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Editorial

Progress in CO_2 Conversion Using Renewable Energy Sources

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Overview

The latest Intergovernmental Panel on Climate Change special report, on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, identified the imperative need to reduce fossil CO_2 emissions. To achieve this goal, in recent years, considerable efforts are being made worldwide to develop CO_2 conversion technologies based on renewable energy and the capability of transforming anthropogenic CO_2 emissions into energy carriers, such as synthetic gas, or value-added chemicals.

In the near future, these systems are expected to expand rapidly, because they can be used to store surplus renewable energy, contributing to greenhouse gas reductions.

In this Special Issue, entitled "Progress in CO_2 conversion using renewable energy sources", we analyze nine contributions from different research areas, ranging from electrochemical systems for CO_2 capture and conversion to syngas production systems via the CO_2 reforming of methane, and their optimization procedures.

A summary of the content associated with each of the selected papers in this Special Issue is presented subsequently.

In the first paper, Mezza et al. [1] described an electrochemical platform capable of capturing CO_2 from a gas mixture and convert it into syngas. This system consisted of two different electrochemical flow cells: the first cell performed a capture and release process of CO_2, whereas the second component was responsible for the conversion of CO_2 into a CO–H_2 mixture (syngas) with a CO selectivity of 56%. The capture/release stage was based on a regeneration process of NaOH and the acidification of $NaHCO_3$ inside a four-chamber reactor, utilizing Pt foils as catalysts. Instead, the conversion process was carried out by the electrochemical reduction of CO_2 based on ZnO as a catalyst and $KHCO_3$ as an electrolyte. The electrochemical platform for CO_2 capture and conversion could be supplied with renewable energy, in order to avoid additional CO_2 emissions and to further exploit the concept of a carbon neutral process.

An alternative option for syngas production from CO_2 is represented by the high-temperature thermochemical two-step cycle, based on metal oxide catalysts. Milanese et al. [2,3] developed a solar reactor model, based on a solid particle circulation loop between two fluidized beds (reduction reactor and oxidation reactor) crossed by two gas streams, N_2 and CO_2, respectively. In the first fluidized bed, under a low-pressure O_2 atmosphere obtained by fluxing N_2, a solar-driven endothermic dissociation of ceria occurs, according to the reaction $CeO_2 \rightarrow CeO_{2-\delta} + \delta/2O_2$, whereas in the second step, exothermic oxidation of the reduced ceria ($CeO_{2-\delta} + \delta/2O_2 \rightarrow CeO_2 + \delta CO$) enables completion of the cycle, producing CO with a maximum ideal efficiency of about 63%.

In order to reduce the very high temperature needed by two-step solar thermochemical cycles for CO_2 splitting, Pan et al. [4] proposed a new solar reactor integrated with a solid oxide electrolysis cell. Their results indicate that the introduction of external voltage as an alternative driving force in the reduction step can produce several advantages: (i) mitigating the reduction temperature, from 1500 °C to 1000 °C; and (ii) the metal oxide (e.g., CeO_2, ZnO, SnO_2, etc.) can be reduced in air instead of a low-pressure O_2 atmosphere. Therefore,

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the thermodynamic evaluations carried out in this study have shown a significant potential for reducing the cost of fuel production.

Bampou et al. [5], in order to reduce greenhouse emissions of the steel industry, investigated the integration of renewable hydrogen into steelworks off-gases for the efficient production of methane and methanol. Particularly, they carried out several numerical simulations by means of AspenPlus™ (Bedford, MA, USA) to study and compare different methanol (200–300 °C, stoichiometric number 1.7–2.1, and pressure 50–100 bar) and methane (200–300 °C, stoichiometric number 1–1.1 and pressure 1–10 bar) synthesis processes. The results of methane synthesis showed that, due to high CO and CO_2 conversion rates, it was possible to almost eliminate the CO_2 emissions from the steel plant, while the methanol conversion rate reached the maximum value of about 40%. Therefore, taking into account the higher market value of methanol with respect to methane, the best economical solution would be the result of estimated production costs, end-product prices, and carbon credits.

