Mobile Small-Scale Methanol Synthesis Pilot-Plant with Internal Recycle Operated with CO_x from Waste Gasification

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Abstract

For the reduction of CO_2 emissions chemical recycling of carbon-containing residuals is of increasing interest. The gasification of non-recyclable waste streams offers a way to convert carbon into valuable base chemicals. One particular example is CO_x based methanol which can be utilized in various ways as an energy storage, clean fuel and building block for chemical industry.
At TU Darmstadt a mobile small-scale methanol pilot-plant was realized, with the aim to study the methanol synthesis process from CO_x including a reactant/product separation through condensation, high-pressure gas recycles and purge as well as different connection possibility of two fixed bed reactors, the separation and recycle. Furthermore, the scale is this small that catalysts can be tested on a pre commercial production scale and lower amount and that approx. 50 mL h^{-1} of liquid product mixture are produced, allowing detailed product characterization but avoiding huge amounts of storage and disposal. Through the small scale the pilot-plant is also mobile and easy to transport to real CO_x sources. The composition of the streams before and after each reactor can be analyzed by a gas chromatograph which detects the permanent gases via TCD and the larger carbon compounds and oxygenates via FID. As a part of the BMWi project VERENA real syngas is obtained from Hochtemperatur-Winkler-gasification (HTW). The 500 kW pilot plant at TU Darmstadt operates at temperatures of up to 1000°C. A subsequent raw gas cleaning removes impurities such as dust, strong acids and organic compounds. One part of the cleaned syngas is afterwards used for methanol synthesis to study the full chain process.
First experiments were carried out with 30 g of commercially available CZA-catalyst (copper zinc oxide on aluminum oxide), a reaction temperature of 230 °C and a pressure of 30 bar. The stoichiometric feed stream of CO_2 and H_2 with 30 g h^{-1} was mixed from bottled gas. The results show that a full conversion of the reactants is possible when increasing the recycle ratio. At the same time a small accumulation of byproducts can be observed in the recycle stream. Nevertheless, no detectible purge stream was necessary. Moreover, the start-up process of the reaction including the recycle can be recorded. When increasing the reactor temperature from RT to 230 °C a first decrease of the off-gas mass flow can be observed at a reaction temperature of about 180 °C. Full conversion is reached at a specific combination of reaction temperature and recycle ratio for the given point of operation. Investigation of dynamic plant behavior shows a pressure dependence for the time until a new stationary point is reached. Further experiments are planned with real CO_x mixtures from the HTW-gasifier to investigate the influence of real syngas on the recycle ratio, the catalyst stability and the spectra and accumulation of byproducts.