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Insight in the Decarbonization of Oil Refining by Integrating High-Temperature Electrolysis

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Abstract

High-temperature electrolysis of steam is one of the most energy-efficient techniques for producing hydrogen. Coupling the process with conventional oil refining plant can help this industry lowers its carbon footprint by using the low-carbon hydrogen instead of hydrogen derived from fossil resources.

This study explores the potential of replacing steam methane reformers with high-temperature electrolysis, utilizing heat sources from a midsize refinery. The integration is facilitated through two interfacing units: a heat recovery steam generator for producing electrolyzer steam feedstock, and a hydrogen processing unit for delivering hydrogen that meets the required specifications. Additionally, the study provides a comparison with alternative low-temperature electrolysis methods. Through process modeling, the study establishes overall heat and mass balances, evaluates energy efficiency, and assesses direct carbon emissions. Integrating electrolyzers within the refinery significantly reduces the CO_2 intensity of hydrogen production.

Introduction

According to +2°C global warming scenario, all energy and industry sectors must consider minimizing their greenhouse gas emissions. Among these industries, oil refineries produce an average of 1.2 million metric tons of CO_2 equivalent per year [1]. Oil refiners have thus to adapt their production strategy to comply with regulations, but also to anticipate the projected drop in the fossil fuel demand [2].

Oil refining consists of the processing of crude oil feedstock and its conversion into petroleum products e.g., liquified petroleum gas (LPG), naphtha, gasoline, kerosene, jet fuel, diesel fuel, fuel oils, wax, asphalt. Petroleum refining includes several unit operations which can be classified as separation, conversion and treatment processes [3]. The separation steps involve the split of crude oil into the main petroleum intermediates via atmospheric distillation, vacuum distillation and light ends recovery. The conversion steps then comprise units to break large molecules into smaller ones (e.g. cracking, coking, visbreaking), units to combine small molecules into larger ones (e.g. alkylation, polymerization), and units to rearrange molecules structure to higher-value ones (e.g. reforming, isomerization). Finally, the treatment processes allow upgrading petroleum products by removing undesirable constituents or heteroatoms such as sulfur, nitrogen, and oxygen (e.g. hydrodesulfurization, hydrotreating, sweetening).

Refineries are currently the largest consumers of hydrogen in industry [4], and although demand from oil refining may drop in a net-zero scenario, the sector is still forecast to be a large consumer in the decades to come. Hydrogen is consumed as a reducing chemical reactant by several conversion and treatment units. The major hydrogen consumers in refineries are the hydrocracking (HCU) and hydrodesulfurization (HDS) units. The hydrogen demand is generally supplied by the catalytic naphtha reforming (CNR) where hydrogen is a reaction by-product. The demand is most of the time complemented by additional steam methane reforming (SMR) units. Substituting fossil-based hydrogen from SMR thus appears as a pertinent route to decarbonize the oil refineries.

Electrolysis technologies can produce low-carbon hydrogen by using water and renewable or low-carbon energy sources (such as solar, wind, hydraulic, biomass, geothermal, and nuclear energy). These technologies comprise low-temperature electrolyzer operating in the range of 20 – 80°C such as proton-exchange membrane (PEMEL) or alkaline electrolyzer (AEL), and high-temperature electrolyzer operating in the range of 650 – 800°C known as solid-oxide electrolyzer (SOEL). The high-temperature electrolysis which is directly fed with steam is one of the most energy-efficient techniques for producing hydrogen [5]. SOEL benefits from utilizing both electrical and thermal energy, significantly reducing overall electricity demand. A substantial portion of the energy required for the electrolysis process is supplied as heat. This high efficiency is due to the effective use of heat and the favorable thermodynamics of the electrolysis process at high temperatures.

This study summarizes the perspectives of coupling SOEL with a midsize refinery of 200 thousand of barrels per day (~ 1125 t/h). The decarbonized scheme thus consists in suitable connections of the high temperature electrolysis system by mean of two interfacing units: (i) a heat recovery steam generator (HRSG) which produces the electrolyzer steam feedstock from available refinery heat sources, and (ii) a hydrogen processing unit (HPU) which delivers hydrogen at the appropriate specifications (pressure and purity) towards the refinery. The assessment is performed by means of process modelling and simulation. The simulations allowed establishing overall heat and mass balances and evaluating energy efficiency and direct carbon emissions.

