

# Advanced materials and processes for CO<sub>2</sub> capture and conversion to fuels

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Carbon dioxide has been identified as the most significant greenhouse gas arising from anthropogenic activities, mainly as a waste by-product in fossil fuels combustion, chemicals production and synthetic fuels manufacturing processes. Thus it is of great importance to reduce CO<sub>2</sub> emissions in order to counteract global warming and climate change. A step towards this direction is the application of CO<sub>2</sub> capture technologies in industrial sector.

Chemical absorption with alkanolamines (or variants) is today the benchmark technology for CO<sub>2</sub> capture from flue gas streams. The sorbed CO<sub>2</sub> can be further sequestered by raising the temperature and/or lowering the pressure, so that the regenerated solvent is recycled in the absorption unit. However, despite the maturity of this process, it still remains energy intensive and costly. Membrane gas absorption (MGA) on the other hand is a novel method which combines membrane gas separation with absorption creating a new way of contacting liquid and gases. It has the advantages of higher efficiency, less required energy and lower costs in a more compact unit compared to the conventional absorption processes. The MGA process has already been tested in industrial applications using mild concentrations of diethanolamine as absorbing agent with excellent behavior (>95% CO<sub>2</sub> recovery) [1].

The captured CO<sub>2</sub> can be directed for subsequent sequestration into depleted oil and natural gas reservoirs, deep coal seams, etc., which is the traditional end-of-pipe approach. An alternative solution is the fixation of CO<sub>2</sub> as a chemical reactant: its advantage compared to sequestration methods is that it involves production of chemicals with high economic value while consuming great amounts of CO<sub>2</sub>.

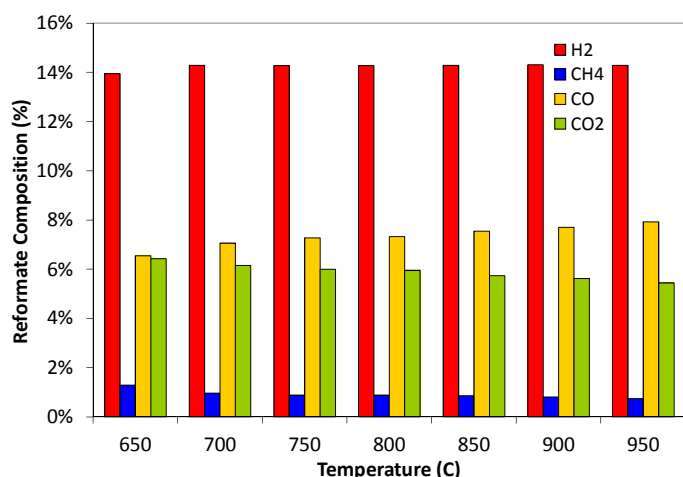


Figure 1: SADRМ performance evaluation test for the LaAl-perovskite with 2% Rh in the temperature range 650-950 °C.

In this line of work a series of experiments is conducted in order to investigate the catalytic performance of Rh-based catalysts for the SADRМ process in fixed-bed configurations and monolithic structures for various conditions. As shown in Figure 1 the syngas formation is high according to all thermodynamic trends. The feed gas composition can be tuned to produce the desired syngas composition.

In the context of the ERANET CARDIOSOL project appropriate initial feed composition including steam and CO<sub>2</sub> (steam-assisted dry reforming of methane – SADRМ) is considered a promising route to convert CO<sub>2</sub> to fine chemicals leading to the production of syngas ratios most appropriate for the production of added value chemicals such as methanol, dimethyl-ether (DME), olefins, etc. or for the production of refinery products via the Fischer-Tropsch synthesis route such as sulfur-free diesel, naptha, LPG, etc.

The general kinetic scheme of the reforming of  $\text{CH}_4$  with steam/ $\text{CO}_2$  was incorporated into a generic 1-D model [2]. All resistances to mass and heat transfer in the bed, the bed-to-particle region (inter-particle), and the particle (intra-particle) itself are included under transient conditions. In order to validate the developed model, the industrial case of the steam-methane reforming (SMR) reactor was set as a base-case; this is done because all resistances are present in severe pressure and temperature conditions for the multi-component feed gas mixture.

