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MACBETH: A Revolution in Catalytic Reaction Technology

Insights, current status and future perspectives

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Membranes and Catalysts Beyond Economical and Technological Hurdles (MACBETH) is a European funded project that aims to implement a catalytic membrane reactor (CMR) technology at Technology Readiness Level 7 (TRL7) in four industrially relevant use cases. This paper gives the background, status quo and future perspective of that innovative technology that could transform current chemical processes into more sustainable ones.

1. Introduction

In all sectors of the process industry, downstream processing requires a significant share of the overall energy and resource consumption and contributes a large portion of the capital expenditure (CAPEX) and operational expenditure (OPEX) of each process. To enhance the competitiveness of the European process industry and contribute to Europe's goal of more sustainable and environmentally friendly processes, it is highly desired to have a broadly applicable concept for an efficient integration of downstream operations in the overall process chain. The consortium of the European Union (EU)-funded MACBETH project aims to provide breakthrough technology by combining catalytic synthesis with the corresponding separation units in a single, highly efficient CMR unit (**Figure 1**).

This disruptive technology has the potential to reduce greenhouse gas (GHG) emissions of large volume industrial processes by up to 45%. Additionally, resource and energy efficiency can be increased by up to 70%. The new reactor design is expected to provide substantially smaller and safer production plants in addition to competitive advantage, since CAPEX may be decreased by up to 50% and OPEX by up to 80% compared to conventional systems.

To achieve this, the MACBETH consortium will combine the catalytic synthesis step with a highly efficient separation step through tailor-made membranes. The predecessor EU funded projects

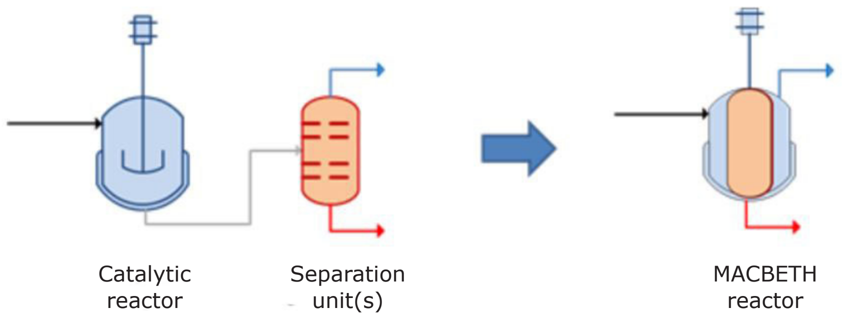

Fig. 1. Schematic presentation of MACBETH technology combining synthesis and separation units in a single reactor

Reactor Optimization by Membrane Enhanced Operation (ROMEO), Biogas Membrane Reformer for Decentralized Hydrogen Production (BIONICO) and Catalytic Membrane Reactors based on New Materials for C1-C4 Valorisation (CARENA) have shown proof of concept for CMRs at TRL5. Successful TRL5 pilot plants are in operation for the following large-scale processes:

- Hydroformylation
- Hydrogen production
- Propane dehydrogenation.

Members of the earlier consortia have now joined MACBETH, aiming to combine the results of their previous projects and bring CMR to TRL7 for all three processes and finally to commercialisation. The broad applicability of CMR will be demonstrated on the foundation of a large variety of building blocks such as catalysts, membranes, support materials and reactor concepts under different conditions in different sectors of process industry that require a separation after a catalytic synthesis. According to SusChem, the chemical industry is worth approximately €1500 billion (1) and more than 80% of the processes depend on catalytic technologies. Therefore, CMRs may be expected to have huge impact.

The MACBETH consortium's goals include two special extensions:

- Transfer of CMR technology to a new sector (biotechnology) already within MACBETH, namely biocatalytic oil cleavage (BOC)
- Creation of the spin-off European Lighthouse Catalytic Membrane Reactors (LCMR) within MACBETH.