Process Modeling, Calibration and Validation

The models are achieved by using Symmetry®, the SLB commercial computational thermodynamic process modelling software. The integrated model considers tree sub-models for the SOEL, the HRSG, and the HPU. The input parameters include oil refinery interface characteristics, the fluid thermodynamic properties, the electrolyzer performances, and the overall system operating conditions.

The models incorporate compounds such as water, hydrogen, oxygen, nitrogen, methane, carbon dioxide, carbon monoxide, and alkanes and alkenes ranging from C1 to C30. The thermodynamic properties for refining processes are determined using the Refinery Soave-Redlich-Kwong (SRK) equation of state model, while Advanced Peng-Robinson (APR) equation of state is used for SOEL, HRSG and HPU. The HRSG considers properties from the revised formulation of 1997 of the International Association for the Properties of Water and Steam (IAPWS-IF97).

For each unit operation (i.e. involving a physical change or chemical transformation), predefined blocks and objects from the modelling software library are utilized. Specific parameterizations are performed according to the type of blocks or objects. Heat exchanger blocks are designed as counter-current flow exchangers and defined by their temperature approach. Pump and compressor blocks are characterized by their discharge pressure and efficiency. Separators and splitters are specified using split factors.

All inlet streams to the model's battery limits are at ambient conditions (25°C and 1.01 bar). The process simulations assume 100% capacity factor with the plant running at nominal capacity.

High Temperature Electrolyzer

The high temperature electrolyzer i.e. SOEL is represented as depicted in Figure 1. Steam is introduced into the process and mixed with a recycle stream to achieve 10 mol.% hydrogen at the system's inlet. This helps prevent oxidation of the electrodes. The resulting stream is heated to the electrolysis temperature of 800°C using successive feed-effluent heat exchangers and an electric heater exchanger. Sweep gas, defined as dry air, is also fed into the process and heated in the same manner.

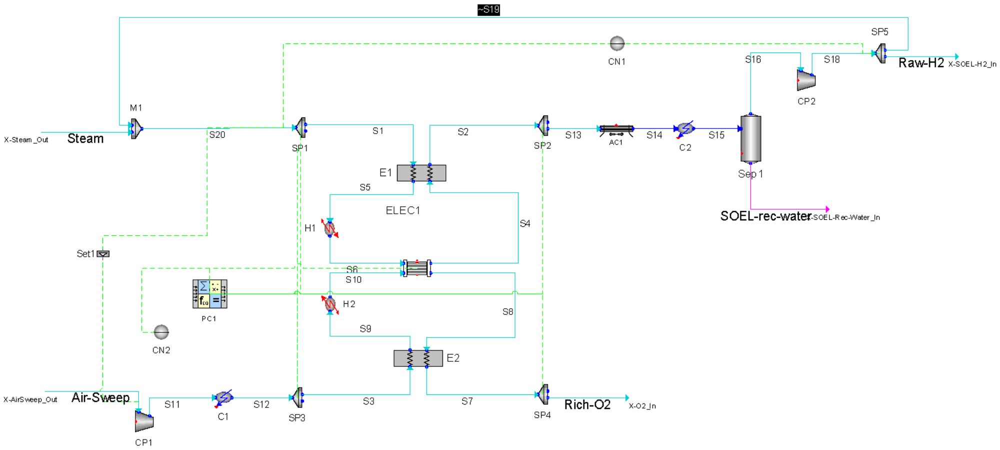

Figure 1—Sub-model of the SOEL high temperature electrolyzer.

Both the hot steam and hot sweep gas enter the electrolysis cell stack, where the electrolysis reaction occurs. The electrolysis cell stack is defined by stack arrangements, electrode geometry, a current density of 1 A/cm^2, cell potential, minimum overpotential, and the system's thermal and hydraulic performance[5, 6].

