

BRIDGING THE SCALES FROM CATALYST SYNTHESIS TO SUSTAINABLE PROCESSES: CO₂ HYDROGENATION TO METHANOL

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Abstract

CO₂ hydrogenation to methanol is a promising strategy for reducing CO₂ emissions. The thermocatalytic conversion of CO₂ and hydrogen relies on heterogeneous catalysts. Recent progress has led to high-throughput catalyst development. New catalysts are typically compared based on conversion, selectivity, or space-time yield in a lab reactor. However, the success of a catalyst is ultimately determined at the plant level. Thus, catalyst assessment should reflect all tradeoffs in environmental and economic performance from the catalyst to the scale of the large-scale chemical plant. This work links lab-scale data on novel CO₂ hydrogenation catalysts to their process-level performance. For each catalyst, a chemical process is optimized to resolve the tradeoffs incorporated through reactor temperatures and pressures, and heat integration. The process performance is determined by techno-economic analysis and life cycle assessment. Out of the three compared catalysts, the industrial Cu-based catalyst outperforms the others due to better utilization of the costly hydrogen feed. The developed workflow guides future catalyst research.

Keywords

CO₂ hydrogenation, heterogeneous catalysis, Life Cycle Assessment

Introduction

CO₂ utilization plays an essential role in a sustainable and environmentally friendly transformation of the chemical industry. Thereby, the conversion of CO₂ and green hydrogen to platform chemicals like methanol plays a key role (Zhong et al. 2020; Kästelhön et al. 2019). Considerable progress has been made in the development of heterogeneous catalysts to enable this conversion (Zhong et al. 2020).

Catalyst development for a thermocatalytic conversion usually feeds CO₂ and hydrogen to a continuous fixed-bed reactor at higher temperatures and pressures. Methanol forms as main product with water, carbon monoxide, and other hydrocarbons as side products. Today, the benchmark catalyst is a Cu/ZnO/Al₂O₃ catalyst which is also used to industrially convert syngas to methanol (Kanuri et al. 2022). Promising new catalytic systems are based on In (Ghosh et al. 2021; Cordero-Lanzac et al. 2022), but Pd, Au, Ag, Co,

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Ni, Ga, and ZnO-ZrO₂ are also explored, among other metals (Jiang et al. 2020; Wu et al. 2021).

Newly proposed catalysts are typically compared and optimized based on selectivity to methanol or space-time yield (Suvarna et al. 2022). However, the objective of applying catalysts in large-scale production plants is the process' overall performance. Besides cost, this process performance should reflect the potential of the process to contribute to climate change mitigation. Thereby, chemical processes need to be optimized for each catalyst. For a sound comparison guiding catalyst development, all tradeoffs should be considered from catalyst to process level (Gertig et al. 2020; Ioannou et al. 2021). For this purpose, the reaction performance of newly developed catalysts should be directly linked to the process level.

The gap between surface chemistry and process modeling is bridged by reaction kinetics and kinetic models (Tripodì et al. 2017). While multiple kinetic models are available for the Cu/ZnO/Al₂O₃ catalyst (Vanden Bussche and Froment 1996; Slotboom et al. 2020; Graaf et al. 1988), only limited kinetic data and models are available for new catalytic systems. Hence, most process design studies focus on the Cu/ZnO/Al₂O₃ catalyst and develop or optimize chemical processes using data from Vanden Bussche and Froment (1996) or Graaf et al. (1988) (González-Garay et al. 2019; Vázquez and Guillén-Gosálbez 2021; Abbas et al. 2022).

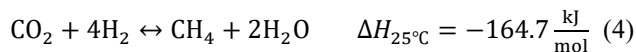
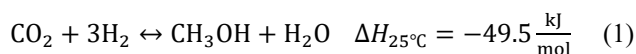
Recently, Cordero-Lanzac et al. (2022) developed a kinetic model for a new InCo catalyst to synthesize methanol. The kinetic model allowed to compare a process with the InCo catalyst with an industrial benchmark process using a Cu-based catalyst. The optimal reaction conditions from a lab reactor were used for an industrial process. However, other reaction conditions might be favorable at plant scale due to recycle streams and economic considerations (Zhong et al. 2020). Furthermore, the underlying assumptions of Cordero-Lanzac et al. (2022) and the benchmark differed, limiting the validity of the drawn conclusion.

