

Solid Oxide Electrolysis Cell-Based Syngas Production and Tailoring: A Comparative Assessment of Coelectrolysis, Separate Steam, CO₂ Electrolysis, and Steam Electrolysis

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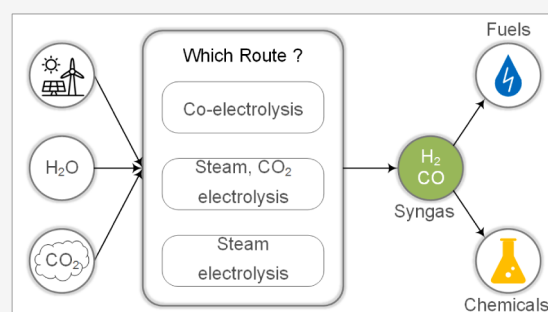
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ABSTRACT: Solid oxide electrolysis cell (SOC) systems offer a promising solution for generating green syngas crucial in decarbonizing challenging sectors like chemicals, steel, and transport. In this steady-state system modeling study, three distinct system concepts for SOC-based tailored syngas production from steam and CO₂ have been investigated. The system models are implemented within ASPEN, and an experimentally validated SOC reactor model has been utilized. At the system level, a parametric analysis is performed by varying inlet composition, fuel utilization, SOC operating pressure, and maximum oxygen content in the SOC exhaust. The results are used to identify system design challenges that differ for the three routes and the most preferable system based on energy efficiency, system complexity, and feasible syngas compositions. System configurations involving purely electrochemical conversion of steam and CO₂ are found to have 2–7% higher system efficiencies. Pressurized electrolysis leads to 5–8% lower system efficiencies when taking into account the maximum O₂ concentration constraint for the exhaust air.



INTRODUCTION

The EU has set out a target of net-zero greenhouse gas (GHG) emissions by 2050 within the European Green Deal.¹ In order to achieve this aim, emissions reduction across all sectors of the economy would be essential. While the increased use of renewable energy sources has contributed to a significant decrease in CO₂ emissions, this progress has primarily been limited to the power sector, where fossil-derived electricity can be readily replaced with renewable alternatives. In recent years, there has been a growing interest in the development of “Power-to-X” technologies that have the potential to enable decarbonization in sectors beyond power generation.² Among these technologies, high-temperature solid oxide electrolysis (SOEL) has emerged as a promising option, particularly for syngas production within the chemical industry.³

Solid oxide electrolysis offers several advantages⁴ in comparison to low-temperature electrolysis technologies and has been the subject of investigation in various experimental and modeling studies. The coelectrolysis of steam and CO₂ has been investigated as a method for efficient syngas production. Experimental studies at the cell and stack level have mainly focused on the electrochemical performance, degradation behavior, reaction mechanisms, feasible syngas compositions, pressurized operation, and cell architectures.^{5–7} The feasibility of producing tailored syngas using coelectrolysis has been demonstrated,⁸ and an agreement between experimental and theoretical predictions of gas composition has been observed.⁹

Similar behavior for steam and coelectrolysis and a higher pressure sensitivity for pure CO₂ electrolysis were observed.¹⁰ The influence of pressurized operation on SOC stacks with different architectures has also been investigated,¹¹ and it was found that the performance improvement at elevated pressures differs significantly depending on the dominant source of resistance. Most of the studies, however, have been performed at the cell and stack levels.

Furthermore, various system modeling studies have explored coelectrolysis for syngas and synthetic fuel production. Samavati et al.¹² studied a pressurized SOEL system for syngas production and reported a 20% drop in overall system efficiency (LHV based) at 25 bar compared to atmospheric pressure, attributed to increased methane content. Becker et al.¹³ investigated an SOC-based syngas production system coupled with a downstream Fischer–Tropsch (FT) unit and reported a 2.6% drop in power-to-liquid efficiency (HHV based) with an increase in SOC operating pressure from 1.6 to 5 bar. Another study¹⁴ comparing 5 process variants of an integrated SOEL and FT system showed a 6% higher efficiency

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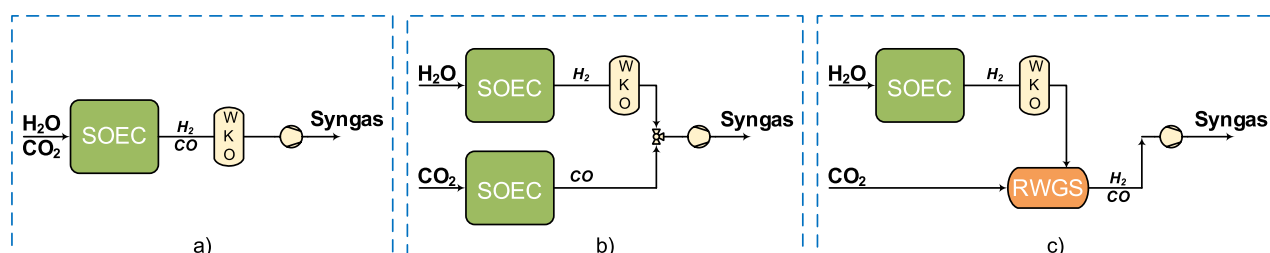


