

## Regeneration Conditions as the Key to Sorption Enhanced Dimethyl Ether Synthesis

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### Highlights

- SEDMES: direct synthesis of DME from syngas by in situ H<sub>2</sub>O adsorption
- Steam adsorbent easily regenerated by pressure swing, without temperature swing
- Catalytic conversion and activity improve by temperature swing regeneration

### 1. Introduction

Dimethyl ether (DME) is one of the most promising alternative fuel solutions among the various ultra clean, renewable, and low-carbon fuels under consideration worldwide [1]. Sorption-enhanced DME synthesis (SEDMES) is a novel process for the production of DME from synthesis gas [2,3], in which water is removed in situ by the use of a solid adsorbent. The concept is based on Le Chatelier's principle stating that reactant conversion to products in an equilibrium limited reaction is increased by selectively removing reaction products. Experimental proof-of-principle has shown increased DME yield, improved selectivity towards DME over methanol and reduced CO<sub>2</sub> content in the product [2]. Periodic regeneration of the adsorbent is typically done by pressure (vacuum) and/or temperature swing. Among other aspects, equipment, material stability, and overall process efficiency depend on the regeneration operation. In the previous proof-of-principle both temperature and pressure swing regeneration were used [2]. This contribution will present extended proof-of-concept for the novel SEDMES process and results of an investigation into the impact of regeneration conditions on catalyst and adsorbent performance for the sorption-enhanced production of DME.

### 2. Methods

Both thermodynamic modelling using Aspen Plus [4] and transient experiments were performed for various feed compositions with a stoichiometric M module of 2 ( $M = ([H_2] - [CO_2]) / ([CO] + [CO_2])$ ) and inert N<sub>2</sub>, Ar. Commercial copper/zinc oxide/alumina catalyst (5-10 g) and commercial zeolite A steam adsorbent (20-40 g, mixed as sieve fractions) were used experimentally. Adsorption was conducted at 275 °C, 25 bar(a) and with different feed gas compositions. Regeneration was done by switching to dry gas, depressurisation and eventual heating up to 300-400 °C. Analysis was done by a combination of mass spectrometry and GC.

### 3. Results and discussion

A representative breakthrough experiment is shown in Figure 2, indicating sorption enhanced DME synthesis.

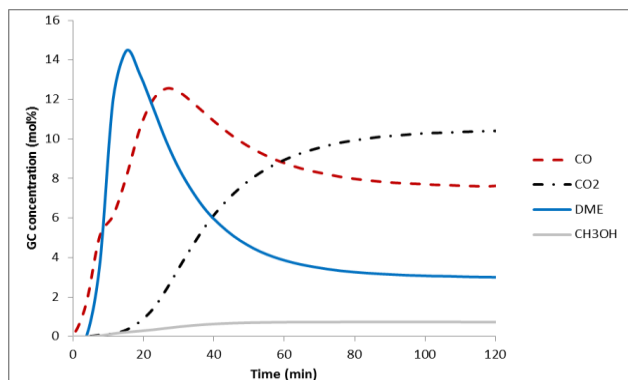


Figure 2. Breakthrough experiment at 25 bar(a), 275 °C, feed H<sub>2</sub>:CO:CO<sub>2</sub> 7:2:1 (regeneration at 400 °C).

