Separation Enhanced Dimethyl Ether Synthesis

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Separation Enhanced Dimethyl Ether Synthesis

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A novel sorption enhanced dimethyl ether synthesis (SEDMES) process is presented using a solid adsorbent to remove produced water in situ. SEDMES experiments from feed mixtures of H_2, CO, and CO_2 have shown an increased yield of DME, an improved selectivity to DME over methanol, and a strongly reduced CO_2 content in the product. Consequently, SEDMES will reduce the downstream separation effort and minimise the recycle streams. Within the European Horizon 2020 project FLEDGED, synthesis gas from biomass gasification will be used as feedstock for the separation enhanced DME-synthesis.

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Introduction

Dimethyl ether (DME) is a promising alternative fuel among the various ultra clean, renewable, and low-carbon fuels under consideration worldwide [1]. In the DME production from syngas, the following equilibrium reactions are involved:

Methanol synthesis

$$CO_2+3H_2 \rightleftharpoons CH_3OH+H_2O \quad (1)$$

Water-gas shift (WGS)

$$CO+H_2O \rightleftharpoons H_2+CO_2 \quad (2)$$

Methanol dehydration

$$2CH_3OH \rightleftharpoons CH_3OCH_3+H_2O \quad (3)$$

Indirect DME production comprises the production of intermediate methanol (1), and methanol dehydration (3) in separate reactors. Both reactions are thermodynamically limited which leads to limited DME yield and extensive separations and recycles. The direct DME synthesis (Figure 1b) proceeds in a single reactor via intermediate methanol (1) as well, yet offers a reduction in process steps and increased overall DME yield. In terms of efficiency, direct DME synthesis process outperforms the indirect synthesis, yet the need for separation and recycling remains. In the direct DME synthesis, the O-surplus of the feed ends up in CO_2, which means that about equal molar amounts of DME and CO_2 are produced. Since the reaction is equilibrium limited, downstream separation produces recycle streams of syngas (CO and H_2), CO_2, and methanol. Syngas and methanol are recycled back to the DME synthesis reactor, while the CO_2 recycle is used in synthesis gas generation via dry or tri-reforming.

A novel process route exists, called sorption enhanced DME synthesis (SEDMES, Figure 1c). It is based on the use of a solid adsorbent for the in situ removal of water. According to Le Chatelier's principle, the removal of one of the products will shift the equilibrium-limited conversion to the product side. The process has been analysed theoretically [2], indicating that in situ water adsorption leads to an increased yield and selectivity to DME. In this contribution, results are presented of an investigation into the sorption-enhanced production of DME.

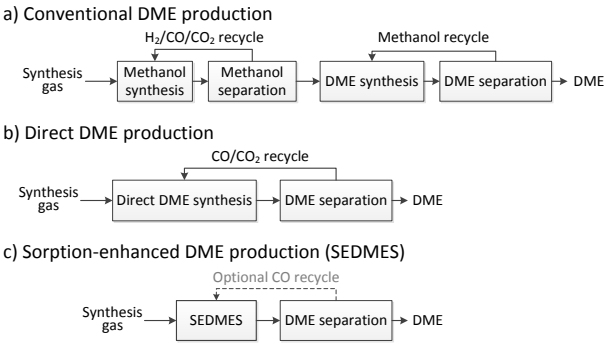

Fig. 1: DME production routes

Table 1: Experimental settings

Composition	1	2	3
Sample weight [g]		50	
Particles sieve fraction [µm]		212-425	
Feed flow rate [Nml/min]		260	
Reactor pressure [bar(a)]		25	
Feed gas composition [mol%]			
N_2	23.0	23.0	23.0
H_2	57.7	51.5	53.8
CO		25.4	15.4
CO_2	19.2		7.7
M module		2	

Approach

A combined approach was taken, comprising thermodynamic modelling and transient experiments. Thermodynamic calculations were performed on different feed compositions with different $H_2/CO/CO_2$ ratios (see Table 1) using HSC Chemistry [3]. All compositions had an *M* module of 2, the stoichiometric molar ratio for DME, defined as $M = ([H_2]-[CO_2])/([CO]+[CO_2])$. The calculations were performed taking into account equilibrium reactions (1-3) from the feed mixtures at 25 bar(a) pressure and as a function of temperature. In addition, the impact of steam separation enhanced reaction was addressed by calculating the thermodynamic equilibrium as a function of

steam content at a total pressure of 25 bar(a) and a temperature of 150-350 °C.