Figure 1. Schematic illustration of the three syngas production routes: coelectrolysis (a), separate steam and carbon dioxide electrolysis (b), and steam electrolysis followed by reverse water gas shift (c).

at 20 bar compared to atmospheric pressure. Sun et al.¹⁵ conducted a thermodynamic analysis of a pressurized SOEL system for synthetic methane and dimethyl ether (DME) production and found that low temperature and higher pressure improved system efficiency for methane production, whereas high pressure and high reactant utilization made high temperature essential for DME production. These results show that there is no general consensus on whether pressurized electrolysis for syngas production is advantageous or not. Another limitation of these studies is that the results of highly integrated systems are interpreted directly at the system level. This tends to convolute the influence of many stack-level and system-level variables.

While high-temperature coelectrolysis for syngas production has demonstrated several advantages, such as the ability to produce syngas with diverse compositions and potential synergistic integration with downstream processes, the scale-up of this technology to the MW scale has been relatively slow, with few such plants in operation.¹⁶ Furthermore, critical process requirements and challenges associated with system efficiency, tailoring capacity, and process safety (e.g., material degradation under a high-temperature oxygen-enriched atmosphere) have not been adequately addressed. The existing literature lacks a systematic investigation into high-temperature SOC-based syngas production routes, particularly with a focus on system efficiency, tailoring capacity, and process safety. Moreover, there is a need to identify relevant key performance indicators (KPIs) for downstream processes and shift the focus from parameters that primarily determine reactor size to those that impact energy efficiency and process viability.

Therefore, this study aims to bridge these gaps by utilizing steady-state system modeling to evaluate different SOEL-based process routes for syngas production using a commercially available SOC reactor. The main objectives are to assess the advantages and disadvantages of each process route, considering factors, such as system efficiency, syngas tailoring flexibility, and process safety. Additionally, the study examines whether pressurized electrolysis offers any benefits for syngas production. Moreover, the influence of reactor level parameters, such as operating temperature, pressure, and utilization, is investigated.

PROCESS DESCRIPTION AND MODELING

Process Routes. Three routes for syngas production using high-temperature SOCs have been investigated. Figure 1 shows simplified process flow diagrams (PFDs) for the three routes. The first route involves the simultaneous reduction of steam and carbon dioxide, or coelectrolysis (Figure 1a). This is the simplest route from the point of view of system design and operation, and allows for the production of tailored syngas in a single step. In the second route, steam and carbon dioxide are

reduced within two separate electrolyzers, and the produced hydrogen and carbon monoxide are mixed downstream to produce syngas (Figure 1b). In the third route, the high-temperature SOEL is used only for steam reduction and the produced hydrogen is supplied to a reverse water gas shift reactor (RWGS) along with carbon dioxide to produce syngas (Figure 1c). This route is the second most investigated concept after coelectrolysis, and the principal advantage it offers is the possibility to combine a low technology readiness level (TRL) technology (SOEL) with a relatively higher TRL technology (RWGS). The terms Route 1, Route 2, and Route 3 are used interchangeably with coelectrolysis, separate steam/ CO_2 electrolysis, and steam electrolysis + RWGS, respectively.

SOC Reactor Model. The SOC reactor model is based on a commercially available reactor from SUNFIRE, which has been characterized under both atmospheric and pressurized operating conditions. Detailed information regarding model development and experimental validation has been published elsewhere.¹⁷ A brief overview of the model has been provided in the [Supporting Information](#).

System Models. The system models have been implemented within Aspen Plus. The RWGS reactor has been modeled as an electrically heated isothermal equilibrium reactor.^{18,19} Standard models available in the Aspen library were used for other process engineering equipments, such as flash vessels, heat exchangers, and pressure changers. Compressors were modeled with 2–3 intercooled stages (maximum pressure ratio of 3), and the heat of compression was not utilized within the process. Key model input parameters have been specified in Table 1, and detailed process flow diagrams have been provided in the [Supporting Information](#).

