ENTER MACBETH

Until recently, catalytic membrane reactors have only been able to demonstrate their performance in laboratories, but now they are about to take the stage in a starring role

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The chemical engineers Linda Arsenjuk (left) and Corina Nentwich from the process technology unit are working on the further development of membrane reactors

Sometimes dramatic changes start out very small. We see chemical engineer Dr. Linda Arsenjuk as she puts on blue rubber gloves at the Evonik Technology Center in Marl. She then carefully pushes a small gray ceramic tube into a metal cylinder the length of her forearm. Seven of these tubes fit into the metal frame—each of them has 30 highly symmetrically arranged holes on its front side. "No grease must get onto the highly sensitive membrane on the exterior of the reactors," says Arsenjuk. "That's why I have to do it wearing gloves."

The object that she is so carefully handling might trigger a revolution for several important reactions in the chemical industry for process technology. "The aim is to develop catalytic membrane reactors, or CMRs for short, for industrial use," says Arsenjuk. Scientists have already shown on the laboratory scale that such CMRs work in principle. The task now is to overcome the final technical obstacles on the path toward larger-scale applications and to investigate the economic efficiency of this approach in practical industrial use.

The experts have two hopes regarding this technique. Firstly, the catalyst that is needed for the reaction is incorporated into the membrane reactors in a way that makes it much more stable than conventional techniques. In addition, the integrated membrane directly separates the resulting product from the other components. Ideally, it will replace the energy-intensive separation techniques that are still commonly used. Depending on the process in question, the researchers are hoping to thus boost energy efficiency by as much as 70 percent. This would also significantly reduce greenhouse gas emissions.

In keeping with its importance, the overall project bears an impressive name: MACBETH. The acronym stands for Membranes And Catalysts Beyond Economic and Technological Hurdles. The fact that project coordinator Prof. Robert Franke is a huge fan of the English playwright William Shakespeare may have played a role in the choice of the name. Under normal circumstances, Franke travels to Shakespeare's place of birth in Stratford-upon-Avon every year in order to enjoy the local theater festivals. Now, he is using the pandemic-related cancellation of the plays to push ahead with his own MACBETH.

A PRECURSOR FOR MANY APPLICATIONS

The project encompasses four sub-projects devoted to a variety of different chemical processes (see box on page 47). One of these sub-projects is being carried out at the Marl Chemical Park. It involves an important process called hydroformylation—also known as oxo synthesis. The process is called hydroformylation by chemists when they make unsaturated hydrocarbons known as olefins react with syngas (a mixture of hydrogen and carbon monoxide) to create aldehydes. In this way, →

the global chemical industry produces 12 million metric tons of aldehydes every year. In Marl, Evonik generally uses aldehydes as intermediates that are on their way to becoming more advanced alcohols, organic acids or esters that are incorporated into solvents for the manufacturing of cosmetics and detergents, for example, as well as in the production of medication or as plasticizers in polymers.

Franke has been working on this approach for more than ten years. As part of the MACBETH project, the technique is now ready to demonstrate its suitability for industrial applications. That this method works in principle was already shown by the predecessor project ROMEO (see text above), which ran from 2015 to 2019. The acronym stood for Reactor Optimisation by Membrane Enhanced Operation, which naturally appealed to the Shakespeare enthusiast as well.

NO TANKS OR COLUMNS

"We now want to conduct tests in a real-life production environment so that we can find out, for example, whether the system also works with the industrial feed in our hydroformylation facility and thus with the gas mixtures that are commonly used there," says Franke. ROMEO still employed very pure input gases, although the olefins that are used at the hydroformylation facility, for example, are part of gas mixtures that come directly from the petroleum cracker, he explains. Franke also wants to know whether the process is suitable for larger production quantities and operates reliably over the long term.

The researchers are currently working on the hydroformylation of the olefin 1-butene, which produces the aldehyde n-pentanal. This reaction will now be transferred to a larger-scale operation that will demonstrate its potential. In the Technology Center, Arsenjuk shows us how much progress they have already made with an experimental setup underneath a hood. It contains a stainless steel cylinder that has a thick wrapping of aluminum foil. The cylinder is strapped vertically into the setup. "It contains our tubes, into which we feed the reaction mixture of butene and syngas from above," explains Arsenjuk. Inside the tubes is the catalyst that causes the components to react. The resulting n-pentanal

