

Synthesis of methanol from biosyngas

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In the last 2 years, 4345 scientific documents have been published regarding carbon dioxide capture and storage (CSS) (research made the 9/2/2018 in the TOPIC field of the Web of Science Core Collection with the keywords "(carbon dioxide capture) OR (Carbon capture and storage)"). Carbon capture technologies rely on the adsorption or mineralization of carbon dioxide over solids or liquids. However, high process costs and technical issues such as corrosion limit the expansion of CSS at larger scale. Hansan et al. estimated that the sequestration of streams with a concentration of CO₂ higher than 10 % costs between 30 and 70 \$/ton CO₂, depending on the flowrate and composition of the exhausted [1].

Converting CO₂ into chemicals or fuel is a strategy that enables the reuse of the carbon instead of landfilling it. An analysis on recent papers (Web of Science Core Collection, year 2015-2017, keywords "(CO₂ conversion) OR (CO₂ hydrogenation)") reveals that the research is focusing on selective hydrogenation to give syngas, methane and various liquid products.

Here, we converted biosyngas, i.e. a mixture of CO, H₂ and CO₂ into methanol. H₂ to CO molar ratio (stoichiometric) was always 2 whereas CO₂ concentration varied between 0 and 13 %vol.

The catalyst was a commercial CZA (mixture of Cu, Zn and Al oxides, from Alpha Caesar ID: 45776), which is the most employed catalyst for methanol production [2]. Its typical composition is: CuO 63.5 %wt, ZnO 24.7 %wt, Al₂O₃ 10 %wt and MgO 1.3 %wt. We collected all the data in a lab scale fixed bed reactor. Its diameter is 6 mm. Four mass flow controllers set the flow of CO, H₂, CO₂, and N₂ (internal standard for the analytical part). A type K thermocouple measured the temperature of the catalytic bed and a Brooks pressure controller back regulated the pressure to a value between 20 and 35 barg, depending on the test. A cold trap at 3 °C condensed water, methanol and eventually any other by-products. A Ritter TG01/05 totalizer quantified the total volume flowed in the plant from the beginning of each test. A micro-GC (Agilent 3000A) measured the unreacted CO flowrate (Eq. 1). SEM, TEM, TPR, and XRD characterized the catalysts. Before each test, we activated the catalyst at 5 bar and 300 °C with 50 NmL min⁻¹ of H₂ for 4 h.

$$CO_{flowrate,out} = N_{2,flowrate} * (A_{CO}/A_{N_2})/F \quad (1)$$

From the mass balance, we derived CO conversion.

Methane and carbon dioxide were the main byproducts. Equation 2 calculated products selectivity:

$$S_i = \frac{C_{flowrate,i}}{CO_{flowrate,in} - CO_{flowrate,out}} \quad (2)$$

where all the flowrates are expressed in mol min⁻¹.

CO conversions increased with total pressure (5 %, 6.3 % and 7 % at 230 °C respectively at 20, 25 and 30 bar). The higher the temperature, the higher the conversion. At 20 bar, CO conversion is 5 % at 230 °C and 12 % at 250 °C while it is 15 % at 270 °C. However, byproducts selectivity raises at 270 °C.

CZA catalyzed methanol production and biosyngas may be employed as new potential feedstock for this process.

References

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