Table 1. Key Model Input Parameters

parameters	values
SOC operating temperature	850 °C
SOC operating pressure	1 bar
SOC reactant utilization	70%
Exhaust O_2 concentration	30%
RWGS operating temperature	850 °C
RWGS operating pressure	1 bar
Mechanical efficiency of turbines/compressors	95%
Isentropic efficiency of turbines/compressors	75%

Syngas Characterization. Syngas compositions are usually characterized using different syngas ratios. The most commonly used ratios are H_2/CO and $(\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2)$. For most of the processes, an H_2/CO ratio between 1 and 3 is required. In addition, for certain processes, the CO/CO_2 ratio is important as well.²⁰ Therefore, within this study,

both H_2/CO and CO/CO_2 were investigated, as these two can be combined to create all the other ratios. This is done using the following coefficients, which take into account the inlet composition and the utilization U_f . A value of 1 for $R_{H_2/CO}$ would imply that the H_2/CO ratio in the produced syngas is equal to the H_2O/CO_2 ratio in the feed gas. A value of 1 for R_{CO/CO_2} would imply that the CO/CO_2 ratio in the syngas is completely determined by the utilization alone. A detailed explanation of this approach is provided in the [Supporting Information](#).

$$R_{H_2/CO} = \frac{H_2/CO}{H_2O/CO_{2inlet}} \quad (1)$$

$$R_{CO/CO_2} = \frac{CO/CO_2}{U_f/(1 - U_f)} \quad (2)$$

Energy Efficiencies. Two definitions of system energy efficiency based on the lower heating value (LHV) of syngas have been used. The first definition considers the LHV of syngas, excluding methane, and the second definition includes the LHV of methane as well. Throughout the study, system efficiencies refer to the first definition, unless stated otherwise. P_{el} represents the total electrical power consumption for the system, including the SOC reactors, RWGS reactor, and the BOP components.

$$\eta_{\text{syngas w/o } CH_4} = \frac{LHV_{\text{syngas w/o } CH_4}}{P_{el}} \quad (3)$$

$$\eta_{\text{syngas}} = \frac{LHV_{\text{syngas}}}{P_{el}} \quad (4)$$

RESULTS AND DISCUSSION

The analysis has been divided into two broad sections. In the first section, syngas production using coelectrolysis is investigated at the reactor level. The influence of reactor level parameters such as operating temperature, utilization, and pressure on the produced syngas composition is studied individually. This is a thermodynamic analysis, and the results are independent of the SOC reactor. In the second section, coelectrolysis is compared with the two alternate routes, and the influence of pressurized electrolysis and O_2 concentration in the exhaust air is assessed at the system level. This is followed by a general discussion of the main findings.

Reactor Level Analysis. Influence of Temperature. Figure 2 panel a illustrates the temperature dependence of the two coefficients $R_{H_2/CO}$ and R_{CO/CO_2} . Both coefficients exhibit a strong temperature dependence. $R_{H_2/CO}$ decreases sharply until 600 °C and more gradually thereafter, while R_{CO/CO_2} increases gradually with increasing temperature. Interestingly, both coefficients approach a value of 1 from 750 °C onward. At ~830 °C, both ratios are equal to 1, above that, $R_{H_2/CO}$ starts to decrease below 1 and R_{CO/CO_2} starts to increase above 1. This phenomenon is due to the shift in the equilibrium of the RWGS and methanation reactions as the temperature increases and has also been observed experimentally in recent studies.^{21,22} As a result, the conversion of CO_2 to CO instead of CH_4 becomes increasingly favorable at higher temperatures. Between 810 and 850 °C, $R_{H_2/CO}$ deviates negligibly from a value of 1. This is the temperature range within which current state-of-the-art reactors operate. To

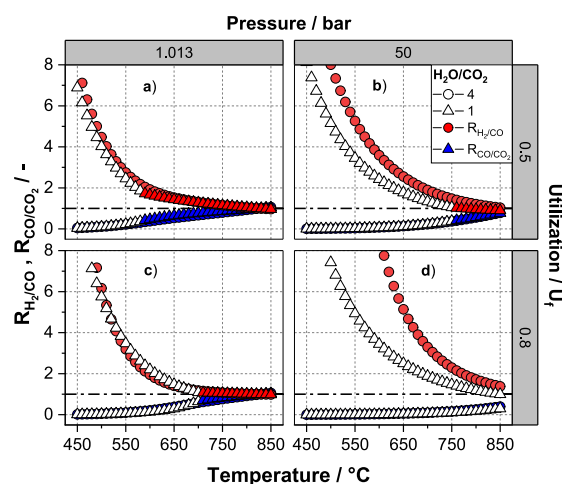


Figure 2. $R_{H_2/CO}$ (red markers) and R_{CO/CO_2} (blue markers) as a function of temperature for inlet H_2O/CO_2 ratios of 1 (Δ) and 4 ($\circ$) at atmospheric and elevated pressures and two different utilization rates. Blank markers represent points at which carbon deposition is expected.

mitigate the effects of degradation in these reactors, a common strategy is to allow the operating temperature to gradually increase over the reactor's lifetime. Since the $R_{H_2/CO}$ value remains practically constant in this temperature range, any temperature drift that occurs will lead to negligible changes in the syngas compositions over the lifetime of the reactor (with no adjustment of the inlet composition).