Yeo et al. [6] optimized the operating conditions of the CO_2 methanation process with Ni-based catalysts using the Taguchi design method coupled with an L16 orthogonal array. Particularly, they performed several CO_2 methanation experiments in a fixed-bed reactor (diameter = 10 mm, height = 60 mm), containing 1 g of catalyst, two thermocouples to measure the temperature, and one pressure regulator. Three parameters, such as the reaction temperature, reactor pressure, and space velocity, at four levels, were investigated as influencing factors. The authors experimentally demonstrated that sufficient methane and long-term operational stability were obtained at 315 °C, 9 bar, and 6000 h^{-1} of space velocity in the range of H_2/CO_2 = 3.6–4.0.

Szima and Cormos [7] presented a techno-economic evaluation of synthetic natural gas (SNG) production based on captured CO_2 and renewable hydrogen. In this study, the process was modeled and simulated by means of Aspen Plus® software (V8.6, https://www.aspentech.com/en/products/engineering/aspen-hysys (accessed on 22 January 2021)), analyzing overall energy efficiency, ancillary energy consumption, capital costs, operational and maintenance costs, SNG levelized cost, sensitivity analysis, etc. Furthermore, five renewable hydrogen production sources (photo-fermentation, dark fermentation, biomass gasification, bio-photolysis, and PV electrolysis) were compared with two reference cases (natural gas steam reforming and electrolysis) from a techno-economic point of view. The results showed that the mean SNG cost was strictly related to the cost of hydrogen, ranging from 67 to 78 EUR/MWh. This cost was around 3.0–3.5 times higher than the old price of natural gas (as quoted prior to the Russia–Ukraine war), but it is absolutely competitive with the current price of natural gas, which has recently exceeded 200 EUR/MWh. Finally, this study also evaluated the effect of 20 EUR/tCO_2 and 100 EUR/tCO_2 credit on the SNG cost, demonstrating that both options could significantly improve the economics of the SNG plant. Therefore, although PV electrolysis currently has the worst economic indicators among renewable hydrogen sources, further development of electrolyzers and PV panels could make this technology very attractive for future applications.

Between the conversion processes of major greenhouse gases into value-added chemicals, the dry reforming of methane (DRM) has gained great attention in recent decades, because it transforms methane and carbon dioxide into synthetic gas, which serves as an important raw material for the formation of liquid hydrocarbons. In this scenario, Ahmad et al. [8] investigated the activity and stability performance of $SrNiO_3$ and $CeNiO_3$ perovskites for syngas production via the dry reforming of methane. The results related to $CeNiO_3$ demonstrated higher CH_4 and CO_2 conversion levels in comparison with $SrNiO_3$: the lower activity of the second perovskites was due to strontium carbonates which covered the nickel active sites. Furthermore, both perovskites deactivated over time due to carbon deposition, as evidenced by the TEM and TPO images.

In another study on the DRM process in a thermally fixed bed reactor, Mazhar et al. [9] assessed the synthesis of various Co-loaded, TiO_2–$MgAl_2O_4$-supported catalysts. Here, the catalysts were prepared by means of a modified co-precipitation method, while the

active metal Co was loaded via the wetness impregnation method. The DRM process was investigated in a reactor with a temperature of 750 °C, a feed ratio (CO_2/CH_4) of 1, a catalyst loading of 0.5 g, and a feed flow rate of 20 mL/min. The best catalytic performance, in terms of CH_4 and CO_2 conversion and stability, was obtained with 5% $Co/TiO_2–MgAl_2O_4$.

Scientific studies on the technologies capable of transforming anthropogenic CO_2 emissions into energy carriers or other value-added chemicals are numerous, but there is a lot of room to explore many physical aspects that are still without a clear answer from both theoretical and experimental points of view.

Conflicts of Interest: The authors declare no conflict of interest.

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