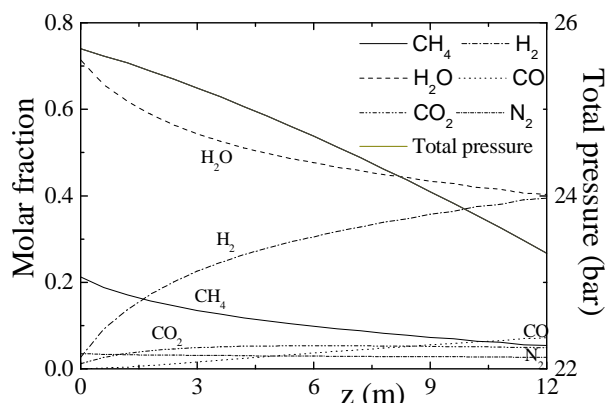


Figure 2. Molar fractions and total pressure under steady-state operation in an SMR industrial reactor.

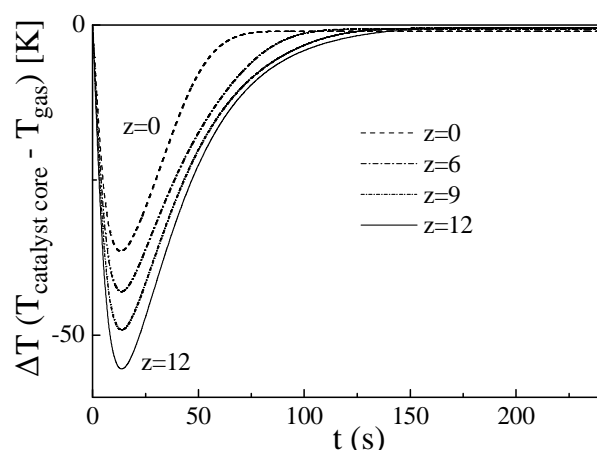


Figure 3. Dynamic profiles of temperature difference between the catalyst core and the gas mixture at various  $z$ -points in an SMR industrial reactor.

As illustrated in

Figure 2,  $\text{H}_2$  is produced at the expense of steam and  $\text{CH}_4$  with a total pressure decrease from 25.7 to 23.33 bar. At the exit, the dry composition of  $\text{H}_2$  is 66.2%. As temperature increases, the reverse water-gas shift reaction is enhanced thereby leading to  $\text{CO}$  formation at the expense of  $\text{CO}_2$  and  $\text{H}_2$ .

Figure 3 depicts the dynamic profiles of the temperature difference of the catalyst core and the gas bulk phase at various axial points.

It is evident that the catalyst does not reach the gas mixture temperature rapidly due to the solid catalyst thermal inertia. This difference may be lower than -50 K at the exit of the reactor for short times, but it becomes very small under steady-state conditions reached after about 120 s for all points along the  $z$ -axis. However, this difference is never eliminated, due to the mass and heat inter- and intra-particle resistances. The proposed formulation is capable of reproducing published data with reasonable accuracy, while results are in accordance with literature findings.

## Acknowledgments

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## References

- [1] Koutsonikolas, D., Pantoleontos, G., Mavroudi, M., Kaldis, S., Pagana, A., Kikkinides, E. S., Konstantinidis, D., Pilot tests of  $\text{CO}_2$  capture in brick production industry using gas-liquid contact membranes, *Int. J. Energ. Environ. Eng.* 2016 [submitted for publication].
- [2] Pantoleontos, G., Skevis, G., Karagiannakis, G., Konstandopoulos, A. G. A heterogeneous multi-scale dynamic model for simulation of catalytic reforming reactors. 9<sup>th</sup> International Conference on Chemical Kinetics, June 28 – July 2, 2015, Ghent, Belgium.