Additionally, the values of both coefficients for the two compositions become practically indistinguishable from 650 °C onward. This is because of the difference in the extent of methanation for different compositions below 650 °C. The higher the H_2O/CO_2 ratio, the greater the extent of methanation at a given temperature. Therefore, it can be inferred that within the temperature range of 750–850 °C, the syngas composition can be expected to be a function of inlet composition alone.

It can also be observed that for an inlet composition of $H_2O/CO_2 = 1$, below a temperature of 600 °C, there is a tendency of carbon deposition. However, for an inlet composition of $H_2O/CO_2 = 4$, no carbon deposition is expected. This is expected as the propensity of carbon deposition is higher for feed gases with a lower O/C ratio and at lower temperatures.²³ It should be noted that the $R_{H_2/CO}$ value is already higher than 1 for a feed gas composition of $H_2O/CO_2 = 1$ in this temperature range, indicating that syngas ratios (H_2/CO) below a certain value would be infeasible due to the risk of carbon deposition. However, it should also be acknowledged that these results are based on equilibrium calculations, which only consider graphite as the solid carbon form. Experimental studies have shown that at least two other forms of carbon are more likely to be present,²⁴ and that these different forms of carbon also have a different temperature dependence.²⁵ Incorporating data for these forms of carbon can potentially reduce the safe operating range at higher temperatures and pressures.²⁶ Additionally, the role of kinetics has not been accounted for in this analysis, and experiments have shown that carbon deposition may not occur under thermodynamically unsafe operating conditions due to slow reaction kinetics.

Influence of Utilization. To study the influence of utilization on the syngas compositions, it was increased from 50% to 80%. A comparison of panels a and c in Figure 2 reveals two key changes in the trend of $R_{\text{H}_2/\text{CO}}$ values with increased utilization. The initial sharp decrease in $R_{\text{H}_2/\text{CO}}$ with increasing temperature now extends up to a temperature of 650 °C, and above 650 °C, the slope of $R_{\text{H}_2/\text{CO}}$ becomes flatter. This flatter slope implies a lower temperature sensitivity of the syngas ratios. The reason for this is an increase in methanation, as evidenced by the lower $R_{\text{CO}/\text{CO}_2}$ values (particularly below 700 °C). The second notable change is an increase in the risk of carbon deposition (for an inlet composition of $\text{H}_2\text{O}/\text{CO}_2 = 1$). This change is expected because with increasing utilization, the O/C ratio in the product gas decreases.

These results show that within a temperature range of 750–850 °C (at atmospheric pressure), utilization has no discernible influence on the syngas ratios. This implies that current state-of-the-art reactors may be safely operated within a wide range of utilizations with minimal or no changes in the inlet composition ($\text{H}_2\text{O}/\text{CO}_2$ ratios). This is in line with experimental observations.⁹ On the other hand, for reactors operating at 700 °C and below, utilization may need to be restricted to lower values due to an increased risk for carbon deposition and significantly higher methane concentrations.

Influence of Pressure. The influence of pressure on the R coefficients can be studied by comparing panels a and b in Figure 2. With increasing pressure, the slope of the $R_{\text{H}_2/\text{CO}}$ increases even at temperatures above 750 °C. This is due to a sharp increase in methanation with pressure (confirmed by a marked decrease in $R_{\text{CO}/\text{CO}_2}$ values over the entire temperature range). Since the extent of methanation also depends on the composition, the difference between the $R_{\text{H}_2/\text{CO}}$ values for different compositions also increases. This is also why these changes become more pronounced at higher utilizations, as can be seen by a comparison of Figure 2 b,d. In addition to methanation, there is also an increase in the risk of carbon deposition, which further limits the safe operating range (for an inlet composition $\text{H}_2\text{O}/\text{CO}_2 = 1$).

As explained previously, a sharper $R_{\text{H}_2/\text{CO}}$ slope implies a higher temperature sensitivity of the syngas ratio, and a difference in $R_{\text{H}_2/\text{CO}}$ values for different compositions means that the relationship between inlet $\text{H}_2\text{O}/\text{CO}_2$ ratio and syngas ratio becomes nonlinear. As a result, a small increase/decrease in the inlet $\text{H}_2\text{O}/\text{CO}_2$ ratio can cause a big change in the syngas ratio at the outlet. In contrast at atmospheric pressures, the $R_{\text{H}_2/\text{CO}}$ values are practically the same for all compositions (and close to 1) within a temperature range of 750–850 °C. This would allow tailoring the syngas ratio by simply setting the inlet $\text{H}_2\text{O}/\text{CO}_2$ ratio equal to the desired H_2/CO ratio divided by the $R_{\text{H}_2/\text{CO}}$ value at that temperature.