Oxygen molecules are produced at the anode and carried away by the sweep gas, resulting in oxygen-enriched air with a purity of 60 mol.% oxygen. If no sweep gas is used, pure oxygen is produced at the anode. Meanwhile, hydrogen molecules are generated at the cathode and leave the electrolysis cell along with unreacted water[5,6]. The water conversion rate is 70 mol.%. The hydrogen-water mixture is then processed through an aero-refrigerant heat exchanger and a cooler to remove most of the unreacted water. The raw hydrogen is routed through a blower, with part of the stream recycled at the SOEL inlet to prevent stack oxidation. The remaining raw hydrogen exits the SOEL unit at 1.4 bar with a purity of 98.5 mol.% hydrogen.

Interfaced Oil Refinery

The hydrogen consumption in refineries depends on the refining complexity and crude oil characteristics[7–8]. Generally, simple refineries consume 1–2 kg of hydrogen per ton of oil equivalent, while complex refineries with HCU and HDS processes use 4–10 kg. Heavy oil upgrading and refining can require 10–40 kg of hydrogen per ton of oil equivalent. Traditionally, 30–70% of a refinery's hydrogen comes from CNR, where hydrogen is a byproduct [3]. In simpler refineries with low hydrocracking needs, naphtha reformers can cover most of the hydrogen demand. Conventional refineries typically obtain 60–70% of their hydrogen from CNR. In contrast, complex refineries with heavy oil upgrading get 30–50% of their hydrogen from naphtha reforming. Refineries processing heavy or sour crude obtain less than 30% of their hydrogen from naphtha reforming. In all these cases, the remaining hydrogen demand is met by SMR.

The study examines an oil refinery with a capacity of 200 thousand barrels per day, classified as a complex refinery with HCU and HDS processes, where it is assumed 30% of the hydrogen demand is covered by CNR. According to literature [8], hydrogen utilization in such refineries averages 6.6 kg of hydrogen per ton of oil equivalent. Therefore, the plant's hydrogen demand is targeted at 7.5 tons per hour, with 5.2 tons per hour coming from SMR, which can be substituted by SOEL. The refinery's hydrogen header is designed to receive hydrogen at 20 bar and Grade B hydrogen with 99.9 mol% purity, as per ISO 14687 standards [9].

Waste heat in refineries is plant-dependent and, if available, can come in various forms and from different units. It may be available as excess utility (e.g., steam network) or directly within the process itself. Since refinery processes are typically well integrated, excess utility appears to be the most convenient option for heat coupling. The assumed heat sources are excess low-pressure (LP) and low-low-pressure (LLP) steam from the refinery's utility network. The LP and LLP steam are specified as saturated steam at pressures of 5.5 and 3.5 bar, respectively.

Heat Recovery Steam Generator

The HRSG, shown in Figure 2, represents a direct heat recovery steam generation system. Demineralized water is supplied to the system via a feed water pump. The water passes through three successive stages: water preheating, water vaporization, and steam superheating.

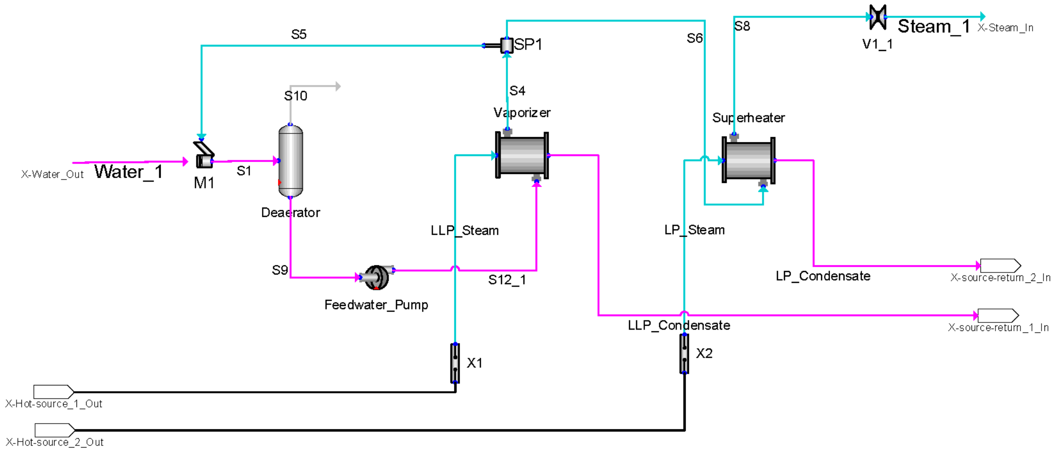

Figure 2—Sub-model of the heat recovery steam generator.

