Improving Overall Hydrogen Utilization by Direct Coupling of Methanol and Formaldehyde Production in a CO_2-based Process Chain

Pia Münzer[1*], Ulrich Arnold[1], Jörg Sauer[1]

1 Karlsruhe Institute for Technology, Hermann-von-Helmholtz-Platz 1, 76244 Eggenstein-Leopoldshafen

**Corresponding author: pia.muenzer@kit.edu*

Highlights

- A directly coupled production of methanol and formaldehyde from CO_2 is suggested.
- Linking both processes could increase overall H_2 utilization by up to 11 percentage points.
- Feasibility of formaldehyde synthesis in the presence of CO_2 was proven.

1. Introduction

For many CO_2-based processes, H_2 is needed as reaction partner to win valuable products like methanol (CH_3OH). Therefore, a drastic increase in H_2 demand is expected in the next decades [1]. At the same time production costs will increase, as future H_2 is supposed to be generated from sustainable sources. Hence, it is essential to not only optimize H_2 production technologies but also the subsequent process chains to maximize overall H_2 efficiency in order to successfully establish a carbon neutral economy. This then leads to the necessity to modify established industrial processes so that any arising H_2-rich waste gas stream may be used as feedstock for chemical syntheses. In this context, the presented work focuses on the coupled operation of CO_2-based methanol synthesis and the subsequent oxidative dehydrogenation (ODH) of the alcohol to gain formaldehyde (CH_2O). Both steps are implemented in individual reactors between which raw methanol and the H_2-rich flue gas of ODH are exchanged as schematically depicted in Fig.1.

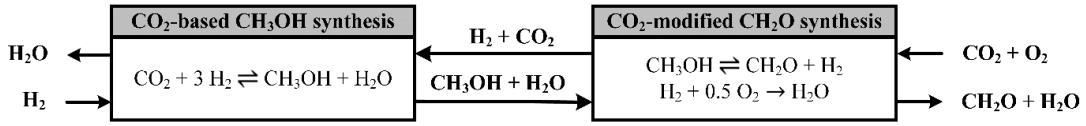

Figure 1. Schematic flow diagram of the coupled production of CH_3OH and CH_2O.

This study aims at exploring the potential improvement of overall H_2 management of the suggested process coupling compared to the conventional production route as well as the assessment of feasibility of industrial installation. Modified silver catalyst processes (SCP) are regarded for CH_2O production. In these modifications, CO_2 replaces N_2 as diluting component to limit reaction temperature. The implemented process for CH_3OH synthesis was adapted from results of previous research [2].

2. Methods

For all considered process chains, detailed flowsheet simulations were performed in Aspen Plus® V11 using a Non-Random Two-Liquid property method (NRTL2). For the methanol converter a Redlich-Kwong-Soave equation (RSKMHV2) and a detailed kinetic model was assumed [3]. To correctly account for the chemical reaction of formaldehyde with water and methanol during the absorption process, a suitable model was chosen [4].

In order to evaluate the feasibility of the concept, experimental investigations on the modified SCP for the production of CH_2O were performed. Experiments were carried out in an electrically heated tubular reactor with an inner diameter of 1 cm. At a constant flow rate of 1 $l_{STP} \cdot min^{-1}$ CH_3OH was converted over a polycrystalline silver catalyst at a fixed concentration of 2.5%. Oxygen was supplied according to a conventional O_2/CH_3OH ratio of 0.4 [5]. Reaction temperature was increased stepwise in a representative range from 540 to 600 °C. The influence of operational parameters on reactant conversion as well as product yield was studied for different concentrations of CO_2 (0-75%) in the feed stream.

3. Results and Discussion

For the evaluation of the concept, different process chains for the production of 90 $kt \cdot a^{-1}$ of CH_2O following a CO_2-based synthesis of CH_3OH were regarded. It was assumed that the introduced CO_2 does not influence formaldehyde formation. Simulations showed that by directly coupling both process steps, H_2 utilization could be increased by up to 11 percentage points reaching a maximum value of 98%. At the same time CO_2 conversions as high as 99% were reached when recycling the waste gas stream of a modified SCP to the feed stream of methanol production.

Evaluation of experimental data confirmed the feasibility of the CO_2-modified SCP. As can be seen in Fig. 2, the measured products were CH_2O, CO, CO_2, H_2 and H_2O matching the expected spectrum for conventional ODH.

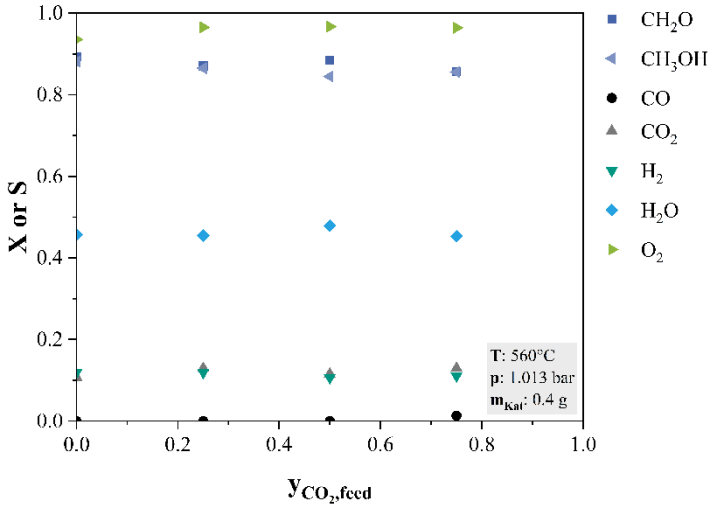

Figure 1. Measured reactant conversion and product selectivity for modified SCP for different CO_2 concentrations (y_{CO2}) in the feed stream.

At suitable temperatures both reactant conversion and product yields remained unchanged with increasing CO_2 content in the feed stream. At higher temperatures a decrease in CH_2O formation was observed with higher CO_2 concentrations. It was then also noted that H_2 and CO yields increased without being directly correlated.

4. Conclusions

Flowsheet simulations complemented by experimental investigations were conducted in order to evaluate the potential improvement of overall H_2 utilization by directly coupling the production of CH_3OH and CH_2O. It was shown that compared to the conventional process a modified silver catalyst process could lead not only to an increase in overall H_2 efficiency but also positively influence CO_2 conversion when directly linked to CO_2-based methanol synthesis. In addition, it was shown that CH_2O can successfully be synthesized in the presence of large amount of CO_2 at industrially relevant conditions. A reduction in product yields at higher temperatures could later be prevented by using larger quantities of catalyst.

References

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Keywords

Methanol, Formaldehyde, CO_2 utilization, H_2 management