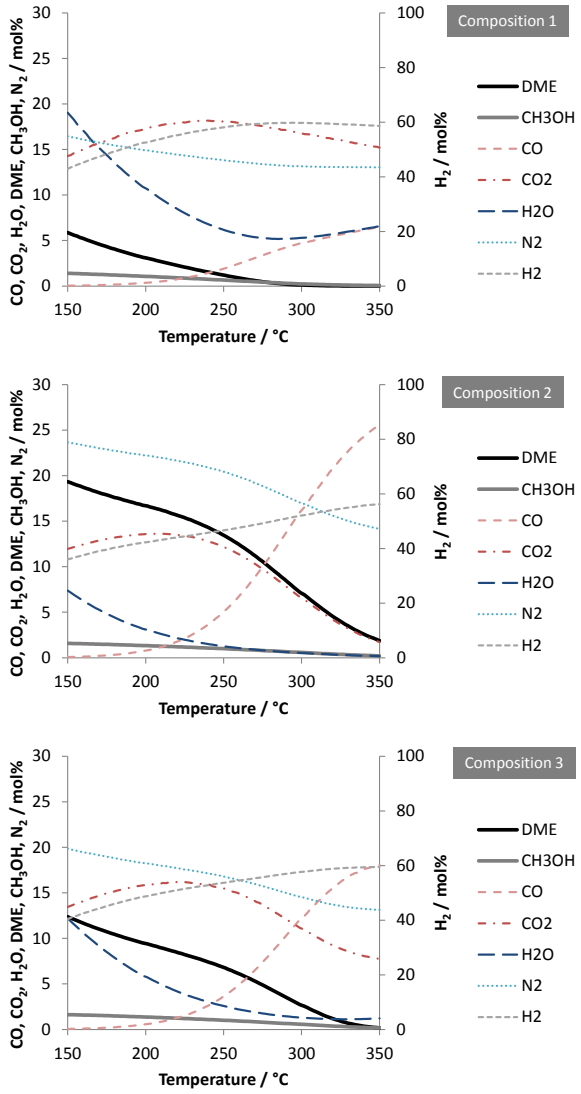

Fig. 2: Thermodynamic equilibrium versus temperature for the compositions in Table 1, 25 bar(a)

Experimentally, a combination of a commercial copper/zinc oxide/alumina catalyst and a commercial zeolite 3A steam adsorbent was used for the demonstration of direct DME synthesis from H_2/CO/CO_2 mixtures. Particles were mixed as sieve fractions. The experimental runs were conducted on a high-pressure reactor setup, allowing 50 g of sample, consisting of 10 g of catalyst and 40 g of sorbent, to be tested in a single reactor of 15.75 mm internal diameter. The catalyst to adsorbent ratio was arbitrarily chosen and not further optimised in this work. Adsorption was done under different feed gas compositions, shown in Table 1. The N_2 balance was used in order to keep the overall pressure stable, considering the shrinking overall reaction. Regeneration was done by switching to dry nitrogen, depressurisation to 1.7 bar(a), and heating to 400 °C. Gas analysis was done by i) MS measuring H_2 (m/z=2), H_2O (m/z=18), CO/N_2 (m/z=28), CH_3OH (m/z=31), CO_2 (m/z=44) and DME (m/z=45), and ii) NDIR measuring CO and CO_2 in the dry sample flow.

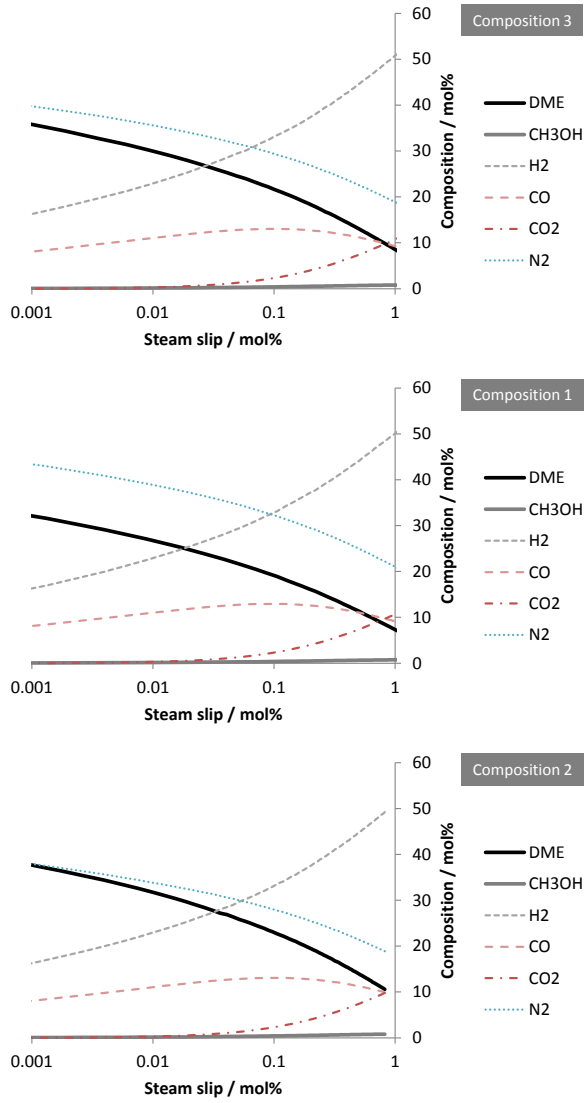

Fig. 3: Thermodynamic equilibrium versus water slip level for the compositions in Table 1, 25 bar(a), 275 °C