Summary. With currently available SOC's operating at atmospheric pressure and temperatures around 800 °C and above, syngas compositions produced via coelectrolysis can be varied within a wide range just by changing the inlet $\text{H}_2\text{O}/\text{CO}_2$ ratio. For SOC reactors being developed for intermediate and low temperatures, temperature control would also be important, and the range of compositions would be very limited to H_2/CO ratios >3–4 due to the risk of carbon deposition. For these reactors, utilization is also important, as the propensity of carbon deposition and methanation increases with utilization.

System-Level Analysis. Syngas production at 230 °C, 50 bar, and with an $\text{H}_2\text{O}/\text{CO}_2$ ratio of 3 (giving a syngas ratio

$((\text{H}_2 - \text{CO}_2)/(\text{CO} + \text{CO}_2))$ close to 2) is considered as the basis for system efficiency comparison of the three process routes. These conditions are typical for methanol synthesis and also fall within the range required for other synthesis processes.²⁷ For the SOC's, only thermoneutral operation has been considered because a practical system will most likely be operated at the thermoneutral point for maximum efficiency. Another reason is that the main focus here is on the comparison of the 3 process routes. Common model input parameters are taken from Table 1. Table 2 presents the energy

Table 2. Energy Balance and System Efficiencies for the Process Routes

system component	route 1	route 2	route 3	unit
<i>Energy Balance</i>				
SOC	76.6	76.9	71.1	%
Steam generator	13.6	13.7	17.4	%
Electric heaters	4.0	3.6	4.1	%
Syngas compressor	5.7	5.7	5.5	%
RWGS	-	-	1.9	%
Total	100.0	100.0	100.0	%
<i>Losses</i>				
WKO	5.2	4.9	9.1	%
Exhaust air	3.0	3.4	3.0	%
Compressor cooling duty	4.3	4.2	3.6	%
<i>System Efficiencies</i>				
Syngas (LHV)	75.2	75.5	71.5	%
Syngas w/o CH_4 (LHV)	75.1	75.5	71.4	%
Efficiency (LHV)	75.1	75.5	71.4	%
<i>SOC Areas</i>				
SOC 1	13.36	11.18	15.06	m ²
SOC 2	-	2.70	-	m ²

balance and system efficiencies for the base case as well as the required SOC areas for a 100 kW (LHV) syngas production system. The energy flows have been normalized by the total electrical power input for each system.

System Efficiencies for the 3 Routes. Similar system efficiencies are obtained with routes 1 and 2. The primary sources of energy consumption for all three routes are the SOC and the steam generator. Together, these two components account for 90% of the energy consumption in the system. The main source of energy loss is in the form of unrecovered waste heat in the water knockout (WKO), exhaust air, and as the cooling duty of the syngas compressor. Downstream syngas compression from atmospheric pressure to 50 bar has a relatively low energy consumption (~5.5%).

In comparison, the system efficiency reached with route 3 (steam electrolysis + RWGS) is roughly 4% lower. The main reason for this is the higher amount of energy required for steam generation. As can be seen from the reactions (S1, S7) involved, this extra steam is required to produce the extra hydrogen necessary for CO_2 reduction in the RWGS reactor. This extra energy is ultimately wasted in the WKO downstream from the RWGS. On the other hand, when CO_2 and steam are reduced electrochemically (simultaneously or separately), a conversion of only 1 mol of steam is sufficient (roughly) for producing 1 mol of CO. These results show that, in terms of system efficiency, coelectrolysis does not offer any significant advantages over the other two routes. While route 3 can clearly be expected to have lower efficiency, the absolute difference is not significant enough for it to not be, considered.

However, the RWGS reactor is still under development (unlike Shift reactors, which are already used industrially). Additionally, the required SOC area is the highest for route 3 which implies higher capital and operational costs.

Syngas Tailoring in the 3 Routes. The aim of this investigation was to determine if system efficiencies vary with the syngas ratio (H_2/CO). Figure 3 demonstrates the

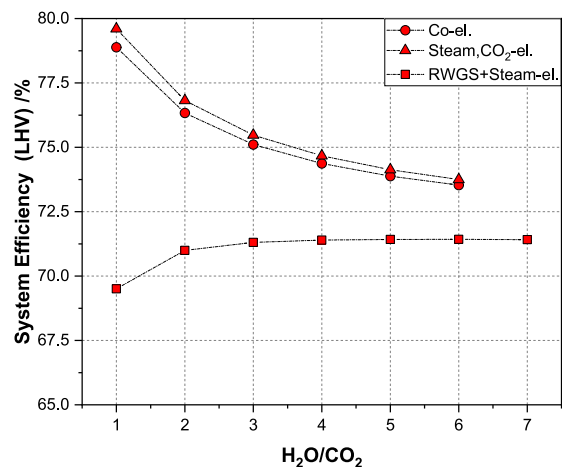


Figure 3. System efficiency (excluding CH_4) as a function of the inlet H_2O/CO_2 ratio for the three process routes.

variation in system efficiency as the H_2O/CO_2 ratio is increased. The results indicate that routes 1 and 2 experience a decline in efficiency with increasing syngas ratios, primarily due to the decreasing lower heating value (LHV) of the syngas caused by the higher H_2 content. Additionally, a higher steam demand results in an increased amount of wasted heat in the WKO. Route 3, on the other hand, displays almost constant efficiency because the increased energy demand for steam generation is balanced by a decreasing energy demand for the RWGS reactor. As the H_2O/CO_2 ratio increases, the conversion of CO_2 to CO in the RWGS reactor rises, leading to a lower energy demand for the syngas compressor and a reduced amount of wasted heat in the WKO.