Preheating is achieved using a thermal deaerator, a direct contact heat exchanger that mixes returned saturated steam with water at ambient conditions. The steam condenses, heating the water, and any dissolved gases in the water feedstock are vented to the atmosphere from the deaerator. The preheated water exits the deaerator at approximately 105°C.

The preheated water is then vaporized in a kettle-type heat exchanger using LLP steam as the hot fluid. This process produces saturated steam at about 2 bars. Approximately 15% of this saturated steam is redirected to the thermal deaerator for the preheating stage. The remaining steam is superheated in a shell-and-tube heat exchanger with LP steam as the hot fluid. This results in superheated steam at a minimum temperature of 150°C, appropriate for feeding the SOEL. Both LP and LLP steam condensates are recovered in the form of saturated liquid.

Note that the HRSG architecture is one possible option, and other configurations can be implemented e.g., using a shell-and-tube heat exchanger for preheating. Depending on the quality of the refinery's boiler feedwater, direct use of LP and LLP steam could also be a more efficient option for feeding the SOEL.

Hydrogen Processing Unit

Based on the refinery's inputs, the hydrogen purity requirement for the hydrogen header is 99.9%, with an operating pressure target of 20 bars. The hydrogen produced by the SOEL has a purity of 98.5 mol% at near atmospheric pressure (1.4 bar). Therefore, a HPU is necessary for both purification and compression as shown in Figure 3.

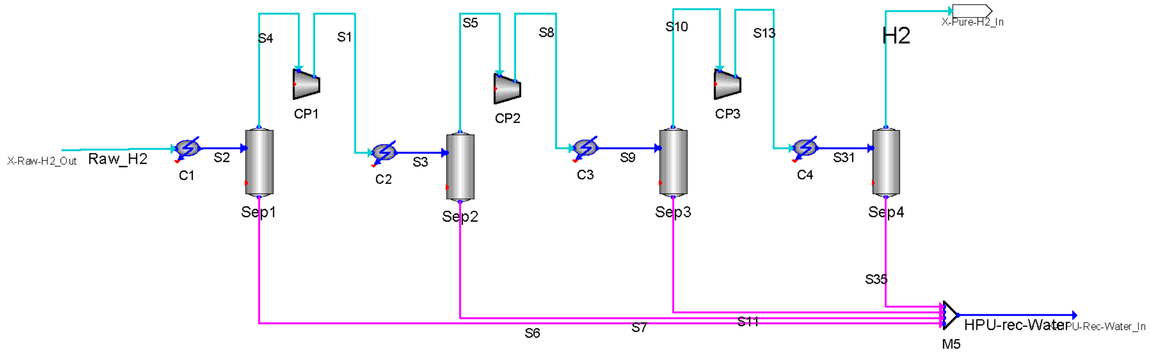

Figure 3—Sub-model of the hydrogen processing unit.

The raw hydrogen stream from the SOEL contains impurities primarily in the form of water moisture and trace amounts of nitrogen. Given that the maximum allowable nitrogen content is 400 ppm for hydrogen Grade B, extensive adsorption purification technologies like pressure swing adsorption (PSA) are not necessary to remove the nitrogen impurity. Therefore, the only impurity that needs to be eliminated from the product is water moisture, which can be removed through multistage compression and intercooling processes. In each stage of compression and cooling, a certain fraction of water is condensed and removed in knock-out drums, until the required purity and pressure specifications are met. The interstage specifications are set at 170°C for the compressor's maximum exhaust temperature, and 15°C for intercooling. The hydrogen recovery rate is 100%.

Results and Discussion

Once the models are built, they are used to simulate the decarbonized scheme as depicted in Figure 4. In this scheme, heat is recovered from the refinery's excess steam utility to produce steam feedstock for the SOEL, which in turn produces hydrogen. This hydrogen is then delivered at the required specifications via an HPU to the refinery's hydrogen header.

