Sorption enhanced dimethyl ether synthesis for high efficiency carbon conversion

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Sorption enhanced dimethyl ether synthesis for high efficiency carbon conversion: Modelling and cycle design

Jasper van Kampen\textsuperscript{a,b,e}, Jurriaan Boon\textsuperscript{a,b}, Jaap Vente\textsuperscript{a}, Martin van Sint Annaland\textsuperscript{b}

\textsuperscript{a} Sustainable Process Technology, ECN part of TNO, P.O. Box 15, 1755ZG Petten, the Netherlands
\textsuperscript{b} Chemical Process Intensification, TU/e, P.O. Box 513, 5600MB Eindhoven, the Netherlands

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\textbf{ABSTRACT}

Dimethyl ether is one of the most promising alternative fuels under consideration worldwide. Both the conventional indirect DME synthesis and the improved direct DME synthesis process are constrained by thermodynamics, which results in limited product yield, extensive separations and large recycle streams. Sorption enhanced DME synthesis is a novel process for the production of DME. The in situ removal of H\textsubscript{2}O ensures that the oxygen surplus of the feed no longer ends up in CO\textsubscript{2} as is the case for direct DME synthesis. As a result CO\textsubscript{2} can be converted directly to DME with high carbon efficiency, rather than being the main byproduct of DME production.

The sorption enhanced DME synthesis process is a promising intensification, already achieving over 80\% single-pass CO\textsubscript{2} conversion for a non-optimized system. The increased single-pass conversion requires less downstream separation and smaller recycle streams, especially for a CO\textsubscript{2}-rich feed. A key optimization parameter for the process performance is the adsorption capacity of the system. This capacity can be improved by optimizing the reactive adsorption conditions and the regeneration procedure. In this work, a detailed modelling study is performed to investigate the impact of various process parameters on the operating window and the interaction between different steps in a complete sorption enhanced DME synthesis cycle, and to compare its performance to other direct DME synthesis processes. The development of sorption enhanced DME synthesis, with its high efficiency carbon conversion, could play a significant role in the energy transition in which the carbon conversion will become leading.

\section{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 \cite{1}. As it can be produced from syngas (defined here as a mixture of CO, CO\textsubscript{2} and H\textsubscript{2}) originating from fossil and renewable feedstocks alike, it is projected to play an important role in the energy transition \cite{1}. DME is also one of the valuable products considered for chemical recycling by carbon dioxide conversion \cite{2}, direct (CCU) as well as indirect conversion via biomass-based syngas.

Conventionally, indirect DME production (Fig. 1a) is a two-step process. Intermediate methanol is synthesized from syngas, subsequently followed by the dehydration of methanol to DME in a separate reactor. The following equilibrium reactions are involved in DME synthesis:

\begin{equation}
\text{Methanol synthesis:}\quad \text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ = -49 \text{ kJ/mol}
\end{equation}

\begin{equation}
\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_4\text{OH} \quad \Delta H^\circ = -90 \text{ kJ/mol}
\end{equation}

Water-gas shift:

\begin{equation}
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -41 \text{ kJ/mol}
\end{equation}

\begin{equation}
\text{Methanol dehydration:}\quad 2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H^\circ = -24 \text{ kJ/mol}
\end{equation}

\begin{equation}
\text{Direct DME synthesis (from CO):}\quad \text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ = -127 \text{ kJ/mol}
\end{equation}
Both the methanol synthesis (1,2) and its subsequent dehydration (4) are thermodynamically limited, resulting in limited yield, extensive separations and large recycles (see Fig. 1a). In recent years a lot of attention is going to the direct production of DME in a single-step process (Fig. 1b), including a major contribution for the development of hybrid catalysts [3–18]. An advantage to operate methanol synthesis and methanol dehydration in one single step is that the subsequent dehydration of methanol removes it from the reaction medium and thereby shifts the reaction equilibrium for the methanol synthesis reaction. Direct DME synthesis (from CO and H₂) (5) reduces the extent of necessary process steps and allows for an increased overall DME yield. However, separation and recycling remain necessary. The oxygen surplus in the feed of direct DME synthesis ends up as CO₂, resulting in equal molar amounts of DME and CO₂ produced. Since the reaction is still equilibrium limited, downstream separation produces large recycle streams of syngas, CO₂ and methanol. Moreover, conventional synthesis of DME from CO₂ is not even viable due to the low CO₂ conversion and DME yield [17].