In this work, we therefore assess catalysts directly in process optimizations using consistent assumptions to resolve tradeoffs between reaction kinetics and process design. Reaction kinetic models connect reaction and process modeling to assess the performance of novel catalysts based on process performance. The process is optimized regarding its operating conditions, e.g., reactor temperature and pressure. The consistent use of methods and assumptions for all investigated catalysts allows for a sound comparison of catalysts in the field of methanol synthesis. Process performance is based on the total annualized cost for methanol production and the environmental impacts associated with the life cycle of the process. The results highlight the differences in the performance of the catalysts and indicate the most important targets for improvement.

Process Design for CO₂ Hydrogenation using Economic and Environmental Objectives

The present work compares catalysts at process level by combining methods from kinetic modeling over process simulation and heat integration to techno-economic analysis and life cycle assessment. The overall workflow is shown in Figure 1.

The flowsheet in Figure 2 is considered for the methanol synthesis from CO₂ and hydrogen (Vázquez and Guillén-Gosálbez 2021). The compressed feed gases CO₂ and hydrogen react in an adiabatic fixed-bed reactor. Subsequently, the reactor outlet is separated using two flash drums and a distillation column. A recycle stream enables the utilization of unreacted CO₂ and hydrogen. A purge stream is taken off the system to prevent the accumulation of side products. In the reactor, CO₂ and hydrogen react to methanol and water (Eq. (1)). The undesired reverse water gas shift reaction (Eq. (2)) leads to the formation of carbon monoxide, which can also react to methanol (Eq. (3)). Depending on the catalyst selectivity, methane is formed as an undesired side product (Eq. (4)).



In this work, the reaction kinetic model by Vanden Bussche and Froment (1996) for an industrial Cu/ZnO/Al₂O₃ catalyst is compared with kinetic models by Cordero-Lanzac et al. (2022) (InCo) and Ghosh et al. (2021) (In₂O₃). The reaction kinetic models follow a Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism. In addition to the three catalysts, a thermodynamic equilibrium reactor is used to benchmark the catalysts. The equilibrium reactor outlet is assumed to be the thermodynamic equilibrium of the reactions in Eq. (1-3). The process is simulated in Aspen HYSYS with the thermodynamic fluid packages Peng-Robinson and NRTL-Ideal based on Vázquez and Guillén-Gosálbez (2021).

The flowsheet simulation results for a given operating point of the process are extracted from Aspen HYSYS. Subsequently, a heat integration problem is solved using Pinch Analysis tools, thereby minimizing the utility demand to drive the process. A detailed description of the optimization is given below. A minimum temperature difference of 10 K is considered for the heat exchanger network design. High-pressure steam (40 bar, 250°C) and cooling water (25°C to 30°C) are provided to satisfy the