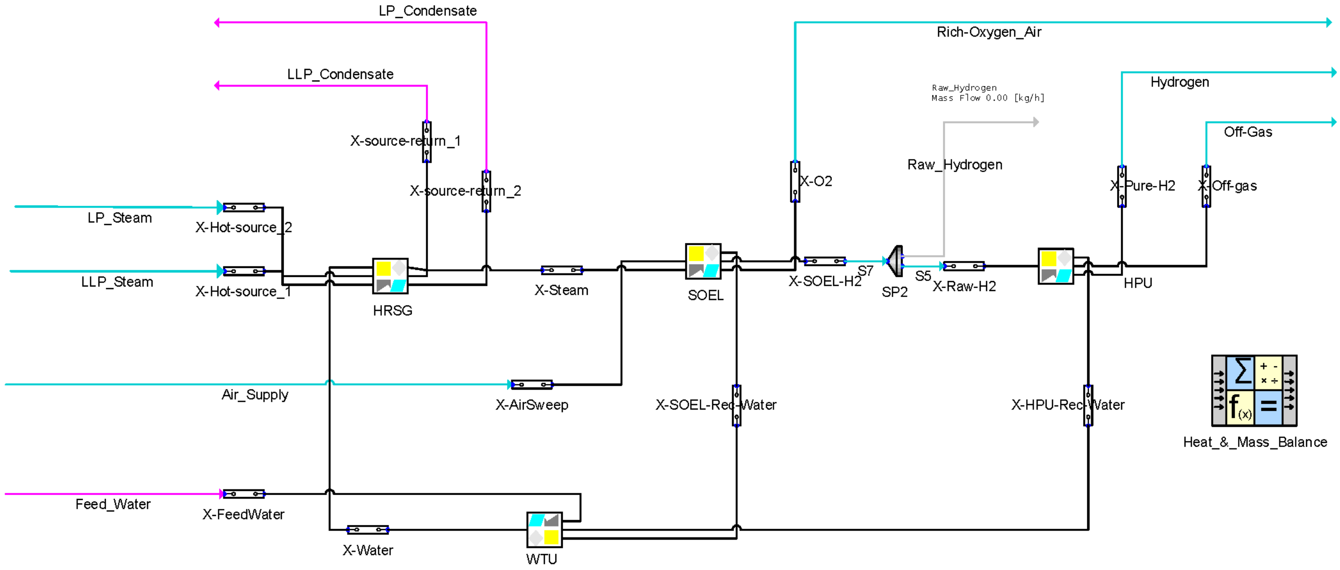

Figure 4—Integrated model of the heat recovery steam generator (HRSG), solid oxide electrolyzer (SOEL), and hydrogen processing unit (HPU).

Additionally, the integrated model incorporates a water treatment unit (WTU) to recover unconverted water from the SOEL and separated water from the HPU's knock-out drum. The WTU operates by mixing all recovered water fractions, removing dissolved gases, and ensuring the quality of water supplied to the HRSG.

The SOEL integration scenarios have been simulated to cover between 0% and 100% of the refinery's hydrogen demand. Results of the simulations are detailed in Table 1 for scenarios where SOEL covers 2%, 20%, 60%, and 100% of the hydrogen demand.

Table 1—Summary of outputs of the simulation for the integration of high-temperature electrolyzer with refinery of 200 thousand barrel per day.

	Units	2% SOEL	20% SOEL	60% SOEL	Full SOEL
Ratio of H_2 from SOEL / H_2 demand	%	2	20	60	100
H_2 Production	t/h	0.1	1.0	3.1	5.2
Rich-O_2 Air Production	t/h	2	16	48	80
Feed Water Consumption	t/h	1	9	28	47
SOEL Electrical consumption	MW_e	4	41	122	203
HPU Electrical consumption	MW_e	0.3	3	10	17
HRSG LLP steam consumption	t/h	2	16	49	81
HRSG LP steam consumption	t/h	0.1	0.2	0.6	1.1

Overall, the model aligns with typical SOEL system efficiency, consuming 39 kWh_e per kg of hydrogen produced and needing a thermal supply of 9 kWh_{th} per kg of hydrogen produced for the electrolyzer steam feedstock production with HRSG.

