. To obtain the desired methanol production, a water flowrate of about 1080 kg/h is required. The resulting hydrogen production is about 120 kg/h (1360 Nm<sup>3</sup>/h).

The model of the AEL was adapted from the electrochemical model developed by Ursua and Sanchis [14] for simulating commercial water AELs. In particular, a module of 37 parallel lines, each consisting of 33 stacks in series, was considered. A specific energy consumption of approximately 44 kWh/kg<sub>H<sub>2</sub></sub> (3.9 kWh/Nm<sup>3</sup><sub>H<sub>2</sub></sub>) was found, which was consistent with values reported in the literature [14,15].

#### Methanol synthesis

Hydrogen and CO<sub>2</sub> are compressed to the operating pressure of the methanol reactor (65 bar) by means of two trains of intercooled compressors. The inlet flow is preheated to the reactor inlet temperature, which is assumed to be equal to 210 °C [16]. In an adiabatic reactor, the exothermicity of the CO<sub>2</sub> hydrogenation reaction leads to an outlet temperature of about 290 °C. Heat exchangers and flash processes within the MSS allow the recovery of heat and the recycling of unreacted gases from the reactor outlet before purification. About 290 kW of external heat are required for water reboiling in the distillation column. This heat is harvested from the SOFC exhaust gases and stored during the discharge phase. Assuming a molar ratio equal to the stoichiometric one, a hydrogen

production of 120 kg/h requires about 880 kg/h of CO<sub>2</sub> to produce 600 kg/h of methanol. The properties, characteristics, and models of the MSS are described extensively in Lonis et al. [11].

#### *Solid oxide fuel cell*

The SOFC operates at a temperature of 850 °C and atmospheric pressure. The stored methanol is mixed with water, sent to the SOFC, vaporised and reformed to obtain a gas mainly composed of hydrogen. Assuming the same duration for the charge and discharge phases, SOFC methanol flow rate is set equal to methanol production in the MSS, while water flowrate depends on the desired steam-to-carbon ratio in the reformer. Within the SOFC, hydrogen is oxidised to produce electricity assuming a fuel utilization factor of 0.85. Residual gases (mainly H<sub>2</sub> and CO) are burnt in a post combustor, reaching a temperature of about 980 °C, and subsequently cooled to preheat the air entering the cell. Residual heat released at about 380 °C is either directly stored in a TES system or supplied to an ORC engine prior to being stored in the TES system at about 195 °C. A comprehensive description of the mathematical and electrochemical models, and of the operating parameters of the SOFC are found in Lonis et al. [11].

#### *Organic Rankine cycle*

Coupling an ORC to the SOFC allows enhanced electricity production, exploiting the heat released by the SOFC. An ORC engine is a relatively simple and low-cost power system using low grade thermal heat (usually below 350 °C). Typically, it is composed of an evaporator, a turbine, a condenser, a pump, and a regenerator [17]. In this study, since the hot circuit is at atmospheric pressure, a separate thermal oil circuit is not necessary. Thus, the ORC working fluid is directly heated up by the SOFC hot gases. A comparison between some of the typical working fluids (benzene, toluene, and butylbenzene [18,19]) was carried out. Benzene was found to be the most convenient (consistently with [19]), due to both its high critical pressure (48.9 bar) and low critical temperature (289 °C) [20].

In the proposed configuration, the ORC system was designed to set an outlet temperature of the exhaust gases equal to 195 °C; they are subsequently required to provide heat to the reboiler of the MSS. Globally, the ORC allows the recovery of approximately 770 kW. An operating temperature of 290 °C and of 46.5 bar, respectively, and a condenser pressure slightly higher

than 0.2 bar were assumed. The regenerator allows an internal recovery of waste heat equal to about 143 kW, increasing the working fluid temperature to 92 °C before the evaporator. The turbine produces 236 kW, while the pump absorbs about 7.5 kW.

### 2.3 Performance indexes

To evaluate and compare the system performance in both configurations, performance indexes were developed, as extensively described in Lonis et al. [11].

Electrolysis efficiency  $\eta_{AEL}$  is defined by (1):

$$\eta_{AEL} = \frac{\dot{m}_{H_2} \cdot H_{i,H_2}}{P_{AEL} + P_{BOP,AEL}} \quad (1)$$

where  $\dot{m}_{H_2} \cdot H_{i,H_2}$  is the chemical power of the produced hydrogen,  $P_{AEL}$  and  $P_{BOP,AEL}$  are the electric power required by the AEL and by its auxiliaries, respectively.

Similarly, SOFC efficiency  $\eta_{SOFC}$  is defined by (2):

$$\eta_{SOFC} = \frac{P_{SOFC} - P_{BOP,SOFC}}{\dot{m}_{MeOH} \cdot H_{i,MeOH}} \quad (2)$$

where  $P_{SOFC} - P_{BOP,SOFC}$  is the net SOFC electric power output (net of the SOFC auxiliaries) and  $\dot{m}_{MeOH} \cdot H_{i,MeOH}$  is the chemical power of the methanol supplied to the SOFC.

The MSS overall efficiency  $\eta_{MSS}$  is defined by (3):

$$\eta_{MSS} = \frac{\dot{m}_{MeOH} \cdot H_{i,MeOH}}{\dot{m}_{H_2} \cdot H_{i,H_2} + \dot{E}_{MSS} + P_{BOP,MSS}} \quad (3)$$

where  $\dot{E}_{MSS}$  is the thermal power needed in the reboiling process of the MSS and  $P_{BOP,MSS}$  is the power required by the MSS compressors.

