Development of an Innovative Concept for Carbon Dioxide Utilization as Side Stream of Integrated Biorefinery Concepts

Acronym: ICOCAD

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Introduction

The increasing share of renewable energy generation sources in Germany creates a surplus of electric energy, when wind or sunlight is available. Therefore the storage of electric energy comes into focus to compensate the drawbacks of its irregular production by renewable sources. The chemical storage of electric energy seems to be a viable solution. One obvious solution is the electrolysis of water to hydrogen and oxygen. However, hydrogen storage in large quantities remains an issue not easily resolved. Alternatively it could be fed into the natural gas grid, which is well developed in Germany. However, the addition of hydrogen to natural gas is limited, because the flame propagation properties of natural gas are affected by hydrogen.

Therefore, the chemical conversion of hydrogen with carbon dioxide from renewable and non-renewable sources such as biogas plants or the steel industry is currently under investigation. The methanation of carbon dioxide, which is also called the Sabatier process, is an exothermic reaction:
High reaction temperatures not only reduce the maximum carbon dioxide conversion through the thermodynamic equilibrium but also favor the undesired competing reverse water-gas shift reaction (RWGS): Carbon dioxide from biogas plants contains significant amounts of Sulphur species, which tend to poison the catalyst.

The aim of the ICOCAD project was therefore to improve the stability of the catalysts against small amounts of Sulphur (below 1 ppm) originating from incomplete removal of these components in the Sulphur trap which needs to be installed in the process. In addition to S-poisoning, the formation of carbonaceous species on the surface and sintering lead to deactivation of methanation catalysts.

Results

Nickel and ruthenium based catalysts for CO_2 hydrogenation were investigated both as fixed bed and in microchannel reactors. The selected catalyst showed constant conversion of hydrogen and carbon dioxide and a constant selectivity towards methane in a long-term test of 1000 h durability.

Promising candidates of high activity and durability were identified and subsequently exposed to H_2S containing feed, which was used as a model compound for Sulphur species. It could be shown that ruthenium containing catalysts deactivate rapidly in presence of Sulphur, while nickel containing formulations showed improved stability - it serves as a “Sulphur-trap”.

A plant concept was developed comprising two step methanation with a first adiabatic reactor stage (figure 3.1.1) followed by a plate heat-exchanger reactor with integrated cooling which allows more than 97 % CO_2 conversion. A pilot plant was put into operation to verify the feasibility of this concept.

On the basis of process simulations 50 m^3/h product gas the energy efficiencies as well as internal and external optimization potentials for the heat network were identified. Overall, it can be stated in the results of the simulations that a high efficiency can be achieved exceeding 80 %. This means that the investigated methanation is comparable with the energy efficiencies of competing processes (eg biological methanation - max 70 %) and has certain advantages over them.

The life cycle assessment was carried out for the impact category climate change applying biomethane (synthetic natural gas). The assumption for the assessment was that CO_2 is used as a by-product of biogas production and regeneratively generated climate-neutral electricity surplus is used for the H_2 generation and that no transport loads arise.

A system with 50 Nm^3/h product gas was considered. Cost calculations as well as sensitivity analyzes were carried out. The economic feasibility studies showed that the innovative methanation concept developed in the ICOCAD project has the corresponding economic attractiveness and thus market opportunities. Scaled up to the potentially marketable order of magnitude of 50 Nm^3/h, this results in a CO_2 saving potential of around 800 tonnes per year.

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Figure 3.1.2: Control unit (front view).

Figure 2: Adiabatic (monolithic) 1st stage reactor (left) and 2nd stage plate-heat exchanger reactor developed in ICOCAD.