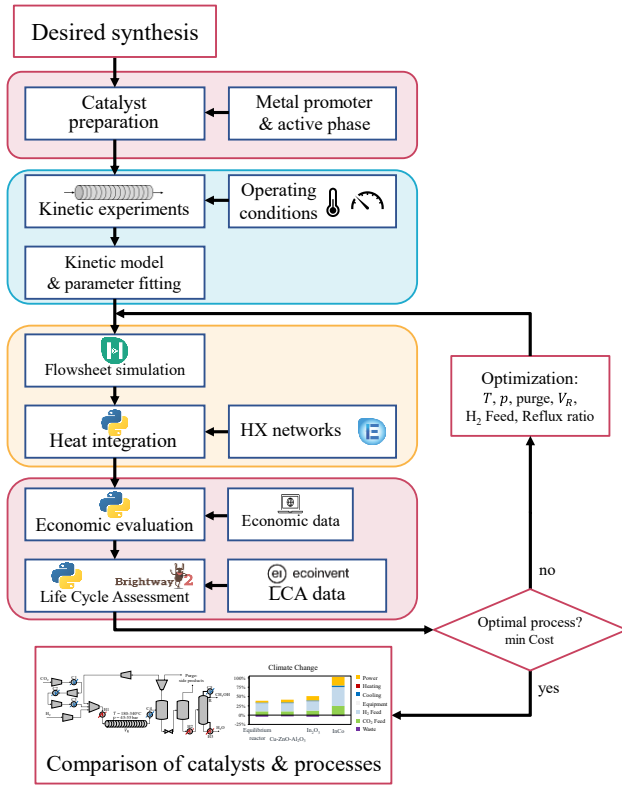


Figure 2: Flowchart of the computational approach for the catalyst comparison.

energy demand. For the designed heat exchanger network, the heat exchanger areas are calculated to estimate the investment cost (Vázquez and Guillén-Gosálbez 2021).

A techno-economic analysis is conducted for the material and energy flows together with equipment size information. Capital expenditures (CAPEX) and operational expenditures (OPEX) are estimated using chemical engineering cost correlations (Towler and Sinnott 2012). Overall, the total annualized cost per mass of methanol (TAC) produced serves as a metric for the economic performance of the process:

$$TAC = \frac{ACCR \cdot CAPEX + OPEX}{m_{MeOH}} \quad (5)$$

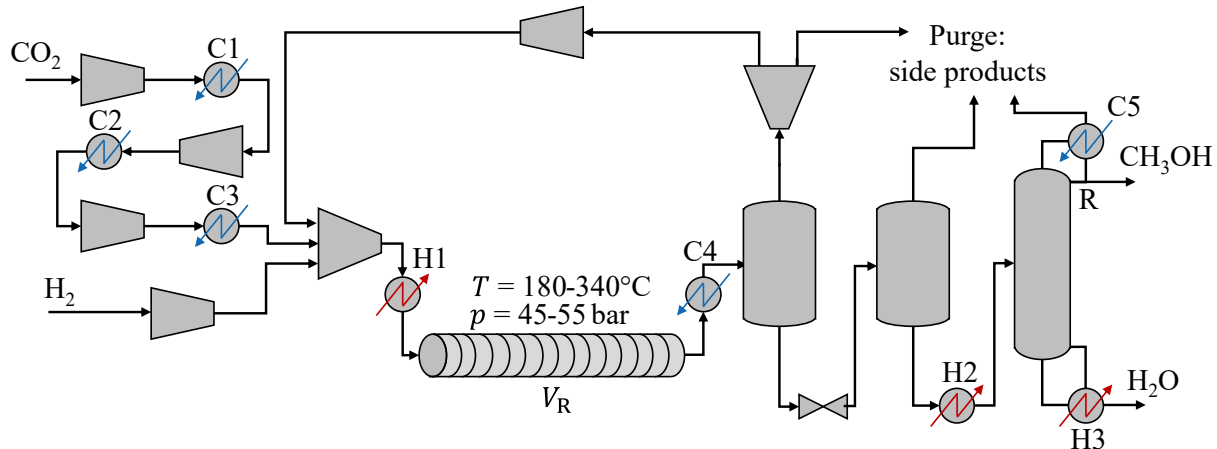


Figure 1: Flowsheet of the methanol synthesis process (redrawn after Vázquez and Guillén-Gosálbez 2021).

where m_{MeOH} is the annually produced mass of methanol, and ACCR is the annual capital charge ratio. An inflation rate of 1.58 % is considered to adjust all prices to 2018, and the plant is operated 8760 h/yr. Green hydrogen from electrolysis and CO₂ from direct air capture are used as feedstocks. The CO₂ feed is defined at 2,000 kmol/h. (Vázquez and Guillén-Gosálbez 2021)

Similar to the economic analysis, raw materials, utilities, and waste streams are used to perform a life cycle assessment of the process (Guinee et al. 2002). The Ecoinvent 3.8 database provides environmental data for the background system (Wernet et al. 2016; Vázquez and Guillén-Gosálbez 2021).