For the HPU, multistage compression with appropriate intercooling requires approximately 3.3 kWh_e per kg of hydrogen produced (with about 40% of the energy used for compression and the remaining 60% for cooling).

Regarding steam utility consumption for the HRSG, water vaporization requires about 1.1 kg of LLP steam per kg of water, while superheating requires about 0.02 kg of LP steam per kg of saturated steam. In general, producing 1 kg of hydrogen via SOEL with the given HRSG requires 15.6 kg of LLP steam for evaporation and 0.2 kg of LP steam for superheating.

To fully integrate electrolytic hydrogen from SOEL, a 220 MW_e system (comprising 203 MW_e for the SOEL and 17 MW_e for the HPU) is required to meet the plant's hydrogen demand of 5.2 t/h. In comparison, low-temperature electrolyzers such as proton-exchange membrane (PEMEL) or pressurized alkaline electrolyzers (AEL) may not require an additional HPU, as the hydrogen produced is already at a pressure of 20 to 30 bars. Considering that low-temperature systems consume about 50 to 55 kWh_e per kg of hydrogen produced [10], a 5.2 t/h hydrogen demand would be met by a 260 to 286 MW_e system. Therefore, SOEL is expected to consume approximately 15 to 23% less electricity, even when accounting for the supplementary HPU.

Carbon Footprint Reduction

The reference carbon emissions for hydrogen production via SMR assume 11.2 kg of CO_2 equivalent per kg of hydrogen produced[11–12]. This includes direct emissions of 9.35 kg of CO_2 equivalent per kg of hydrogen, with an additional 1.87 kg of CO_2 equivalent per kg of hydrogen accounting for upstream emissions. This figure represents the fraction of carbon emissions attributable to grey hydrogen production. Consequently, assuming net-zero carbon emissions intensity for the electricity used, replacing grey hydrogen production units with SOEL will lead to a corresponding reduction in carbon emissions from the refinery. However, since electricity still has a carbon footprint, the net carbon emissions should also include the contribution from the electricity consumption of the SOEL.

When using a low-carbon electricity mix with an average carbon footprint of 27 g of CO_2 per kWh_e (average carbon intensity of France's electricity mix in 2024), the SOEL emissions will increase in line with the system's electricity consumption. With partial integration of SOEL with SMR (see Figure 5), as the SOEL contribution to hydrogen demand increases (i.e., the ratio of hydrogen delivered by SOEL relative to the refinery's hydrogen demand increases), the CO_2 emissions from SMR decrease while those from SOEL increase. However, the overall emissions still decrease for the combined hydrogen production from SMR and SOEL. For full integration of SOEL, approximately 6 t/h of CO_2 is emitted, compared to 58 t/h for full integration of SMR. This represents an 90% reduction in emissions related to hydrogen production.

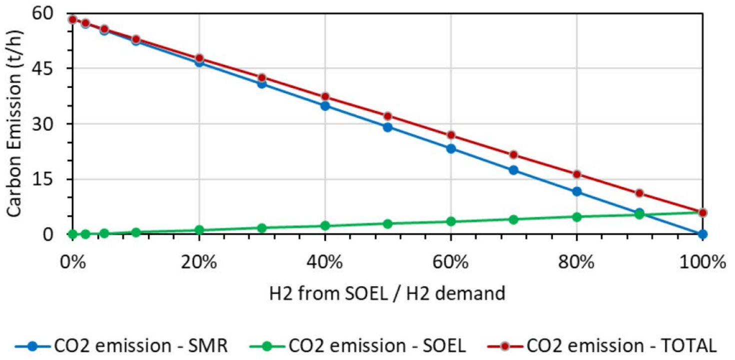

Figure 5—Carbon emission function of the ratio of hydrogen delivered by SOEL by reference to the refinery's hydrogen demand, for combined hydrogen production from SMR and SOEL.

The carbon intensity of electricity generation varies by location and production technology. If the electricity mix has a carbon footprint of 265 g of CO_2 per kWh_e, SOEL emissions are comparable to those of SMR. This sets the maximum allowable carbon footprint for electricity to achieve refinery decarbonization. Using SOEL is advantageous if the carbon footprint of the electricity mix stays below this limit.