These results demonstrate that the flexibility in syngas tailoring demonstrated at the reactor level does not necessarily translate to the system level in a straightforward manner. Although the system efficiency decreases with increasing ratios, for many applications, the ratio will be kept more or less constant, typically around 1–3, at which point the efficiencies are still reasonable.

Pressurized Electrolysis. To investigate the impact of pressurized SOC operation on system efficiencies for the three routes, the calculations conducted in the base case are replicated at an operating pressure of 8 bar. This value is chosen as experimental results for coelectrolysis at 8 bar are available, and at this pressure, a methane content of 2–5% (dry basis) can already be observed.¹⁰ The compression from 8 bar to the syngas delivery pressure of 50 bar is performed in the downstream syngas compressor. Figure 4a illustrates the results, showing a notable decline in system efficiency for route 1 when transitioning from atmospheric pressure to 8 bar. The system efficiency decreases from approximately 75% at atmospheric pressure to 64% at 8 bar. This drop can be attributed to two primary reasons. First, there is an increase in methanation at elevated pressures, contributing to the decrease

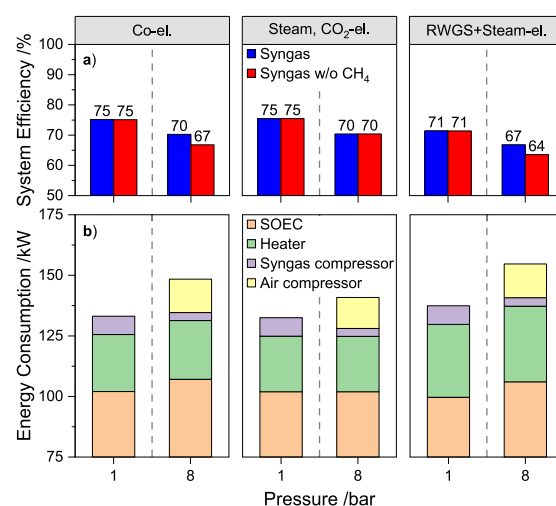


Figure 4. System efficiencies, including CH_4 (blue bars) and excluding CH_4 (red bars) (a), and primary sources of energy consumption for the three process routes at 1 and 8 bar, considering 100 kW as the LHV of the produced syngas (b). Heaters include the energy consumption for steam generation and preheaters.

in system efficiency. Second, the additional energy required for compressing the sweep gas (air) is nearly twice the corresponding reduction in syngas compression power. Figure 4b provides a clearer depiction of this relationship between sweep gas compression energy and syngas compression power. A similar trend is also observed for route 3. In route 2 since there is no possibility of methanation the system efficiency only decreases by 5%.

An effective solution to mitigate the energy loss from compression would involve incorporating a recovery turbine or expander to recover some of the energy. The system efficiencies (excluding CH_4) when an expander is utilized are presented in Table 3. It can be observed that the energy

Table 3. Comparison of System Efficiencies with an Expander

parameter	route 1	route 2	route 3
Efficiency (LHV)-1 bar, %	75.1	75.5	71.4
Efficiency (LHV)-8 bar, %	66.8	70.4	63.6
Efficiency (LHV)-8 bar-Exp, %	68.8	72.4	67.8

recovery is only partial, and the system efficiencies at atmospheric pressure remain 3–6% higher compared to the expander-equipped system. However, the efficiency for route 3 becomes comparable to that of route 1. The utilization of expanders for energy recovery is already demonstrated in certain processes and frequently considered in system modeling studies, affirming its practicality.^{28,29} Nevertheless, it is important to acknowledge that implementing such a solution would entail additional capital expenditure and introduce increased system complexity.

Process Safety. Figure 5 illustrates the influence of the O_2 concentration in the exhaust air on the system's efficiencies. The O_2 concentration is varied between 30 and 90% corresponding to a specific air flow (with respect to H_2O , CO_2 mole flow) between 2.72 and 0.05. The specific air flow requirement is calculated by dividing the molar air flow rate with the total reactant (H_2O , CO_2) flow rate in the system and is presented in Table 4 for two different utilizations.