Sorption enhanced DME synthesis (SEDMES) (6) is a novel process for the production of DME from synthesis gas (Fig. 1c) [19,20], in which water is removed in situ by the use of a solid adsorbent, typically a LTA zeolite [21]. 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, which is utilized for various processes and products mainly considering CO₂ separation [22,23]. By the removal of H₂O as reaction product, the
oxygen surplus of the feed no longer ends up in CO₂, as is the case for direct DME synthesis. As a result, CO₂ can be used as feed, rather than being the main byproduct, as illustrated in Fig. 2.

Reactive steam adsorption has been studied for various reactions, such as the synthesis of dimethyl carbonate (DMC), DME and methanol [24]. The first experimental studies regarding sorption enhanced reactions, such as Kim et al. and Ressler et al. for DME synthesis, focus merely on the enhancement effect of the adsorbent on the reaction, not on a description of the intrinsic adsorption behavior and neither on a description of the process conditions and their implications [25,26]. Sorption enhancement for DME synthesis was first modelled by Iliuta et al., showing the potential of in situ H₂O adsorption for DME synthesis [19]. SEDMES has been evaluated theoretically [19,20] and a proof-of-concept has been demonstrated experimentally [20,27], showing increased DME yield, improved selectivity towards DME over methanol and reduced CO₂ content in the product [20]. Fig. 2 clearly shows this advantage of sorption enhanced DME synthesis over conventional direct DME synthesis. Not only do the experimentally obtained results show a possible DME yield of more than 80 % for SEDMES, the CO₂ content in the product is less than 1 %. The resulting increased single-pass conversion requires much less downstream separation, and smaller recycle streams especially for a CO₂-rich feed [24,27]. A further experimental study has clarified the importance of the regeneration process in the SEDMES technology [27].

In a sorption enhanced system, as the SEDMES process, the periodic regeneration of the saturated adsorbent is typically done by pressure swing, temperature swing, purge/concentration swing or combinations of these methods. While the different regeneration procedures have their own typical duration (timings), the timing of adsorption and regeneration have to be carefully tuned. The simplest case would be a two-reactor column system, in which one column is producing the sorption enhanced product, while the other column is regenerating. However, the regeneration procedure typically consists of multiple steps and in general requires more time than the reactive adsorption. Therefore, multicolumn systems are usually designed for sorption enhanced processes. Fig. 3 provides a schematic overview of the SEDMES process and the involved consecutive steps that a reactor column goes through during one full SEDMES cycle: one reactor is fed with syngas and produces DME during reactive adsorption, while the other reactors are regenerated by feeding a purge gas, are repressurized/depressurized for a pressure swing cycle, or heated/cooled for a temperature swing regeneration. Each of the columns continuously goes through the different steps of the SEDMES cycle consecutively. This relatively simple three-column SEDMES process is used as a base for the model study in this work and is shown in Fig. 4.

This contribution presents an elaborate model study on the SEDMES process, investigating in detail the impact of various process parameters on the operating window, as well as the interaction of different cycle steps. Finally, the performance of the SEDMES process is compared to other direct DME synthesis processes at demonstration scale.

This work first introduces an elaborate model description, followed by a comparison of the model with experimental results. A full SEDMES cycle is described and its performance is extensively studied. Finally, a comparison of SEDMES and direct DME synthesis is made.

2. Model

To analyze the sorption enhanced DME synthesis process a cyclic one-dimensional, dynamic reactor model was developed, based on previous modelling experience for the sorption enhanced water-gas shift process [28,29]. The cyclic model solves the consecutive steps in the cycle using a fixed-bed pseudo-homogeneous reactor model, assuming a homogeneous mixture of direct DME synthesis catalyst and LTA zeolite particles. The different aspects of the model, viz. the conservation equations on the reactor and particle scale, reaction kinetics and adsorption isotherms and the model parameters and numerical solution strategy, are shortly outlined in the next sections.

