Socio-political interests of reducing GHG emissions towards the environment have led to significant technological improvement of efficient methods to capture CO₂, then dispatched to either sequestration (CCS) or re-utilization (CCU/CDU) applications. While CCS can be considered as a well-established technology, it treats carbon dioxide as a waste, which is to be disposed of. On the contrary, CCU line of reasoning accounts CO₂ as an economic asset: CO₂ is a useful commodity that not only favors emissions mitigation, but also novel business opportunities. For this, CCU transforms environmental liability to an economic asset, with the generation synthetic of fuels and chemicals to displace their fossil-based counterparts. The main challenge of CCU is CO₂ itself: its thermodynamic stability needs to be overcome to form further products. For this reason, much researching effort is spent on efficient conversion solutions of CO₂ to CO—a more reactive molecule—and when achieved, it is then used to feed innovative end-products generation technologies. The present work describes a novel CCU integrated system that comprises of Solid Oxide Electrolysis Cell (SOEC) integrated with a small-scale Fischer-Tropsch (FT) reactor for production of the so-called FT-syncrude. The proposed configuration is of the typology Power-to-Liquid (PTL), in which multiple innovative solutions are integrated together, implementing a technology that produces substitute fuels/products, starting from industrial CO₂ separated from flue gases, and creating a net-zero carbon dioxide emission. The Fischer-Tropsch synthesis allows reaching high flexibility of the syncrude composition: it mainly consists of paraffins (CₙH₂ₙ₊₂ with n=1-100) and olefins (CₙH₂n with n>=2), and to a less extent oxygenated products. In the case of short-chain hydrocarbons, they can be used for methane, diesel and jet fuels production, while long-chain hydrocarbons can be a substitute of fossil-based white oils and waxes, used in the chemical sector, or cracked down to lower molecular weight molecules and applied again for the energy generation. Depending on the selected catalysts and the operating conditions of the FT reactor, the syncrude composition can be modified. In the present work, it has been considered to target long-chain hydrocarbons (C₁₅⁺) and increment their production yield.

In this study, we model the CO₂ captured from an industrial process, otherwise vented to the atmosphere. The CO₂ comes as waste of a biogas upgrading plant that uses an amine-based acid gas removal unit generated biomethane and a CO₂ stream having 99.9% (mol) CO₂ purity. The SOEC section consists of co-electrolysis stack modules, in which both CO₂ and H₂O are fed and split into CO and H₂. The resulting syngas is the feed of the FT reactor. The SOEC operates at 850 °C and atmospheric pressure to reduce the selectivity of methane (CH₄ < 0.1% mol of the outlet stream). A recirculation solution allows to produce an H₂/CO ratio of 2.1 mol/mol, that is ideal for the subsequent Fischer-Tropsch synthesis. Furthermore, the SOEC is considered to be alimented by excess electricity of renewable source. Such a solution permits, on the one hand, to reduce the amount of CO₂, by erasing its production in terms of fossil fuels used, on the other, to store renewable energy into chemical energy that, due to the intermittency of the energy vector, would be lost otherwise.
For syngas upgrade to syncrude, a Low Temperature Fischer-Tropsch (LTFT) reactor using a Co-based catalyst has been chosen. The Co-based catalyst enhances the production of syncrude with a better selectivity towards higher hydrocarbons, which are the raw material for manufacturing white oils and waxes with high molecular weight. The reactor operates at different temperatures (220°C and 240°C), with a pressure of 25 bar. A detailed kinetics based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach has been applied to fully describe the complexity of the catalytic FT synthesis. Specifically, a mechanistic approach based on carbide chain-growth mechanisms has been followed, with the main assumption of considering the desorption of α-olefins dependent on the carbon number: such desorption influences the final products distribution\(^7,^8\). The FT kinetic model has been validated with experimental data available in literature, and then applied on a commercial software for process analysis. Also for this reactor, a recirculation solution is considered to increment the yield of syncrude production.

Ultimately, the whole process undergoes an optimization pinch analysis, to reach the most effective configuration in terms of energy integration between components and energy streams. For instance, the high exothermicity of the Fischer-Tropsch synthesis (-158 kJ/mol of converted CO) can be exploited to vaporize the water fed to the SOEC. Similarly, FT off-gases can feed an ICE to generate electricity spent by the plant auxiliaries.