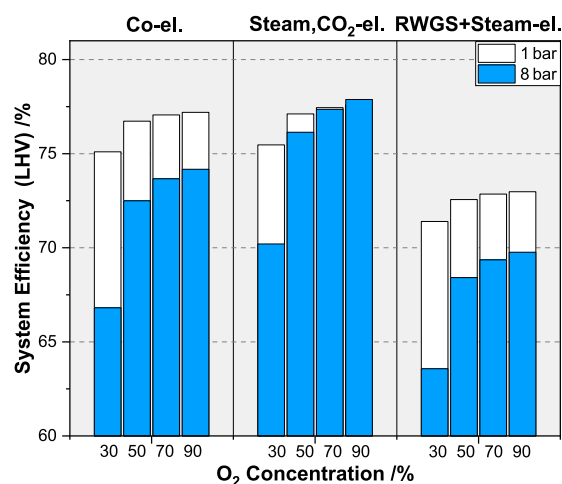


Figure 5. System efficiency (excluding CH₄) as a function of O₂ concentration (mol %) at the stack outlet for the three process routes at 1 and 8 bar.

Table 4. Specific Air Flow Requirement for Different O₂ Concentrations and Utilizations

O ₂ concentration (mol %)	specific air flow (mol/mol)	
	U _f = 70%	U _f = 80%
30	2.72	3.11
50	0.6	0.69
70	0.21	0.24
90	0.05	0.06

System efficiencies increase with increasing O₂ concentrations at atmospheric pressure for all three routes. This increase in efficiency is due to the decrease in the air flow rate, resulting in a reduction in the amount of energy wasted as unrecoverable heat in the exhaust air. At an elevated pressure of 8 bar as well, it can be observed that system efficiencies increase with increasing O₂ concentration, and the efficiency gap between atmospheric and pressurized conditions decreases. For route 1, the efficiency gap is around ~8% at a 30% O₂ concentration, which reduces to around 2.5% at a 90% O₂ concentration. A similar trend is observed for route 3. However, as explained earlier, lower system efficiencies at elevated pressures are due to increased energy requirements for air compression and increased methanation. While a decrease in the air flow rate reduces the energy requirement for air compression, it has no influence on the loss due to methanation. For route 2, with separate steam and CO₂ electrolysis, there is no methane production, resulting in a reduction in the efficiency gap from ~5% to ~0 at 70% and ~0.3% at 90% O₂ concentration. It should be noted that the efficiency gaps shown in Figure 5 will be bigger at higher utilizations due to a higher specific air flow requirement at any particular O₂ concentration.

These results suggest that producing pure oxygen (90% and above) would allow the system efficiency in route 2 to be slightly higher in the pressurized configuration. However, it is essential to note that high temperature oxygen-enriched air poses a significant process safety risk, which is further increased at elevated pressures.³⁰ Experiments with currently available SOC stacks have been performed safely with an O₂ concentration of up to 50%.³¹ However, the risk may not be acceptable for MW-scale plants since an increased plant scale is

accompanied by an amplification of the consequences of any accident, an increased likelihood of failure scenarios, and increased economic and environmental impacts of any incident. This underscores the need for inherently safer system designs.³²

Summary. Coelectrolysis and separate steam, CO₂ electrolysis routes achieve similar system efficiencies, but the RWGS route can be expected to have a relatively lower efficiency. System efficiencies are generally lower for higher syngas ratios (H₂/CO) with coelectrolysis and separate steam/CO₂ electrolysis. Pressurized electrolysis leads to a drop in energy efficiencies and an increased process safety risk.

Discussion. The findings show how translating reactor-level advantages to system level is not straightforward and that downstream process requirements and practical system-level challenges should be assessed together when developing SOC reactors for any application. It is shown that for coelectrolysis, inlet composition is the determining factor for H₂/CO ratios with current state of the art reactors operating above 800 °C, but for upcoming SOC reactors, pressure and utilization will also play a role as at temperatures below 700 °C carbon deposition and methanation become significant. This increased propensity for carbon deposition and methanation below 700 °C also implies that it would not be possible to obtain H₂/CO ratios below a certain value using these reactors, and the ratios would need to be adjusted downstream.

At the system level, it is shown that pressurized electrolysis generally leads to lower system efficiencies (for all the routes), increased system complexity, increased reactor development challenges, and increased process safety risk. Coelectrolysis only has a single-step advantage over separate steam and CO₂ electrolysis but has the disadvantage of methanation, which increases with operating pressure and utilization.