Electricity is supplied by the electricity grid, while heating and cooling are provided by the utility system of a chemical park. The equipment size is used to estimate the steel demand for the installation of the plant. The equilibrium reactor is neglected as equipment. The environmental performance described by the environmental impact per mass of produced methanol is calculated for different impact categories using the Environmental Footprint 3.0 methodology. The environmental impact on climate change is of particular importance since the climate change mitigation potential motivates CO₂ utilization.

Finally, the methanol process is optimized to minimize the total annualized cost per mass of methanol TAC. The optimization variables x are reactor temperature, reactor pressure level, hydrogen feed, reactor size, purge split, and reflux ratio in the distillation column. The overall general Mixed-Integer Non-Linear Programming (MINLP) problem can be formulated as:

$$\begin{aligned} \min_{x,y} TAC(x,y) \\ \text{s.t. } h(x,y) = 0 \\ g(x,y) \leq 0 \\ LB \leq x \leq UB \\ x \in \mathbb{R}^n, y \in \{0,1\} \end{aligned} \quad (6)$$

where y denotes binary decision variables for the heat exchanger connection in the heat integration problem mentioned earlier. The equations $h(x,y)$ and $g(x,y)$ are equality and inequality constraints, respectively. LB and UB refer to the lower and upper bounds of the continuous variables x .

Due to the fixed flowsheet (Figure 2), the heat integration problem can be solved separately from the process optimization for the variables x . Pinch Analysis and the Aspen Energy Analyzer are used to develop optimal heat exchanger networks. To reduce the calculation time, temperature level scenarios for the heat integration problem are defined, and an optimal heat exchanger network is calculated for each scenario. During process optimization, the optimizer chooses the heat exchanger network with the lowest cost from the set of network scenarios and checks whether the Pinch Analysis targets are fulfilled.

The separation of the heat integration optimization problem and the process design problem results in a Non-Linear Programming (NLP) problem:

$$\begin{aligned} \min_x \text{TAC}(x) \\ \text{s.t. } h(x) = 0 \\ g(x) \leq 0 \\ LB \leq x \leq UB \\ x \in \mathbb{R}^n \end{aligned} \quad (7)$$

All calculations except the flowsheet simulation are implemented in Python 3.8.5, using NumPy 1.22.2 and a COM interface between Python and ASPEN HYSYS to extract the required process data. The optimization problem is solved using the SciPy package (The SciPy community 2021). An extensive grid search is combined with the SciPy minimizer to optimize the variables x .

Results

The process design results in four optimized flowsheets for the three investigated catalysts and the thermodynamic equilibrium. The optimal reaction temperatures for the three catalysts are in the range proposed in the literature (compare **Error! Reference source not found.**) (Vanden Bussche and Froment 1996; Cordero-Lanzac et al. 2022; Ghosh et al. 2021). The reactor pressure of all cases is in the same range due to a tradeoff between higher conversion at higher pressures and higher compression cost in the recycle stream.

The single-pass conversion of CO_2 is lower than reported in the literature for lab reactors (Cordero-Lanzac et al. 2022; Ghosh et al. 2021; Vanden Bussche and Froment 1996). A higher conversion would require significantly larger reactors and causes higher overall costs.

Table 1: Optimal operating conditions for different catalysts.

Catalysts	Cu/ZnO/Al ₂ O ₃	In ₂ O ₃	InCo
Reactor inlet temperature T_R	215°C	321°C	282°C
Reactor inlet pressure p_R	4910kPa	5061kPa	5180kPa
CO ₂ conversion X_{CO_2}	10.6%	4.7%	4.7%
Methanol selectivity S_{MeOH}	99.6%	99.1%	58.4%

The lower selectivity for the InCo catalyst is in line with the experimental observations and caused by the significant formation of methane and a fast catalyzation of the reverse water gas shift reaction to carbon monoxide (Cordero-Lanzac et al. 2022).