The MACBETH reactor is still being optimized at the Technology Center

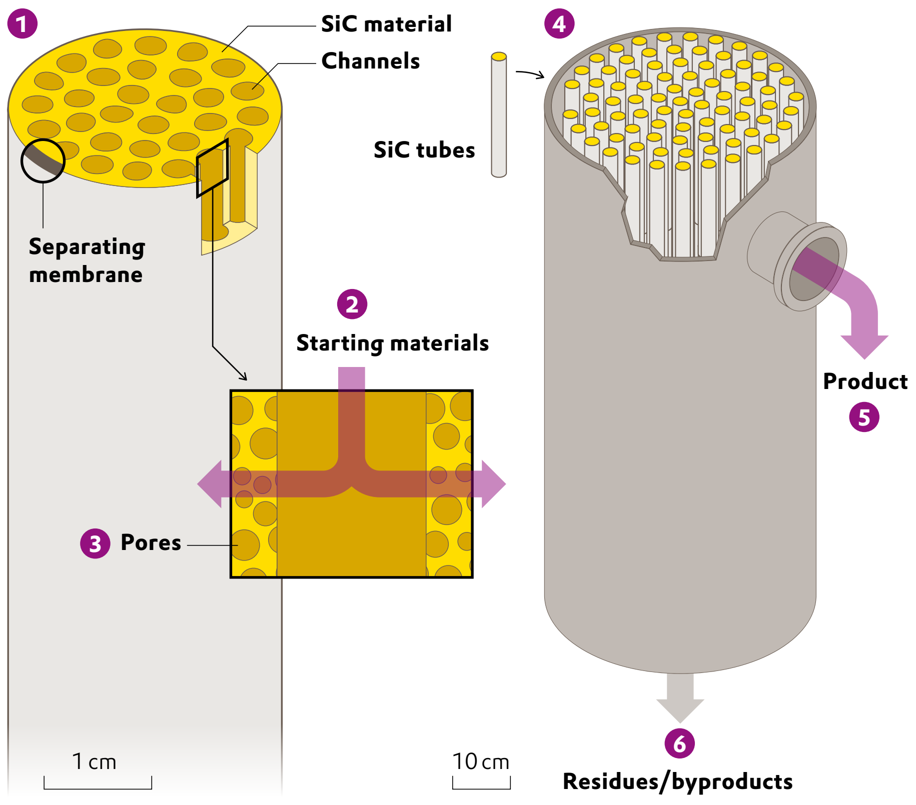
ROMEO lives—the history of solid catalyst development

In hydroformylation processes, catalysts are normally dissolved in the reactor liquid. Known as homogeneous catalysis, this process is very efficient, but also has its drawbacks. "The catalyst mixes with the product and then has to be separated with great effort," explains Robert Franke, the head of hydroformylation research at Evonik. Moreover, it breaks down over time and has to be reprocessed. Although a solid catalyst prevents such mixing, the yield is generally much lower because the reactants and the catalyst do not come into contact as closely. In the ROMEO project, researchers looked for a way out of this dilemma. Their idea was to take advantage of the fact that very porous materials have a large surface area. What would happen if the surface of the pores was coated with the catalyst, in the form of a viscous film, for example? Franke had read about researchers from Denmark and Erlangen who dissolved catalysts in ionic liquids that were used to coat the pores. Ionic liquids are salts that liquefy at temperatures of about 100 degrees Celsius. Experts in this field also took part in the ROMEO project, as did the Danish company LiqTech and its very porous ceramic tubes. In addition, the outer wall of the tubes was coated with a membrane that only lets the reaction product of the hydroformylation pass through. This is not a trivial matter. For example, the aldehyde molecules that are produced during hydroformylation are larger than the starting materials that remain in small amounts in the gas flow. During the ROMEO project, the researchers found a siloxane polymer to be the right material for the membrane. It holds back the starting materials while the aldehyde molecules dissolve in the polymer. Once they have dissolved in the membrane, the molecules travel to the outside, where they are released and can be channeled away.

A reaction in tubes

The MACBETH reactor enables catalysis and filtration in a single step.

1. The MACBETH reactor contains tubes made of silicon carbide (SiC). Each tube has 30 channels and is sheathed in a membrane.
2. The starting materials are fed into the channels and pass through the highly porous SiC material.
3. The pores are coated with a viscous liquid that contains the catalyst. As the starting materials flow through the pores, they dissolve in the coating and react there to form the product that then leaves the liquid.
4. The actual reactor contains numerous SiC tubes connected in parallel.
5. The reaction product passes through the membranes to the exterior and is then channeled away along the side.
6. Residues and byproducts are kept back and channeled downward.



can escape through the exterior wall along the side and then be extracted from the stainless steel cylinder via a connection. If it is sufficiently pure, it can be directly processed further (see the graphic above).

The actual gray reactor tubes are only two and a half centimeters in diameter and 20 centimeters long. However, this isn't a drawback as far as Franke is concerned. On the contrary, he thinks that this gives the setup its "special charm." He says, "The small dimensions allow us to use a modular design with which we can scale the process as desired. If we want to produce larger amounts we simply have to connect sufficient numbers of tubes together."

The possible dimensions can be seen at a site about 800 meters from the Technology Center. Here, in the midst of the six-square-kilometer Marl Chemical Park, is the hydroformylation facility. The hydroformylation is currently carried out in huge tanks that are several meters tall and can hold tens of thousands of liters. The distillation columns that are then needed to separate the product are even taller. However, the new generation of reactors might make these systems superfluous.