The results of the study can be used to draw some inferences w.r.t downstream applications of syngas. The most interesting applications being considered at the moment are FT, synthetic natural gas (SNG) and methanol synthesis. These applications have different requirements and consequently offer different synergies with the syngas production system. Utilizing the waste heat from downstream processes for production of steam for the electrolyzer is feasible for all the three routes and can be expected to lead to similar improvements in system efficiencies. Previous studies have claimed that methanation during coelectrolysis may be advantageous for applications such as SNG where a high methane content is desirable, however, the findings of the present study suggest that even for these applications the system efficiency may be lower at elevated pressures if the maximum O₂ concentration constraint is taken into account. Although there could be system level solutions such as using pure nitrogen or oxygen depleted air as sweep gas instead of air the impact of such solutions on system efficiency has not yet been investigated thoroughly.

In applications like FT or methanol synthesis, the primary source of energy consumption typically lies in the syngas production step.³³ The energy requirement for downstream compression of syngas up to 50 bar accounts for approximately 5% of the total energy consumption. Any potential benefits of avoiding or partially eliminating this compression step need to be carefully evaluated in terms of increased system complexity and potential capital costs.³⁴ It is worth noting that compressors exhibit their highest efficiency at the design point and in larger sizes. If the electrolyzer is operated at a lower pressure than the required syngas delivery pressure (as in

this study), then the syngas would need to be further compressed at downstream plants, and the existing compressors at those plants would need to operate at a partial load. Furthermore, a smaller compressor would need to be added at the syngas production plant for sweep gas compression. Such a solution could result in reduced efficiency and increased costs.

The chemical industry often faces unique requirements, such as the need to establish plants close to urban areas with limited space and feedstock availability, as well as stricter safety regulations. The findings presented in this study provide an intriguing possibility of combining alkaline electrolysis (AEL) or proton exchange membrane (PEM) technologies for H₂ production with SOEL for CO production (Route 2). For a 100 kW syngas production system presented above, the capital costs of electrolyzers would be around 124 and 166 k€ using AEL or PEM combined with SOEL, compared to 217 k€ using SOEL only (assuming current state-of-the-art capital costs).³⁵ In addition, operating low-temperature electrolyzers under pressure offers advantages in terms of simplicity (no need for pressure vessels) and enhanced safety due to lower temperatures and the ability to handle significant pressure differentials between the anode and cathode. AEL technology, in particular, has already been successfully deployed at the MW scale and continues to undergo efficiency improvements. By adopting Route 2, additional benefits can be obtained by avoiding methanation and the need for compression of sweep gas or liquid. Consequently, there is a potential energy advantage in eliminating downstream H₂ compression, which could become a viable and beneficial option. However, the lower efficiency of low-temperature electrolyzers and the electricity costs would also need to be taken into account.

The market deployment of electrolyzers will be influenced by various factors, such as efficiencies, capital, operational costs, cell area, stack size, and lifetime. Manufacturing and scale-up challenges differ for different technologies. Raw material requirements and criticality also vary.³⁶ For SOC, this is further complicated due to the availability of various cell designs (ESC, ASC, MSC, tubular, etc.). Increasing cell areas for SOC is not trivial. These issues need to be considered by the chemical industry while selecting an electrolyzer technology and developing a strategy for the long term and the short term.

CONCLUSIONS

The present study focused on investigating SOEL-based syngas production and tailoring. A parametric analysis was conducted at the reactor level to examine how operating temperature, pressure, and utilization influence the composition of syngas produced through coelectrolysis. To enable effective comparison across a wide range of parameters, a new metric incorporating the influence of inlet compositions and utilization was introduced for evaluating syngas ratios. The results revealed that, in contrast to high-temperature reactors operating above 750 °C, intermediate and low-temperature reactors are more vulnerable to methanation and carbon deposition. This susceptibility may restrict their viability for syngas production through coelectrolysis unless catalysts capable of suppressing these reactions while promoting the reverse water gas shift reaction can be developed.

At the system level, a thermodynamic comparison of three different system concepts in terms of system efficiency, syngas tailoring flexibility, and pressurized SOC operation was performed. Coelectrolysis and separate steam, CO₂ electrolysis

achieved similar efficiencies, and the RWGS+steam electrolysis route was found to have a 2–7% lower efficiency. It was also found that pressurized electrolysis leads to significantly lower system efficiencies. This drop in efficiency is primarily due to an increase in the energy required for sweep gas compression for all the three routes. For coelectrolysis and RWGS+steam electrolysis routes, an additional source of loss is increased methanation. The analysis showed that the energy spent in sweep gas compression can be partly recovered by the use of expanders. This would be advantageous for route 2 (separate steam, CO₂ electrolysis), but for routes 1, 3 the loss due to methanation will still be present and, atmospheric operation would be preferable.

The scale-up of SOC-based syngas production plants can be accelerated by focusing on nonpressurized, simple, and inherently safe system designs, prioritizing the use of off-the-shelf BOP components and standardizing the interfaces between SOEL systems, upstream renewable energy sources, and downstream synthesis processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c03674>

Process flow diagrams, syngas composition characterization methodology, and SOC reactor model (PDF)

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Notes

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