AIDIC EFCE
ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Methanol Synthesis based on Steel Mill Exhaust Gases: Lab-Scale and Close-to-Practice Investigations

Kai Girod*, Klaas Breitkreuz, Stefan Schlüter, Thomas Marzi, Stefan Kaluza

Fraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany

**Corresponding author: kai.girod@umsicht.fraunhofer.de*

Highlights

- Effect of CO/CO_2-ratio on MeOH productivity
- MeOH-synthesis with H_2 enriched steel mill exhaust gases
- Synthesis in close-to-practice test reactor system with intrinsic heat gradients
- Optimization of test conditions by sophisticated process simulation

1. Introduction

State-of-the-art steel mills as large and highly integrated sites comprise different sources of CO_2, CO and hydrogen. Besides the current energetic utilization, these gases provide promising potential to be utilized as feedstock for bulk chemical production while simultaneously reducing the CO_2 footprint of the steel mill. Methanol is one of the most important platform chemicals. Its production by synthesis gas conversion is well established on industrial scale with a worldwide production capacity of more than 80 million tons per year [1]. However, the commercial Cu-based catalyst applied in industrial methanol synthesis is optimized for constant gas streams of high purity and fixed compositions. The scope of this work is to evaluate the possibility of applying a commercial methanol synthesis catalyst in the conversion of synthesis gas derived from steel mill exhaust gases exhibiting fluctuating compositions. The present contribution assesses the influence of altering CO/CO_2-ratios in the inlet gas stream on the performance of the catalyst. In addition, gas streams with specific compositions from different steel mill productions sites are investigated, including CO_2- and nitrogen rich blast furnace gases as well as gas streams originating from steel processing (converter gas). For sufficient methanol productivity, these typically hydrogen-poor gases have to be enriched with H_2 – ideally based on sustainable sources. The experimental investigations are performed in a lab-scale and a pilot plant fixed-bed reactor system, respectively, and supported by process simulation in order to reveal optimal test conditions.

2. Methods

For evaluating the suitability of different syngas sources it is important to differentiate between the gas composition that enters the methanol process as make-up gas and the gas composition that the catalyst is exposed to inside the reactor. The latter one is determined by the product separation and the recycling of the unconverted syngas. For operating a methanol process with high C-conversion a stoichiometric number $(H_2-CO_2)/(CO+CO_2)$ of slightly above 2,0 is required [2]. First, the achievable methanol equilibrium concentration was simulated as a function of the respective hydrogen addition in order to identify appropriate test conditions. In a second step, a synthesis process simulation was developed including a kinetic model for the heterogeneously catalyzed methanol synthesis reaction, a product separation procedure and the possibility to consider different syngas recirculation ratios. The model was used to simulate the methanol synthesis reaction as a function of different gas compositions depending on the recirculation mode. The aim is to achieve high C-conversion rates and to limit process costs that come along with high recirculation streams. The previously identified test conditions were subsequently applied in practice using two different

test facilities. The first system that is close to industrially applied geometry consists of a tubular fixed bed reactor with a total volume of 340 ml (19 mm inner diameter). The modular construction of the system allows large-scale testing of heterogeneous catalysts in a fixed-bed providing a wide range of test conditions with regard to gas composition, pressure and reaction temperature and catalyst shape and particle size. This system is most suitable for long term tests with fixed gas compositions at the same time revealing intrinsic heat gradients. It was used for investigating the conversion of H_2-enriched blast furnace and converter gases. A second complementary test system with a total reactor volume of 15 ml (9 mm inner diameter) is characterized by a higher grade of automatization and allows reproducible variation of the gas composition at given homogenous temperatures. It was used for altering the CO/CO_2 ratio in order to reveal the impact on catalyst durability and productivity. Due to high CO_2 concentration in steel mill gases the impact of different CO_2 concentrations was examined systematically. Starting from a highly active syngas including 3,5 Vol.% CO_2 and 13,5 Vol. % CO the CO_2/CO ratio was increased stepwise while keeping the overall CO_x content constant. To investigate if the methanol catalyst is irreversibly affected by high CO_2 concentrations, tests are subsequently conducted with the initial gas composition. The results are compared with the data obtained from the primary tests with the highly active syngas.

