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Shaping Methanol Synthesis from CO_2: Phase Transitions, Residence Time, and Reactor Design

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Abstract

Methanol synthesis from CO_2 and ‘green’ hydrogen is a promising strategy to reduce fossil carbon dependency and establish circular carbon flows. This study investigates the influence of phase transitions and hydrodynamics on methanol formation using a ternary $CO_2/H_2/N_2$ (24/66/10 mol%) feed gas in two reactor configurations: a plug flow tubular reactor (PFTR) and a continuously stirred tank reactor (CSTR, Berty type). The work is structured in three parts: (1) phase equilibria studies using a high-pressure view cell, (2) residence time distribution analysis *via* tracer experiments, and (3) catalytic methanol synthesis over a commercial $Cu/ZnO/Al_2O_3$ catalyst at elevated pressures.

Although the system exceeded the critical pressure of pure CO_2, phase equilibrium measurements up to 95 bar showed that the ternary gas mixture remained subcritical under the investigated conditions. Nonetheless, near-critical effects may enhance methanol formation at industrially relevant temperatures. Residence time distribution experiments confirmed the expected backmixing in the Berty reactor, resulting in improved reactant–catalyst contact and smoother temperature profiles.

Catalytic testing with a commercial $Cu/ZnO/Al_2O_3$ catalyst demonstrated that the Berty reactor achieved up to 36% methanol selectivity and 38% CO_2 conversion at 280 °C and 2400 rpm. By contrast, the PFTR yielded significantly lower methanol output under similar conditions, highlighting mass transport limitations and underscoring the role of reactor design and flow dynamics.

Looking ahead, methanol has the potential to serve as a flexible hydrogen carrier and carbon-neutral fuel. Its compatibility with existing infrastructure and versatility as a precursor for alkenes and aromatics establish it as a cornerstone of future Power-to-X (PtX) strategies. These findings underscore methanol’s central role in connecting renewable hydrogen production with the defossilization of chemical manufacturing.