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Model-based investigation of methanol and DME synthesis

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Highlights
- Methanol and DME synthesis has been studied comparing alternative kinetic models
- A rigorous parameter estimation has been performed to discriminate the alternative models
- The effect of water injection in the inlet stream have been analyzed

1. Introduction

There is the urgency in reducing our CO_2 emissions, while meeting the growing demand for fuels. Among the carbon capture and utilization technologies, methanol and DME synthesis are promising routes as they can be used as alternative fuels, or precursors for other valuable compounds, and they can be distributed using the existing fuel distribution network.

Nowadays, large scale methanol production is almost exclusively from syngas, using heterogeneous catalysts of Cu/ZnO, and DME synthesis is usually carried out in an independent reactor, which uses an acidic catalyst (e.g.: γ-alumina). Two interesting alternatives are to produce methanol from direct CO_2 hydrogenation and to develop two catalyst reactors (or a bifunctional catalyst) to perform a coupled methanol and DME synthesis. The advantages are in the first case that CO_2 can be used to produce a more valuable compound, instead of releasing it in the atmosphere, and in the second case that methanol is converted to DME before reaching the equilibrium yield, hence increasing the overall methanol production. However, both high CO_2 concentration in the feed and DME synthesis lead to high water concentrations in the reactor compared to conventional syngas, which in turn may results in catalyst deactivation. It is therefore paramount to analyze the effect of water in the catalyst stability and rigorous kinetic models can be of great help for a better understanding of the underlying kinetic mechanism and to identify the key performance constraining parameters.

In this work a general methodology to precisely identify a kinetic model is proposed, which ultimately will lead to an exploration of the differences between the CO_2 rich and traditional syngas compositions in the reactor performances.

2. Methods

Although the Cu/ZnO catalyst has been used for the methanol production for a long time, the actual reaction mechanism is still debated. Several global kinetic models have been proposed in the literature and two important ones are those of Bussche and Froment [1] and Graaf et al. [2], which have been developed for methanol production from standard syngas but have been considered in recent literature also for methanol synthesis from pure CO_2 and H_2 [4,5]. The main difference between the two models is that [2] claimed that direct CO hydrogenation must be considered while [1] proposed a kinetic model based only on the CO_2 hydrogenation and the reverse water gas shift (RWGS) reactions.

In this work the models in [1] and [2] for methanol synthesis will be coupled with a model for the methanol dehydration [3]. To calibrate the models, we will use experimental data from a gradient-less internal recycle reactor operated at constant temperature and pressure, considering different inlet composition and inlet flowrates. Moreover, two case studies have been considered: a methanol-only synthesis case study, using only a Cu-based catalyst, and a coupled methanol and DME synthesis case study, where γ-alumina is added in the catalytic bed (for the complete dataset see [5]). Additionally, new data obtained for the same catalytic systems, injecting in the inlet stream a variable amount of water, have been used for model validation. The simulations and parameter estimations were conducted in the modelling environment gPROMS (Process System Enterprise, gPROMS v 5.0, www.psenterprise.com/gproms, 1997-2017).

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3. Results and discussion

The preliminary calibration results suggest that the model in [1] is capable to represent accurately the experimental data. In Figure 1 we report the case of methanol only synthesis for several syngas compositions. However, despite the fitting quality is quite good additional analysis is needed to correctly assess the importance of the direct CO hydrogenation considered in model [2]. The introduction of CO hydrogenation can increase the fitting quality for inlets with CO_2 fraction lower than 0.5, where the outlet CO_2 fraction is slightly underestimated, but is also important for high CO_2 feeds, as it affects the predicted water production.
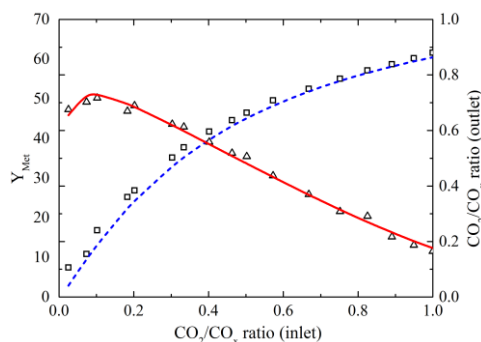
Figure 1. Measured and predicted methanol yield and exit CO_2 fraction in methanol only synthesis for different CO_2 fraction in the inlet. Feed conditions: $CO_x = 18\%$, $H_2 = 72\%$ and $He = 10\%$. $T = 250°C$, $P = 50$ bar, inlet flowrate $= 2.84 \cdot 10^{-4}$ mol/s.

In order to better investigate the effect of water in the catalytic activity, data of water injection has been considered. Here we used the parameter values obtained in the preliminary calibration for the models [1] and [3] to simulate the methanol yield drop after the injection of water in the system. The predictions of the steady states along with experimental values are reported in Table 1.

Table 1. Measured and predicted steady state methanol yield for a methanol and coupled methanol and DME synthesis, considering different amount of water injected in the feed. Feed conditions: same as Figure 1 with $CO_2/CO_x = 0.1$.

	Methanol only		Coupled Methanol and DME	
Injected water (mol/mol)	$Y_{Met, meas}$ (%)	$Y_{Met, pred}$ (%)	$Y_{Met, meas}$ (%)	$Y_{Met, pred}$ (%)
0.0 %	51.0	51.2	53.7	56.4
6.6 %	37.0	38.2	38.3	38.8
9.2 %	25.1	25.6	26.4	26.3
11.9 %	18.0	17.6	18.5	18.1

4. Conclusions

In this work methanol synthesis and coupled methanol and DME synthesis has been studied. Two literature models for the methanol production has been coupled with a model for DME synthesis and have been calibrated against historical data. The effect of water injections in the feed has been simulated considering the preliminary calibration and the predictions are in good accordance with the experimental data.

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Keywords
Methanol synthesis; DME synthesis; Cu/ZnO catalyst; kinetic model