The MACBETH project started in 2019 and will be finished by end of 2024. In the following, the four use cases of MACBETH are briefly described by their case specific background, goal and current status.

2. Outline of the MACBETH Demonstration Cases

2.1 Hydrogen Production Line

2.1.1 Background

Hydrogen production is often carried out through equilibrium limited reactions like reforming of hydrocarbons. These reactions are endothermic which means high temperatures are required to achieve higher conversions and high yields. MACBETH investigates the reforming of natural gas and biogas. These reaction systems usually require a number of reactor steps in series followed by one or more separation steps. By integrating palladium-based membranes in the reactor the equilibrium is shifted towards the products. In this way two benefits are achieved: namely a reduced number of steps (accompanied by a reduction of CAPEX) as well as reduction of temperature (average decrease of 300–350°C compared to conventional systems) allowing for a consequent reduction of OPEX and process emissions.

2.1.2 Goal

Two prototypes will be built at TRL7 to be tested as standalone units for pure hydrogen production from natural gas and biogas. The prototypes will be tested for up to 8000 h of operation to assess the stability and reliability of the intensified process.

2.1.3 Current Status

At the time of writing, the production target of more than 200 palladium-based membranes for the prototypes has been reached. These membranes were produced with perm-selectivity and permeation flux above the project targets (selectivity of 20,000–60,000 *vs.* target of 10,000; permeation of 2.5×10^{-6} mol m^{-2} s^{-1} Pa^{-1} *vs.* target of 1×10^{-6} mol m^{-2} s^{-1} Pa^{-1}).

Apart from standard membranes on ceramic supports, a new procedure to produce thin layer membranes on cheap metallic supports has been developed. These membranes have perm-selectivities three times the target of the project, while the permeation of hydrogen is slightly lower than the target of the project (selectivity of 30,000 and permeation 8×10^{-7} mol m^{-2} s^{-1} Pa^{-1}). Current work aims to improve the performance further. These membranes are stable, robust and easy to implement in reactors. In the near future the lifetime of the membrane reactor may be improved. The demonstration reactors have also been designed and are under construction.

In the meantime, reactor models have been optimised and used to map the operating conditions of the systems, showing that under several operating conditions the targets of the MACBETH project in terms of production rate and purity can be reached. The models have also been instrumental to define the minimum amount of fluidisable catalysts for both prototype and technoeconomic analysis.

These models have been transferred to the MACBETH spinoff company MODELTA BV (The Netherlands), who will further explore the technology and provide services on modelling of membranes and membrane reactor systems for industries interested in the technology.

2.2 Hydroformylation Case

2.2.1 Background

Hydroformylation is one of the most widely industrially applied reactions. More than 10 million tonnes of chemical products (2) rely on this homogeneously catalysed reaction step every year. Thus, a permanent improvement of the hydroformylation process is of utmost interest for many chemical companies. Especially, it is researchers' and companies' aspiration to find a heterogeneous-like catalyst. Improvements within Evonik Industries AG, Germany, have followed several approaches in the past including optimising process technology as well as the catalytic system.

The current approach aims to combine a catalytic reaction with the separation step on a single support structure. This combination in an innovative 'two-in-one' reactor opens the possibility to omit or at least significantly downsize the subsequent separation units. For catalytic processes that are performed close to chemical equilibrium, the constant removal of one reaction partner from the reaction may enhance the efficiency. Thus, the concept allows the yield of catalytic reactions to be increased not only by immediately removing undesired side products from the reaction zone but also by using new heterogenised catalyst systems.

2.2.2 Goal

Within the MACBETH project a pilot plant unit of the hydroformylation CMR will be planned, built and operated in bypass to the current world-scale production plant at Evonik Marl, Germany. It is the goal to demonstrate the maturity of the technology at TRL7 in long term runs under production conditions.