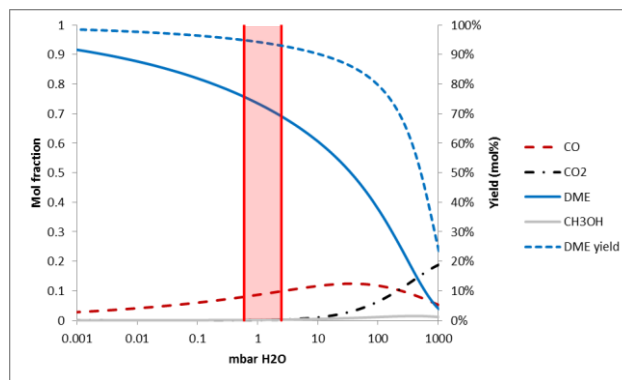
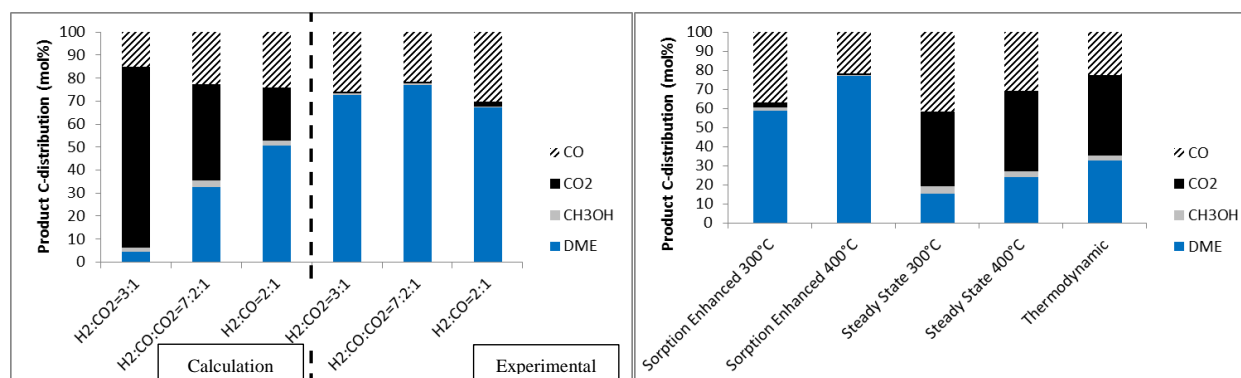


Figure 3. Calculated SEDMES product distribution and yield, 25 bar(a), 275 °C, feed H<sub>2</sub>:CO<sub>2</sub> 3:1.

Pre-breakthrough of steam, CO and DME are the primary products. After steam breakthrough the concentration of DME drops, accompanied with the breakthrough of CO<sub>2</sub> and methanol. Feed flexibility is obtained since the sorption enhancement is similar for different CO/CO<sub>2</sub> compositions of the feed (Figure 4a). For direct DME synthesis 4-50% of the feed carbon ends up in DME as a product, with SEDMES this is enhanced to 65% and more. In addition, the amount ending up in CO<sub>2</sub> is largely reduced to only 2% or less, simplifying downstream separation and recycle. These findings indicate the major benefits of the SEDMES process for the production of DME. In Figure 3 results of thermodynamic calculations for DME synthesis as a function of steam content are shown, addressing the effect of steam separation enhanced reaction. Already after pressure swing regeneration, zeolite A is able to reach the low steam slip levels at which the enhancement is especially significant (Figure 3, red area). Figure 4b shows the experimentally obtained enhancement in conversion towards DME. However, the expected conversion of 90%, as shown in Figure 3, is not reached. In addition Figure 4b shows there is an impact of the regeneration temperature on conversion; a higher regeneration temperature leads to a higher conversion, resulting in almost pure DME together with unreacted CO. A possible explanation for this effect is the catalyst response as function of the regeneration temperature. From Figure 4b it can be clearly observed that the conversion towards DME is improved by regeneration at higher temperature also in steady state when the adsorbent is fully saturated, suggesting that the catalyst activity is influenced by the regeneration.



**Figure 4.** a) Conventional (calculation, left) versus sorption enhanced (experimental, right, 400 °C regeneration) direct DME synthesis, 25 bar(a) and 275 °C, and b) C-distribution in steady state and sorption-enhanced DME synthesis (25 bar(a), 275 °C) versus regeneration temperature for H<sub>2</sub>:CO:CO<sub>2</sub> 7:2:1.

#### 4. Conclusions

The feasibility of the sorption-enhanced DME synthesis (SEDMES) process relies on efficient regeneration of the system. The zeolite adsorbent is readily regenerated by pressure swing. For SEDMES, regeneration with additional temperature swing to 300 °C results in significant conversion enhancement. Regeneration with temperature swing to 400 °C further improves the DME yield, which appears to be related to improved catalyst activity. Within EU Horizon 2020 project Fledged, further optimisation of the SEDMES process will be pursued.

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#### Keywords

Dimethyl ether; Regeneration; Sorption-enhanced reaction; Steam adsorption.