The facility will show how well the separation works and how pure the resulting aldehyde actually is. A small area is already being kept free for the planned demonstration facility. The researchers have also laid out the access points to the huge existing plant. However, some issues still need to be clarified at the Technology Center before the new reactor system can be built. "We are still working on the final design," says Arsenjuk. In this process, the researchers are also examining several innovations that weren't contained in the ROMEO reactor. One example of this is an additional membrane material that was suggested by one of the project partners, the Helmholtz-Zentrum Hereon. There is now a promising alternative to the previously used ionic liquid for the coating of the pores in the reactor. Moreover, tests are now being conducted with a longer version of the ceramic tubes from the Danish partner LiqTech.

SIMULATION OF THE MATERIAL FLOWS

The researchers also have to determine what the optimal settings are for the temperature, pressure, and flow speed of the process in practice. The aim is not only to achieve the best possible product yield, but also to prevent interfering side reactions. "One of the potential problems is always that pentanal molecules react with one another to form larger units that then condense to clog the pores like honey," explains Dr. Corina Nentwich, who is also a chemical engineer at the process technology unit. Within the MACBETH team, Nentwich is responsible for the process simulation, and that means she has to integrate the processes within the new reactor into the corresponding software as precisely as possible. Ultimately, this precise numerical description will help the researchers to theoretically simulate certain scenarios and optimally plan the reactor. →

Linda Arsenjuk and Corina Nentwich next to the distillation facility that might be replaced by the new technology

“The system lets us scale the process as desired”

ROBERT FRANKE, PROJECT COORDINATOR MACBETH

The MACBETH project

Hydroformylation is one of four areas of application for which MACBETH is researching catalytic membrane reactors. In the other project strands, further project partners are working on using the technique to produce hydrogen from biogas, to isolate pure fatty acids from vegetable oils, and to hydrogenate propane into propene. In all cases, the work involves combining suitable catalysts with membranes for separating the desired products. Although catalysts, membrane materials, and reactor conditions vary widely, all of the processes would, if successful, help to save large amounts of energy and prevent greenhouse gas emissions. From 2019 to 2024, 24 partners from ten countries are working on eight work packages in four sub-projects. The EU is funding this research with €16.6 million. Evonik is responsible for the overall coordination of MACBETH.

The project is supported by the European Union’s research and innovation program Horizon 2020 as part of the funding agreement No. 869896.

Nentwich also takes an overarching perspective and examines how the membrane reactor affects the material balances at the facility in Marl. “After all, the reaction of butene to form pentanal doesn’t occur in isolation at the chemical park,” says Nentwich. “On the contrary, the process is incorporated into an entire network of chemical reaction paths and material flows that influence one another.” For example, if the new reactor turned a certain amount of butene into more or less pentanal than the conventional process, this would have consequences for other synthesis lines because they might then have more butene available than before. Nentwich is currently working on ways to depict such interrelationships as well.

Despite the difficult conditions posed by the coronavirus pandemic, the tests at the demonstration facility are scheduled to begin in 2022, if possible. If the innovative membrane reactor shows its worth in practice, it will be a real highlight for Arsenjuk and Nentwich, who are still at the beginning of their careers. “It isn’t every day that you develop a completely new type of reactor. It’s fantastic to be part of such a project,” says Arsenjuk enthusiastically.

TWO THIRDS LESS GREENHOUSE GASES

Another achievement is the calculated effect on the sustainability performance. “To determine this effect, we conducted a life cycle assessment that compared the new method with an extensively studied conventional process,” says Nentwich. This comparison included the further processing of pentanal into 2-propylheptanol (2-PH). “The analysis showed that the new reactor can reduce the total greenhouse emissions of 2-PH production by almost 70 percent,” says Nentwich,adding that this calculation doesn’t even include the effect of the membrane. The impact will thus be even bigger if MACBETH demonstrates that the membrane purifies aldehydes so well that the energy-intensive distillation steps are no longer needed.

No matter whether it concerns the membrane or the catalytic coating, the respective project partners contribute important expertise for many of the details. “We wouldn’t be able to do it on our own,” says Franke, adding that this also applies to the financial aspect. The EU is supporting MACBETH with €16.6 million. Franke says that this assistance is substantial, especially in view of the fact that it involves a certain amount of risk. “That’s because we don’t precisely know whether everything will eventually work as well in practice as we think it will and if a new process can actually be derived from it,” says Franke.

In Shakespeare’s drama MACBETH, three witches predict the eponymous character’s future. Although Robert Franke can’t rely on such arcane arts, he and his team will know by October 2024 whether catalytic membrane reactors are suitable for commercial hydroformylation. That’s how long the MACBETH project will run. In order to make the best possible use of the remaining time, Franke is calling on everyone to heed a command from MACBETH’s opponent Macduff in the fourth act of the Shakespeare play: “Cut short all intermission.”

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At the hydroformylation facility in Marl, Evonik turns olefins and syngas into aldehydes