The consideration of recycle streams in the flowsheet changes the reactor inlet composition compared to typical lab conditions. A mixture containing carbon monoxide and methane as well as impurities of methanol and water enters the reactor, which is different from the pure H_2/CO_2 feed reported in literature for lab experiments. This issue has been addressed by considering carbon monoxide in the reactor feed (Araújo et al. 2021), but many kinetic models are derived with a pure H_2/CO_2 feed. Therefore, considering side products in the lab reactors' feed stream could enhance the understanding of the catalyst performance under industrial conditions. Additionally, the H_2/CO_2 feed ratio is in the range of 2:1, which is under-stoichiometric and lower than in the experimental literature. A lower hydrogen feed is favored by the cost optimization due to the high hydrogen cost.

The solution to the heat integration problem results in the same heat exchanger network for all catalysts and the thermodynamic equilibrium case. The resulting heat exchanger network is shown in Figure 3. The available heat from the cooler C4 at the reactor outlet satisfies the entire heat demand to heat the reactor inlet and to run the distillation column.

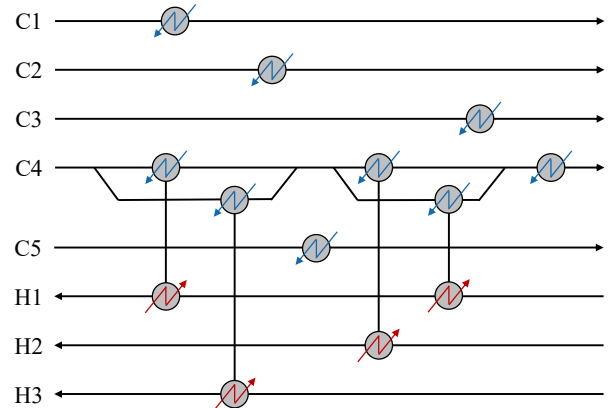


Figure 3: Optimal heat exchanger network for the methanol process.

The economic performance of the processes is shown in Figure 4 in relative costs compared to the least-performing catalyst. For comparison, the thermodynamic equilibrium reactor is added as a benchmark. The Cu-based catalyst reaches almost the performance of the thermodynamic equilibrium (36% vs. 38%). The remaining gap is caused by the investment cost of the reactor and higher recycle streams due to lower conversion. The In₂O₃ catalyst requires higher investment costs for a larger reactor and higher recycle streams due to lower catalyst activity compared to the Cu-based catalyst (56%). The InCo catalyst shows significant methane formation (29.5% selectivity to CH_4), increasing hydrogen loss, which is the largest

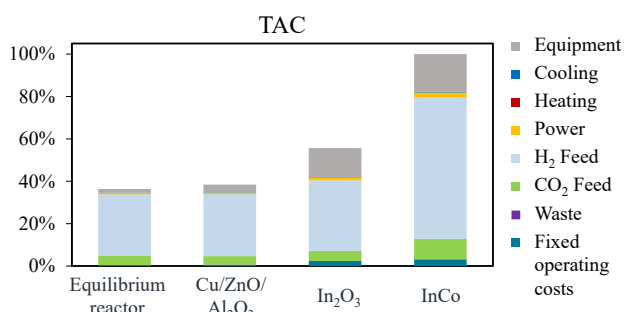


Figure 4: Economic assessment for the methanol synthesis with different catalysts.

contributor to the overall costs. Lower conversion also raises investment costs for reactor and equipment in the recycle stream compared to the other catalysts.

The high costs for green hydrogen emphasize the importance of the utilization of hydrogen (between 59% and 80% contribution). High selectivity is, therefore, key for catalyst development. A lower conversion increases investment costs but is less critical than selectivity. Furthermore, the higher reactor temperature for the In₂O₃ catalyst does not contribute directly to the overall costs. Due to heat integration, the temperature increase does not cause additional energy demand. However, additional costs might occur in the detailed equipment sizing due to high-temperature equipment.