3. Results and discussion

The calculation of the methanol equilibrium concentration as a function of the hydrogen addition revealed the apparent optimal stoichiometric number for the two different gas streams. Figure 1 depicts the required H_2-stream to achieve a certain methanol equilibrium concentration as a function of the stoichiometric factor for two different gas streams a) blast furnace gas and b) converter gas.

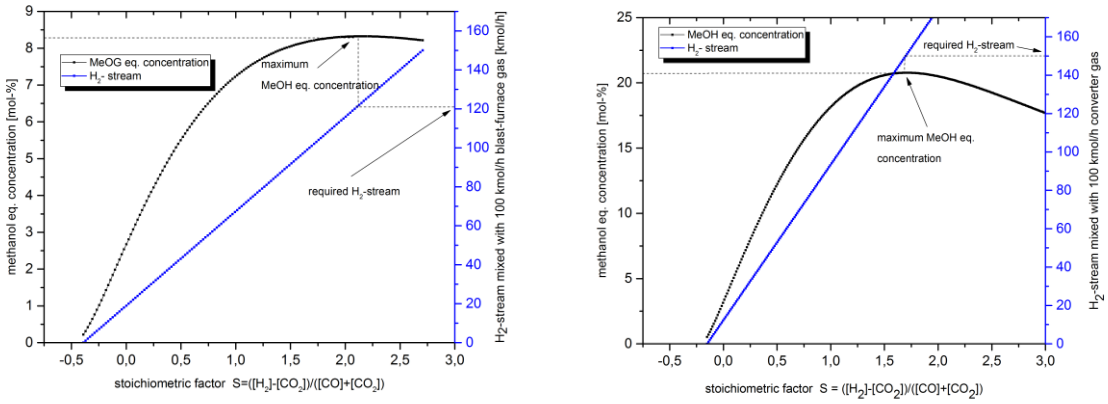

Figure 1. Methanol equilibrium concentration for a) blast-furnace gas and b) converter gas as a function of hydrogen addition,

The computational model provided reactor inlet conditions for different base cases. The reactor inlet gas composition is the result of an optimization in terms of minimized carbon and hydrogen losses that occur due to the required purge stream. The recycle stream is kept in an economically reasonable range. The reactor inlet gas composition is characterized by excess of hydrogen, high CO_2 concentration and significant nitrogen content depending on the origin of the syngas.

All methanol synthesis tests were performed with a commercial catalyst for methanol synthesis. During activation and synthesis the axial temperature profile inside the catalyst bed was monitored. In lab-scale experiments temperature control during activation and initial synthesis conditions is usually achieved by the use of small reactor diameters and low volumes of the powdered catalyst. However, temperature control becomes a major issue under large-scale conditions. It turned out that the temperature distribution was strongly depending on the particle size of the catalyst pellets, the dilution of the catalyst and the type of heating system. As expected, methanol productivity was significantly decreasing with increasing CO_2

content. After exposing the catalyst to high CO_2 concentrations the productivity is apparently irreversible reduced.

4. Conclusions

Catalyst development and testing is usually performed with rather small amounts of catalyst. However, transferring the results about performance and lifetime of the catalyst to industrial relevant pilot-scale application is hardly feasible. Here, larger amounts of differently shaped catalyst particles are usually applied resulting in a non-ideal temperature distribution and transport phenomena that can influence the overall performance of the catalyst. In order to close the gap between lab-scale and large-scale catalyst testing a new test system was developed. The obtained results proof that methanol synthesis with H_2-enriched steel mill gases as feedstock is possible. However, the CO_2/CO-ratio has a crucial effect on catalyst performance. The gathered experimental data is valuable for evaluating new methanol synthesis routes based on steel mill gases.

References

[1] M. Alvaro, IHS Chemical Bulletin, Issue 3, 2016, pp. 10-11
[2] J. Ott et al.: Methanol, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2012

Keywords
Methanol; CO_2; Steel-Mill; Catalysis