Editorial

Special Issue "Methane Reforming Processes"

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1. Preface

This Special Issue, entitled "Methane Reforming Processes", of the MDPI journal *Processes*, embraces wide-ranging aspects of interest in the exploitation of methane reforming reactions and related chemical species, from a point of view that aligns with the scope of this open access journal. Methane reforming has well-established practices, although this Special Issue is oriented toward innovations and improvements that could transform those practices into new processes to face the current sustainability challenges from the Paris Agreement.

In this sense, in the next few years fossil methane can still contribute to easing the hoped energy transition, compared with other fossil carbon feedstocks. However, this transition must include the sustainable production and exploitation of methane (e.g., biomethane), as well as intensified processes including carbon capture (e.g., sorption-enhanced processes) and utilization (e.g., dry reforming). In addition, wiser usage and management of methane is needed to avoid emissions, as planned in November 2021 through the Global Methane Pledge from UNFCCC COP26 (26th Conference of the Parties of United Nations Framework Convention on Climate Change). The COP27 ascertained the need for rapid actions to limit global warming to +1.5 °C compared with preindustrial levels, proposing a reduction in greenhouse gas emissions (including methane) by 43% before 2030 compared with 2019 levels.

In this light, methane reforming and complex processes involving this reaction have recently received renewed academic and industrial attention. Efforts have been devoted to lowering their environmental footprint, focusing on simplification and intensification, as well as on the choice of feedstocks and catalysts according to green chemistry and green engineering principles.

As Guest Editors, we had the chance to propose some experimental and modeling research studies for peer-review that aligned with these premises to *Processes*, and we hope that the final collection of the Special Issue entitled "Methane Reforming Processes" may be as inspiring for the readers as it was for us.

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Guest Editors of *Processes* for the Special Issue "Methane Reforming Processes"

2. The Papers

Knoelchemann et al. [1] focused on several methane reforming processes on a Ni–γAl_2O_3 catalyst. They compared the processes with a kinetic study based on simulations of a packed-bed reactor. The methane reforming processes included dry reforming with carbon dioxide (DRM, feed: CH4/CO_2), autothermal reforming (ATRM, feed: $CH_4/H_2O/O_2$), and combined reforming (CRM, feed: $CH_4/CO_2/H_2O/O_2$). A microreactor model (2 g of catalysts with an average particle diameter of 50 μm) was developed. The kinetic laws of the three considered reforming were implemented in that model at 1023 K and atmospheric pressure. Kinetics were based on dedicated mechanisms for each reforming process. Regarding the kinetic selectivity of H_2, the best results were attributed to CRM.

Barisano et al. [2] situated the investigation of methane conversion by steam reforming on a broader framework, as a part of the steam-gasification process of lignocellulosic biomass. The process was performed in the 1 MW$_{th}$ pilot plant of ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) in the Trisaia Research Centre (Italy); the pilot included an auto-thermal bubbling fluidized bed reactor. Experimental tests were carried out at different equivalence ratios (0.25–0.28), steam-to-biomass ratios (0.4–0.5), and temperatures (750–850 °C), with almond shells as the solid biomass fuel and olivine as the fluidized bed material. Aspen Plus simulations of the auto-thermal gasifier were also performed. In both experimental and simulative studies, Barisano et al. [2] considered the main gasification products and polluting components, such as HCl, H$_2$S, NH$_3$, and tars. Methane was developed by biomass gasification, and steam reforming had to be duly considered within the complex system of gasification reactions, because reforming contributed to the formation of H$_2$, the product of interest in the process. Experiments demonstrated the innovative integration, directly in the reactor freeboard, of a bundle of ceramic candles for high-temperature in situ gas filtration (bringing in process intensification), obtaining dedusted syngas with a lower heating value of 10.9 MJ/Nm^3 $_{dry}$. The Aspen Plus model responded well in terms of the main products, but could be improved as far as predictions regarding H$_2$S and HCl are concerned.

Micheli et al. [3] experimentally investigated the synthesis and reactivity of several bi-functional catalyst/sorbent materials for sorption-enhanced reforming processes (with varying Ni and CaO contents), to be applied in biomass gasification. Systems of CaO/Ca$_{12}$Al$_{14}$O$_{33}$ solid CO$_2$ sorbent, upgraded with Ni as a reforming catalyst, were synthesized and characterized by X-ray diffraction, pore analysis, temperature-programmed reduction, and scanning electron microscopy. Their reactivity at 650 °C was tested by a packed bed laboratory-scale reactor, concerning sorption-enhanced steam reforming of methane and toluene (as the key component representing tars). In the best cases, the sorption-enhanced reforming of toluene had 99% conversion, whereas reforming of methane was not so efficient: this was attributed to the significant excess of CaO phase in the bi-functional material, which was supposed to cause detrimental interactions with Ni (CaO constituted the support at least by 56 wt.%).

The contribution from Fatigati et al. [4] addressed the development of sorption-enhanced steam methane reforming (SESMR) from an energy-efficiency point of view. Ni/CaO/Ca$_{12}$Al$_{14}$O$_{33}$ combined sorbent–catalyst materials were previously tested in a packed bed reactor for 205 cycles of SESMR/sorbent regeneration by calcination (i.e. thermal swing). The experimental results were used by Fatigati et al. [4] to develop a comprehensive thermodynamic model to perform an energy retrofit of the investigated process, enabling the evaluation of energy contributions from its different steps. They demonstrated that sorption-enhanced steam methane reforming offers advantages in terms of the energy content of the final product and overall thermal power recovery, compared with plain steam reforming at the same process conditions (650 °C, 1 atm, milder than the current industrial practice of steam methane reforming).

The paper by Arutyunov et al. [5] was included in this Special Issue to expand the borders of evaluations about exploiting methane and hydrogen (a reforming product) as fuels. They investigated the autoignition of methane–hydrogen mixtures below 1000 K through experiments and kinetic modeling. The autoignition delay of stoichiometric methane–hydrogen–air mixtures was experimentally measured using the high-pressure bomb method in a static-type setup, at different conditions (temperature from 850 to 1000 K, initial pressures of 1 and 3 atm, and hydrogen concentrations from 0 to 50%). The collected results were interpreted by kinetic approaches, e.g., the temperature dependence of the autoignition delay time was analyzed according to Arrhenius type expression. The authors concluded that a hydrogen concentration of 40% is the upper limit of hydrogen content in a mixture with methane, which enables the use of current gas equipment and safety rules for the transportation sector, as well as other practical uses of methane–hydrogen mixtures.

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