The overall trends and ranking for the three catalysts are also observed for the climate change environmental impact (Figure 5): The industrial Cu/ZnO/Al₂O₃ catalyst causes the lowest climate change impact, and its performance is close to the equilibrium reactor (-30% vs. -38%). The In₂O₃ catalyst has higher climate impacts but is comparable to the Cu-based catalyst (-11%). The InCo catalyst leads to significantly higher climate impacts. However, the relative shares of the contributors change compared to the economic assessment: The electricity production for the compression power demand has a high impact on climate change (14-24% relative contribution) but a low cost contribution (1.4-3.4% relative contribution). Furthermore, the high electricity demand for green hydrogen and CO₂ capture underlines the importance of electricity.

The environmental footprint methodology allows for comparing different impact categories to avoid burden

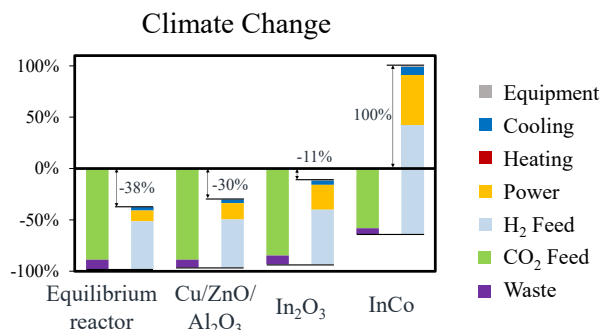


Figure 6: Relative climate change impact of the methanol synthesis with different catalysts.

shifting. The water use impacts show similar trends as the climate change impact (Figure 6) since the underlying processes and reasons are the same. This tendency can also be observed in other impact categories in the Environmental Footprint 3.0 methodology.

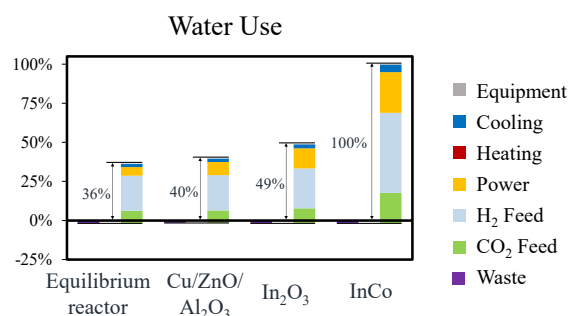


Figure 5: Relative water use impact of the methanol synthesis with different catalysts.

Overall, the trends in the comparison of the catalysts are similar to the comparison of experimental selectivity and conversion. However, this work resolves tradeoffs between selectivity, conversion, and operation conditions, which cannot be addressed on the reactor level. The efficient utilization of hydrogen is the key driver of both economic and environmental process performance indicators. Hence, high selectivity is crucial for CO₂ hydrogenation. The industrial Cu-based catalyst achieves the highest selectivity and performs best. A lower activity of alternative catalysts can be compensated for the most part by larger reactors. Nevertheless, the costs and environmental impacts increase, albeit less than with reduced selectivity.

Conclusions

The present work takes a step toward the integrated development of catalysts and sustainable processes for CO₂ utilization to methanol by considering multiple scales, from catalyst lab testing to reaction kinetics and then plant scale. Tradeoffs between recycle streams, reactor temperature, and investment cost are considered to compare three catalysts based on their process cost and environmental impacts. A kinetic model of an industrial Cu/ZnO/Al₂O₃ catalyst is implemented together with kinetic models for new catalysts using In₂O₃ and InCo. The industrial Cu-based catalyst outperforms the others, and the performance is close to the thermodynamic equilibrium. The results guide experiments by giving insights into the relevant feed conditions for industrial reactors for CO₂ hydrogenation to methanol and identifying key performance indicators.

The combination of methods from kinetic modeling over process simulation and heat integration to techno-economic analysis and life cycle assessment provides a step toward capturing tradeoffs on all scales, from catalyst to process level.

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