Figure 6 illustrates the CO_2 emissions from combined hydrogen production using low temperature electrolyzers (PEMEL/AEL) and SOEL. As the SOEL contribution to hydrogen demand increases, the overall electricity consumption decreases due to the higher efficiency of the SOEL system. This reduction in electricity consumption leads to a corresponding decrease in overall carbon emissions. When fully integrating low temperature electrolyzers consuming around 55 kWh_e per kg of hydrogen produced, the CO_2 emissions are approximately 8 t/h. This is 23% higher than the emissions from SOEL.

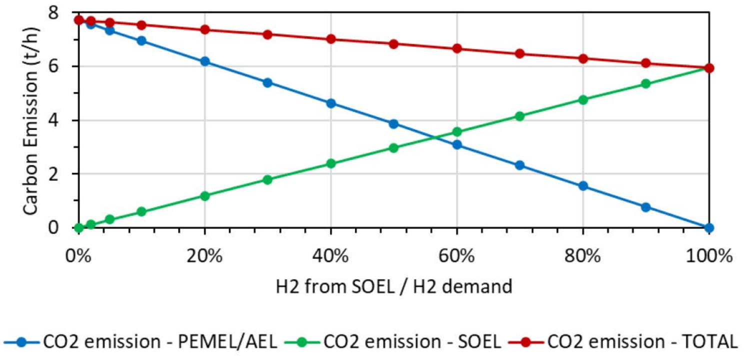

Figure 6—Carbon emission function of the ratio of hydrogen delivered by SOEL by reference to the refinery's hydrogen demand, for combined hydrogen production from PEMEL / AEL and SOEL.

The overall system efficiencies (electrical and thermal requirements) and the corresponding emissions for producing 1 kg of hydrogen (based on an electricity footprint of 27 g CO_2 per kWh_e) are summarized in Table 2. This provides clear evidence that water electrolysis is a viable substitute for SMR for decarbonization purposes. It becomes even more attractive when available heat can be used to further reduce CO_2 emissions through high temperature electrolysis.

Table 2—Summary of efficiency and carbon footprint data for SMR, SOEL, and PEMEL / AEL.

		Electrical efficiency	**Thermal efficiency**	**Carbon footprint**
		kWh_e/kg^{H2}	kWh_{th}/kg^{H2}	kg^{CO2eq}/kg^{H2}
SMR[11–12]		-	-	11.2
SOEL + HRSG + HPU (*this study*)		42.3	9	1.1
PEMEL / AEL [10]		50 – 55	0	1.5

Conclusion

In this study, the potential of integrating solid oxide electrolyzers (SOEL) with a midsize refinery is evaluated using a commercial process modeling software, Symmetry®. The process models are developed and calibrated to simulate the performance of a SOEL system interfaced with a heat recovery steam generator (HRSG) and a hydrogen processing unit (HPU).

The simulations establish overall heat and mass balances, highlighting the utility consumption requirements of the HRSG for efficient steam production for SOEL and the electrical consumption of the HPU for hydrogen delivery according to refinery specifications.

Scenarios of combined hydrogen production from steam methane reforming (SMR) and SOEL, as well as from low temperature electrolyzers (PEMEL/AEL) and SOEL, are examined. The integrated SOEL system (including HRSG and HPU) is found to be more energy-efficient and less carbon-intensive compared to SMR and PEMEL/AEL. The integrated SOEL system consumes approximately 42.3 kWh_e per kg of hydrogen produced at the refinery's specifications and emits 1.1 kg CO_2 equivalent per kg of hydrogen (for a low-carbon electricity mix with an average carbon footprint of 27 g of CO_2 per kWh_e). This suggests that SOEL, although not yet a fully mature and widely industrialized technology, promises to be a relevant solution for integration into oil refineries.

However, the successful integration of SOEL technology in the refining industry will depend on the availability of renewable or low-carbon electricity (which is necessary for any type of electrolyzer technology), as well as surplus of hot utilities like steam.

As a follow-up to this technical assessment, an economic analysis could provide insights into the feasibility, viability, and competitiveness of integrating SOEL into oil refineries.

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