2.2.3 Current Status

Starting with the results from the predecessor project ROMEO, the catalytic system has been modified to meet the safety requirements of an industrial setting. In addition, various support structures for both catalyst and membranes have been prepared, tested and optimised. Scale-up of the deposition procedure of the membrane materials on the outer skin layer of the silicon carbide support was optimised. Finally, the catalyst recipe was adjusted allowing for long-time experiments with a membrane coated monolith reactor in laboratory scale so far with >2000 h of stable performance. Besides the optimisation work at laboratory scale, the construction of the demonstration unit has started.

2.3 Propane Dehydrogenation

2.3.1 Background

Propylene is currently mostly produced as a side product of industrial processes such as steam cracking and fluid catalytic cracking. Due to growing demand, several technologies have been introduced in the market to increase propylene production. Propane dehydrogenation (PDH) uses fixed bed reactors in parallel to convert propane into propylene. Typically, one of the reactors is in regeneration phase to remove the coke formed on the catalyst. Since the dehydrogenation reaction is endothermic, high temperatures are required to increase conversion and yield.

2.3.2 Goal

The implementation of a CMR concept, shifting the equilibrium towards the products and removing hydrogen, allows the unit to operate at lower temperature (500–550°C *vs*. 600–650°C). This dramatically reduces catalyst deactivation due to coke formation. This has a positive impact on the onstream factor as well as on CAPEX, OPEX and GHG emissions.

CMR can be operatively realised in an integrated membrane reactor (membranes installed inside a fixed catalytic bed) or in a cascade of catalyst beds and membrane separations (membranes installed in a dedicated shell between two separate catalytic beds). The cascade architecture allows the catalytic reactors and membranes to operate at different temperatures, namely 500–550°C for reactors and 350–400°C for membranes.

2.3.3 Current Status

At this stage of the MACBETH Project, catalyst formulation (platinum-tin on hydrotalcite support) has been fully defined and double skin palladium-based membranes on ceramic support are being produced and tested. Scale-up activities on catalyst and membrane building blocks are in progress. In the meantime, unit arrangement and reactor design have been defined. The detailed design and procurement phase of the MACBETH PDH Pilot Unit, to be installed and operated at ENGIE Lab CRIGEN, France, are in progress. Activities on modelling the catalytic reactor and of the overall system are also ongoing.

2.4 Biocatalytic Oil Cleavage Case

2.4.1 Background

Omega-3 polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are vital for human psychological, neural, prenatal, maternal and ocular health. They help to prevent cardiovascular disease (3), inflammation, hypertension and other chronic disorders (4). Furthermore, EPA and DHA play a crucial role as potential treatment for neurodegenerative and neurological disorders such as Alzheimer's and Parkinson's disease (5). However, the human body does not efficiently produce these valuable omega-3 PUFAs. Therefore, it is necessary to obtain adequate amounts through nutrition (6).

To enrich those valuable fatty acids in fish oil, an enzyme catalysed approach was chosen. Enzymes can selectively cleave certain fatty acids from the glycerol backbone of natural oils as shown in the predecessor project COSMOS (7). Enzymes are also used on a large scale to make specialty and bulk chemicals (8).

2.4.2 Goal

Our objective is to adopt the CMR approach and demonstrate its commercial applicability to the field of biotechnology. We will utilise the selectivity of both the catalyst (enzyme) and the membrane to enrich the omega-3 content in fish oil. Another novelty will be the introduction of a liquid-state reaction to the CMR technology. In particular, our aim is the enrichment of EPA and DHA in an enzyme catalysed reaction system. First, initial operation will be demonstrated in a continuous manner. Afterwards, long-term tests will be performed in an industrial environment.