Results

Figure 2 shows the thermodynamic results on the formation of DME as a function of temperature for the gas compositions given in Table 1, without in situ water adsorption. DME formation is dependent on the different H_2/CO/CO_2 ratios as well as temperature. At decreasing oxygen content in the gas mixture (order of composition 1, 3, and 2) the conversion to DME is higher, indicating that the presence of excess oxygen is hampering the formation of DME. Oxygen removal can be realised by removing the reaction product steam and thus promote the conversion to DME. This is essentially the removal of steam from the reactions (1-3). Figure 3 shows the results of the thermodynamic calculations of the formation of DME as a function

of steam content at 25 bar(a) for the three gas compositions given in Table 1. Because $M = 2$ for all three cases, the graphs appear very similar and clearly show that the removal of steam results in higher conversions towards DME for all gas compositions. The carbon conversion to DME is very high, especially at lower steam slip levels. The concentrations of methanol and CO_2 reduce significantly, suggesting that the conversion of oxygen rich feedstock CO_2 into DME can be realised when removing steam.

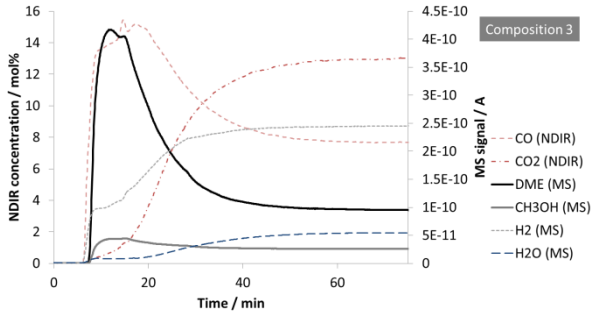

Fig. 4: Breakthrough experiment with Composition 3, 25 bar(a), 275 °C

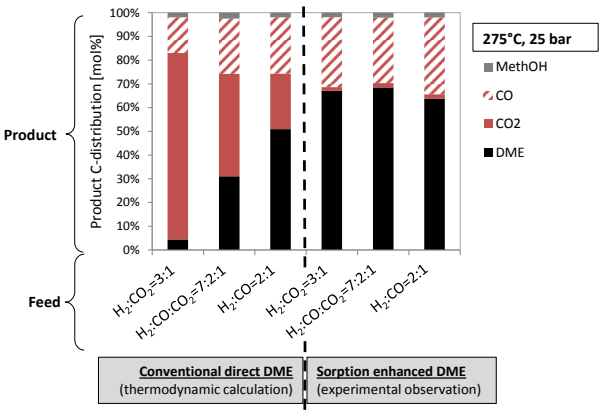

Fig. 5: Conventional versus sorption enhanced direct DME synthesis, 25 bar(a), 275 °C

Experimental proof-of-concept of SEDMES is indicated in Figure 4 by breakthrough measurement of Composition 3. Before the breakthrough of steam, which starts at about 16 minutes on stream, the main carbon-containing products are CO and DME. A small amount of methanol is being produced, and small amounts of H_2O and CO_2 slip through the not yet optimised bed. After 16 minutes on stream, H_2O and CO_2 break through together and the DME concentration drops. Similar results were obtained with the other feed gas compositions, and the observed pre-breakthrough sorption enhancement for each of the settings is shown in Figure 5. The amount of feed C ending up in DME is enhanced from 4-50% for the direct DME synthesis to around 65% for SEDMES. Additionally, the amount ending up in CO_2 is strongly reduced from 20-80% to below 2%. Moreover, the product distribution depends much less on the feed CO/CO_2 composition (at the same value of the *M* module). When comparing the obtained pre-breakthrough concentrations (Figure 5) to the thermodynamic equilibrium (Figure 3), it shows that the experimental product spectrum is according to thermodynamic equilibrium. It is anticipated, therefore, that removal of balance N_2 will further enhanced the conversion to DME. These observations for the sorption enhanced mode have several important implications for DME synthesis. The feed to the SEDMES reactor can contain CO_2 as well as CO. Secondly, the CO_2 content of the reactor effluent is largely suppressed, simplifying the downstream separation section and largely eliminating the CO_2 recycle. These findings have led to a recent patent application on SEDMES [4].

Summary

A novel sorption enhanced dimethyl ether synthesis (SEDMES) process is presented using a solid adsorbent to remove produced water in situ. SEDMES experiments from feed mixtures of H_2, CO, and CO_2 have shown an increased yield of DME, an improved selectivity to DME over methanol, and a strongly reduced CO_2 content in the product. Consequently, SEDMES will reduce the downstream separation effort and minimise the recycle streams.

Outlook

Fledged is a recently started EU H2020 project which aims at developing a flexible process for the production of DME from biomass gasification with sorption enhanced processes. In Fledged, the SEDMES process is being developed further, targeting higher conversions to DME. Specific attention is paid to elucidation of the reaction mechanism. The objective of the project is an experimental validation of a full cyclic SEDMES process for 3 kg/h DME production at ECN laboratories.

Acknowledgement

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