Methanol from Steel-Mill-Gases: Long-Term Catalyst Testing with Real Cleaned Gas Streams

Kai Girod[1]*, Heiko Lohmann[1], Stefan Kaluza[2], Stefan Schlüter[1]

1 Fraunhofer UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, Germany; 2 Hochschule Düsseldorf, University of Applied Sciences, Germany

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

Highlights

- Real-gas catalyst testing in an on-site laboratory for methanol synthesis.
- Combination of process simulation and close-to-practice catalyst testing.
- Long-term testing with Clariant´s methanol synthesis catalyst.
- Methanol synthesis with real cleaned steel mill gases.

1. Introduction

Currently, methanol is produced catalytically using syngas, which is derived from fossil raw materials such as natural gas or coal. Alternative syngas sources to produce methanol are CO_x-containing metallurgical gases. The successful establishment of a direct utilization or a carbon capture and utilization process involving steel-mill-gases would not only enable the reduction of climate-damaging CO_2 emissions, but also a sustainable production of methanol. Within the framework of the Carbon2Chem® joint project, the sustainable methanol synthesis from metallurgical gases is being investigated. The scope of this work is to evaluate the possibility of applying a commercial methanol synthesis catalyst in the conversion of syngas derived from steel mill exhaust gases exhibiting fluctuating compositions. First, it is mandatory to produce syngas that contains no detrimental concentrations of minor and trace compounds, which deactivate the methanol catalyst. This task requires suitable conditioning and purification processes for syngas production which are investigated in an on-site technical center at thyssenkrupp Steel Europe in Duisburg, Germany [1].

2. Methods

For the described work, a recently developed process model for a large-scale methanol-process corresponding to the Lurgi low pressure process and a test-setup for heterogeneous catalysts is applied. The model comprises a 1-dimensional reactor model of a large-scale boiling-water cooled tube-bundle reactor, a raw product separation (cooling trap) and a gas recycle of the unconverted syngas. The process model is used to calculate realistic reaction conditions for practical catalyst tests with real gas streams [2]. The investigated gas streams are pre-cleaned Blast Furnace and Basic Oxygen Furnace Gas. For synthesis, all cleaned steel-mill-gas streams must first be enriched with H_2. Different H_2 sources are available in the laboratory. H_2 can be extracted from coke oven gas by pressure swing adsorption. It can also be produced by water electrolysis or provided from bottles [1,3]. The quality of the CO_2 separated by amine wash is of particular interest. Long-term methanol synthesis was performed with real separated CO_2. The practical tests were performed in a lab-scale test set-up with direct access to the on-site gas-cleaning unit [3]. In the test system used, the catalyst is exposed to a higher gas load, compared to demonstration scale test set-ups with product separation and gas recycle. If catalyst poisons are present in detrimental concentrations, poisoning of the catalyst can be observed earlier. All tests were performed with Clariant´s methanol synthesis catalyst.

3. Results and discussion

For methanol synthesis with pure CO_2 a theoretical productivity maximum was identified at a simulated recycle ratio (RR) of 3.2 which is shown in Figure 1.

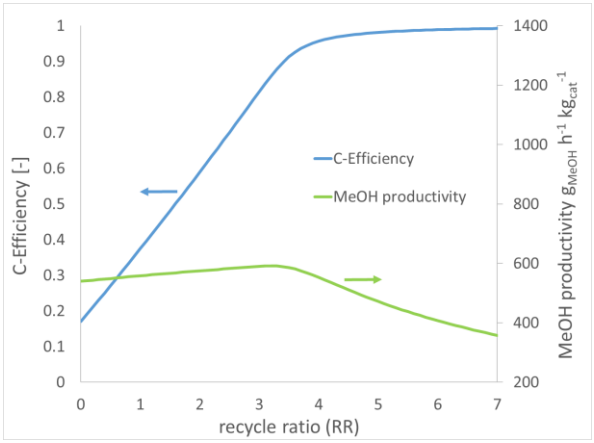

Figure 1: Simulated Methanol Productivity and Carbon Efficiency

The corresponding calculated reactor inlet gas composition was subsequently applied for long-term catalyst testing with real CO_2 separated from pre-cleaned Basic Oxygen Furnace Gas by amine wash. After a slight initial decrease of catalyst activity that always can be observed, the catalyst exhibited a nearly constant productivity over a period of more than 1400 h time on stream. In an additional test, pre-cleaned Basic Oxygen-Furnace-Gas was converted in a Water-Gas-Shift unit. The separated CO_2 was used for methanol synthesis as well. A similar trend as before was observed over a period of 1100 h time on stream. Non-converted pre-cleaned Blast-Furnace-Gas was investigated over a period of more than 3500 h, which was the longest test campaign. The observed catalyst productivity was overlaid by the effect of a fluctuating feed-gas composition regarding the main compounds. Feed gas measurements were used to distinguish the causes of the observed changing catalyst productivity. Methanol could be synthesized with all examined cleaned real-gas streams over long periods. Apparently, no additional catalyst deactivation due to catalyst poisoning was observed.

4. Conclusions

Process simulation of a large-scale methanol synthesis process was successfully applied to provide realistic test conditions for on-site catalyst testing to evaluate the stability of Clariant´s industrial methanol synthesis catalyst. The combination of both, simulation and lab-scale testing turned out to be very beneficial for a close-to-practice approach of catalyst testing in a comparatively simple one-pass test set-up. The conducted methanol synthesis lab-scale tests indicated that syngas generated from steel-mill-gases was sufficiently cleaned to synthesize methanol over long periods.

References

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Keywords

methanol synthesis, steel-mill-gas, catalyst testing, process simulation