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Optimization of Temperature Profile for di-methyl ether synthesis by CO₂ hydrogenation.

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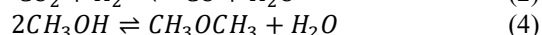
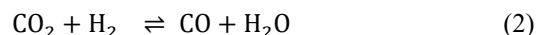
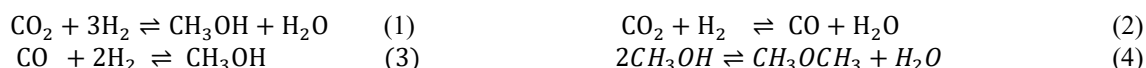
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Highlights

- Di-methyl ether can improve CO₂ hydrogenation compared to methanol synthesis.
- Optimal Temperature Profiles (OTP) increase CO₂ conversion into methanol and DME.
- Low residence times and optimal temperature profiles are recommended.
- Heat exchanger-reactor has to be compatible with low residence time and OTP.

1. Introduction

Harnessing renewable energies to produce green hydrogen capable of converting CO₂ into fuels and chemicals, with the potential to replace fossil feedstocks in the chemical industry, is a remarkable alternative for mitigating greenhouse gas emissions and reducing dependence on fossil fuels. Thermal catalytic *hydrogenation of CO₂*, efficient and easy to industrialize despite its energy consumption and the catalyst deactivation, refers to the process of converting carbon dioxide into value-added molecules, such as methanol and di-methyl ether (DME), using hydrogen (H₂). The hydrogenation of CO₂ to methanol (CTM) is a combined process of three reactions (1 -3), and in the direct hydrogenation of CO₂ to DME, methanol is formed as an intermediate and successively dehydrated (4) in a single reactor containing bifunctional catalysts or mixture of two catalysts optimized for both the reactions separately. The relative occurrence of these parallel or consecutive reactions is difficult to quantify under operating conditions and generally depends on the thermodynamic conditions and the catalysts chemical nature.



All the reactions are, a priori, balanced, and thermodynamic limitations lead to low conversions and selectivities under acceptable kinetic conditions. The aim of this study was therefore to work on the operation of a catalytic reactor in order to improve the conversion per pass of a fixed-bed reactor, by examining its possible temperature control.

2. Methods

This study consisted of three parts: (i) calculation of the gas composition at thermodynamic equilibrium; (ii) estimate of the kinetic parameters from our experiments; (iii) assessment of the several scenarios for temperature profile optimization.

The gas composition and CO₂ conversion at thermodynamic equilibria were calculated by RGibbs under Aspen Plus V12 for the same conditions than the experimental ones. The equation of state used was SRK. The experiments were carried out in a 200mm x 4mm diameter stainless steel fixed-bed reactor in a furnace using a mechanical mixture of catalysts (0-200µm): CuO-ZnO-Al₂O₃ (Alfa Aesar) (CZA), and ZSM5 (ACS Material). The experimental set-up is precisely described in [1]. The ranges of pressure and temperature were [26-36 bar] and [463-593 K] for H₂/CO₂ inlet ratios of about 1, 3 and 9 with 10% N₂ added to calculate balances accurately. The outlet gas was analyzed by gas chromatography. Kinetic modeling was classically carried out, but considering the molecular contraction along the reactor and the existing deactivation on the CZA catalyst [2]. The kinetic laws were derived from Langmuir-Hinshelwood-type models, independent for each catalyst. The ODE system was solved using the *ode45* Matlab routine and the parameter estimate was performed using the *lsqnonlin* Matlab solver.

For the temperature profile optimization, a fixed bed piston reactor was simulated. When reversible exothermic reactions occur, the Arrhenius law suggests to begin at a high temperature to achieve higher

rate and conversion (kinetic limitation), but due to the thermodynamics limitations, it is necessary to decrease the temperature to maximize the conversion. Thus, there is an optimum temperature profile to identify to attain a maximum conversion with a minimum volume by changing temperature as a function of a given reactant conversion (X_j). The compound mass balances were discretized into at least 100 cells to avoid numerical errors. In each cell, considering the upstream gas composition, the temperature required to achieve the target criteria was determined and fixed and the gas composition calculated. Several target criteria were used, either maximizing the extents of the reactions (X1) and (X4), the CO₂ conversion (X CO₂) or the methanol and DME production (FMD) or minimizing the extent of the reaction (X2). The optimizations were performed for several reactor inlet temperatures [473-607 K], H₂/CO₂ inlet ratios from 1 to 9, pressures [31, 36 bar] and catalyst masses and inlet gas flow rates to vary the residence times [1-130 s].

3. Results and discussion

For the reactions taken place on the commercial CZA catalyst, the kinetic model developed by Quezada [2] was retained. For the reaction 4, the model proposed by Ortega et al. [3] assuming the reaction equilibrium was modified taking into account the slower rate of the reverse reaction than that expected assuming thermodynamic equilibrium. 13 kinetic parameters were estimated. A regression analysis validated the model on 39 experiments.

Figure 1 shows that the optimization of temperature profiles in the reactor allows a sharp increase of CO₂ conversion into methanol and DME (from 10 to 40% on fig. 1.c), minimizing the CO production. While without optimization, that is to say in isothermal conditions, the outlet CO₂ conversion is the conversion at the thermodynamic equilibrium of the inlet temperature, conversions keep on increasing when decreasing temperature along the bed. The choice of the target criteria led to different optimized temperature profiles and the optimization of X1 (proportional to FMD) led to better CO₂ conversion and methanol and DME production. Our set of optimizations demonstrated that if long residence times are chosen (small flowrates or/and high catalysts weights), working at low temperatures give the best results but for a bigger production minimizing the catalysts amounts, the best is to work with low residence times, enter the reactor at high temperature and follow the optimized temperature decreasing profile.

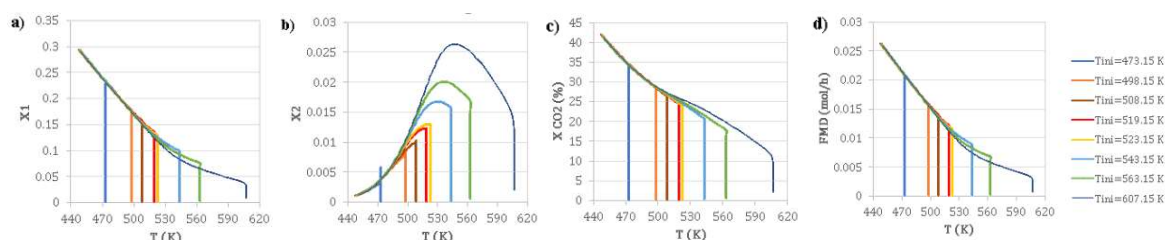


Figure 1. Effect of the inlet temperature on CO₂ conversion, X1, X2 reaction extents and value-added molecule production maximizing the target criteria X1. P=31.1 bar, H₂/CO₂=2.8, N₂=10%. Residence time 6 s.

4. Conclusions

A tool for scaling-up a reactor for the hydrogenation of CO₂ to DME and methanol has been developed, maximizing the conversion of CO₂ and/or the production of methanol and DME by optimizing the residence time and the optimal temperature profile to be followed. This tool needs to be improved by considering any limitations due to internal transfer in the catalyst grains. However, we assumed in our method that a perfect removal of the heat produced by the exothermic reactions can be performed, that could be unrealistic. Hence, designing a heat exchanger reactor from our kinetic models is our next goal.

References

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Keywords

Optimal Temperature Profile ; CO₂ Hydrogenation ; DME synthesis ; Kinetic model