2.4.3 Current Status

As of now, crucial reaction parameters have been identified and optimised in laboratory experiments ready to scale up. This includes enzyme selection, optimisation of reaction temperature and reaction mixture composition. Immobilised enzyme formulations have been developed and produced. Different carrier materials and immobilisation techniques were tested, aiming for the optimal enzyme-carrier combination for a continuous process. A membrane separation unit will perform the first purification step and will be an integrated part of the pilot plant. A wide range of membrane configurations and materials have been tested and a suitable solution was found to achieve the ambitious goal of this project. Feasibility studies were successfully conducted first in 10 l batch experiments and in a continuous flow setup up to 1 l h^{-1}. Satisfactory results were achieved in the laboratory experiments with regards to the level of omega-3 enrichment in the final product.

3. Summary

The European-funded project MACBETH aims to introduce a revolutionary process technology by combining the relevant reaction and separation steps in a single apparatus at TRL7. After two years of research and development, the project and four demonstration cases are on track. Great saving potentials in terms of costs and GHG emissions are envisioned.

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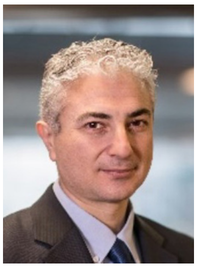
The Authors

Frank Stenger studied Chemical Engineering at the University of Karlsruhe, Germany, where he obtained his diploma in 1999. His PhD on nanoparticle technology followed at the Technical University of Munich, Germany, in 2004. He started his industrial career as a process engineer at Degussa AG, Germany, in 2004 and became head of Reaction Technology Group in 2011 at Evonik Operations GmbH, Germany. He also heads the technology platform modular plants within Evonik. Since then he has been active in several EU-funded research projects (F3 Factory, ROMEO). Frank chairs several working groups at DECHEMA, Germany, and the Association of German Engineers (VDI) in the field of reaction technology and modular plants.

Robert Franke studied chemistry at the University of Bochum, Germany. He earned his doctorate degree in 1994 in the field of relativistic quantum chemistry under Professor W. Kutzelnigg. After working for a period as a research assistant, in 1998 he joined the process engineering department of the former Hüls AG in Germany, a predecessor of Evonik Performance Materials. He was awarded the professorial research degree in 2002 and in 2011 he became adjunct professor at the University of Bochum. He is now director of innovation management hydroformylation, Evonik Operations GmbH. His research focuses on homogeneous catalysis, process intensification and computational chemistry.



Fausto Gallucci studied Chemical Engineering at the University of Calabria, Italy, where he obtained his MSc in 2001 and PhD in 2006. He performed his PhD research on hydrogen production from methanol in membrane reactors. In 2007, after having held a position as a postdoctoral researcher at the Research Institute on Membrane Technology, Italy, Gallucci moved to the University of Twente, The Netherlands, where he was appointed Assistant Professor in 2009. The following year, Gallucci moved to the Eindhoven University of Technology, The Netherlands, where he was appointed Associate Professor in 2015. In 2018 he was appointed full Professor at the chair of Inorganic Membranes and Membrane Reactors.

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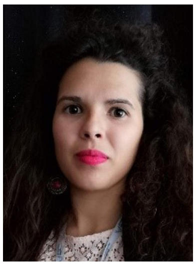
Fabio Angelini graduated as a chemical engineer at the University of Rome 'La Sapienza', Italy, in 2000. Since 2001, he is Senior Process Engineer in KT – Kinetics Technology SPA, Italy. For more than 20 years, he has worked on a huge number of basic, front-end engineering design (FEED) and engineering, procurement and construction (EPC) projects, mostly on sulfur recovery and tail gas treatment. He had the chance to perform several field activities in KT licensed plants all over the world, successfully collaborating with companies of different countries and cultures. Since 2018, he is collaborating with the research and development (R&D) department of KT – Kinetics Technology SPA on EU funded projects.



Vittoria Cosentino graduated as a chemical engineer at the University of Salerno, Italy, in 2018. She is currently Strategic R&D Engineer. She is continuously involved in execution of EU funded projects, mainly related to the application of membrane reactor technology in the hydrocarbon processing industry.