Also, a PtL efficiency can be defined by (4):

$$\eta_{PtL} = \frac{\dot{m}_{MeOH} \cdot H_{i,MeOH}}{P_{AEL} + P_{BOP,AEL} + \dot{E}_{MSS} + P_{BOP,MSS}} \quad (4)$$

Finally, the global efficiency of the overall system is reported in (5):

$$\eta_G = \frac{P_{SOFC} - P_{BOP,SOFC}}{P_{AEL} + P_{BOP,AEL} + \dot{E}_{MSS} + P_{BOP,MSS}} \quad (5)$$

The introduction of the ORC leads to the efficiency of the electricity production ( $\eta_{SOFC+ORC}$ ) and to the global efficiency of the overall system ( $\eta_{G,ORC}$ ) reported in (6) and (7), respectively:

$$\eta_{SOFC+ORC} = \frac{P_{SOFC} - P_{BOP,SOFC} + P_{ORC} - P_{BOP,ORC}}{\dot{m}_{MeOH} \cdot H_{i,MeOH}} \quad (6)$$

$$\eta_{G,ORC} = \frac{P_{SOFC} - P_{BOP,SOFC} + P_{ORC} - P_{BOP,ORC}}{P_{AEL} + P_{BOP,AEL} + \dot{E}_{MSS} + P_{BOP,MSS}} \quad (7)$$

### 3. RESULTS AND DISCUSSION

Table 1 shows the performance indexes calculated for the three different cases analysed: the system based on AEL without ORC, the system based on AEL with ORC, and the reference system based on RSOC [11].

Table 1 Performance indexes of the main systems

Efficiency	Present work (no ORC)	Present work (ORC)	Ref. work (no ORC)
$\eta_{electrolysis}$	0.763	0.763	0.950
$\eta_{MSS}$	0.702	0.702	0.702
$\eta_{PtL}$	0.548	0.548	0.671
$\eta_{SOFC}/\eta_{SOFC+ORC}$	0.491	0.565	0.491
$\eta_G/\eta_{G,ORC}$	0.269	0.310	0.329

While in the reference system, the thermal energy discarded by the SOFC is completely re-used to preheat various flows among the different subsections, coupling a high temperature SOFC and a low temperature AEL allows for the recovery of the thermal energy released by the SOFC, to produce more electricity in an ORC engine.

Since the high temperature water electrolysis process reduces the electricity input, the SOEC has an efficiency that is considerably higher than that of AEL (0.95 vs 0.76). Consequently, as the methanol synthesis process is the same in all of the three cases analysed ( $\eta_{MSS}$  equal to 0.7), the reference case based on RSOC leads to a higher PtL efficiency (0.67) with respect to the AEL based cases (0.55). PtL efficiencies  $\eta_{PtL}$  are consistent with the data in the current literature, showing the effectiveness of such systems in a PtL perspective. All three cases are based on a SOFC that shows an efficiency  $\eta_{SOFC}$  slightly lower than 0.5. The integration with the ORC provides a 235 kW power increase, increasing the efficiency of the electricity production  $\eta_{SOFC+ORC}$  up to 0.57. Globally, the base AEL process, without the ORC, shows poorer performance ( $\eta_G = 0.27$ ), since the MSS reboiling process only partially recovers the heat released by the SOFC. The introduction of the ORC, a low-cost technology which slightly increases the system complexity, allows the heat released by the SOFC to be fully exploited, boosting the global efficiency to 0.31. On the other hand, an innovative technology such as high temperature RSOC allows for a global efficiency of up to 0.33.

The comparison between the two AEL and RSOC technologies is not easy. An RSOC is convenient since only one device is necessary, allowing savings in investment costs, even though the degradation rate is higher and therefore the lifespan is shorter [21,22]. Moreover, electricity consumption is lower than AEL, owing to high temperature operations. However, RSOC is not yet a mature technology, and so it is not yet economically convenient. Nowadays, RSOC technology is about 15 times more expensive than comparable commercially affirmed systems, which prevents a wide diffusion of these devices [23]. Nevertheless, future RSOC costs are predicted to decrease substantially, reaching the same costs as AEL technology [23,24]. RES costs are also expected to drop considerably in the next few years [25].

Generally speaking, the advantage of such systems (both AEL with ORC, and RSOC) is that with an efficiency of about 30% it would be possible to run an energy storage plant capable of performing a closed carbon cycle with energy coming from RES and captured CO<sub>2</sub>. Theoretically, by coupling these technologies to direct air capture of CO<sub>2</sub> would allow for the building and installing of distributed systems to store energy and produce chemicals anywhere, without the need for concentrated CO<sub>2</sub> sources.

### 4. CONCLUSIONS

A PtL energy storage system based on an alkaline water electrolyser, a high temperature SOFC, and a TES system was analysed, with and without integration with an ORC plant. The two configurations were compared with each other and with a system based on an innovative high temperature RSOC. The introduction of the ORC in the PtL energy storage system allows a better use of the heat released by the SOFC, improving the global efficiency by 4 percentage points, from 0.27 to 0.31. Given the slight increase in complexity and the efficiency increase resulting from the introduction of the ORC, the solution without ORC is not convenient. The solution based on the RSOC system is characterised by a higher global efficiency (0.33), but it is not yet a mature technology. Thus, the system based on AEL might be a short-term solution as a PtL energy storage system, while the innovative RSOC system might be further developed for a convenient deployment in the long-term future.

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