2.1. Mass, momentum and energy conservation for gas and particle phase

For the description of the fluid flow and mass transfer, the 1D non-steady isothermal differential mass and momentum balances are solved. The total mass and momentum balances, component material balances and overall energy balance are given in Table 1. Constitutive equations have been taken from the literature [30–34].
2.1.1. Particle-scale model

For both the particle concentrations and the adsorbent species concentrations a linear driving force (LDF) approximation is used (Table 2), to account for intraparticle transport (expressed by the flux $N_i$), reaction and adsorption (Eq. 12), and to account for intracrystalline transport and adsorption (Eq. 13). Glueckauf has shown that when the conditions are close enough to equilibrium ($D_i/t_{p} > 0.1$) a LDF approximation holds [32]. In these equations $\bar{c}$ is the average concentration in the particle, whereas $\bar{q}$ is the average amount adsorbed in the adsorbent particles. $q'$ is the amount adsorbed in equilibrium with the (bulk) concentration. This is given by the adsorption isotherm of steam on the zeolite adsorbent (see Section 2.3). The equations for the intraparticle model are derived from the common linear driving force approximation for porous spherical particles, including the effective macro- and micropore diffusion ($D_{pr}, D_{c}$) [30].

2.2. Reaction kinetics

The direct DME synthesis catalyst is a bifunctional catalyst [20,27], which is considered to be a mixture of a methanol synthesis catalyst (Cu/ZnO/Al2O3) and a methanol dehydration catalyst (γ-Al2O3) [21]. For the methanol synthesis (1,2) and the water-gas shift reaction (3) the kinetic expressions by Graaf et al. and Vanden Bussche et al. are used.

### Table 1
Reactor model equations.

| Continuity | $\frac{dN_i}{dt} = \frac{dN_i}{dV} = \frac{1}{\rho} \frac{d\rho}{dt} \frac{dV}{d\rho} + \frac{1}{\rho} \frac{d\rho}{dt} \frac{dV}{d\rho}$ (7) |
| Momentum | $\frac{d\rho V}{dt} = -\rho V \frac{d\rho}{dt} + F + \frac{1}{\rho} \frac{d\rho V}{d\rho} + \frac{1}{\rho} \frac{d\rho}{dt} \frac{dV}{d\rho}$ (8) |
| Species mass balance | $\frac{dN_i}{dt} = \frac{dN_i}{dV} = \frac{1}{\rho} \frac{d\rho}{dt} \frac{dV}{d\rho} + \frac{1}{\rho} \frac{d\rho}{dt} \frac{dV}{d\rho}$ (9) |
| Overall energy balance | $(\rho \dot{C} + \dot{c})_V = -\rho \dot{C} \dot{\rho} \frac{dV}{d\rho} + \frac{1}{\rho} \frac{d\dot{C} \dot{\rho}}{d\rho} \frac{dV}{d\rho} + \frac{4}{\rho} \frac{d\rho}{dt} + \dot{q} (\sum \Delta H_i | \dot{r}_i + \Delta H_{ads} | \dot{\bar{q}})$ (10) |
| Equation of state | $PM = \rho RT$ (11) |

### Table 2
Intraparticle equations.

| Intraparticle mass balance | $\frac{d\bar{c}}{dt} = k_{LDF} \left( \frac{\bar{c}}{\rho} - \bar{c} \right) + f_{eq} \frac{\bar{c}}{\rho} - \frac{\bar{c}}{\rho}$ (12) |
| Intraparticle mass balance | $\frac{d\bar{q}}{dt} = k_{LDF} \left( \frac{\bar{q}}{\rho} - \bar{q} \right)$ (13) |
| Mass transfer coefficients | $k_{LDF,1} = \frac{\bar{c}}{\rho}$ (14) |
| Mass transfer coefficients | $k_{LDF,2} = \frac{\bar{q}}{\rho}$ (15) |

[15,35,36] (Table 3). In Table 4 the kinetic and adsorption constants are defined according to Van’t Hoff relations [15,35]. The equilibrium constants are taken from Graaf et al. [37].

For the methanol dehydration reaction (Eq. 4) the kinetic expression by Berčič et al. is used [21,38]. The kinetic and adsorption constants by Ng et al. (adapted from Berčič et al.) are again defined according to Van’t Hoff relations [15]. The equilibrium constant is given by Zhiliang et al., from Hu et al. [39].

Because Eq. (18) (reaction rate expression for the methanol synthesis from CO2) can be written as the stoichiometric sum of Eqs. (16) and (17), $K_{p3}$ can be calculated as:
\[ K_{p3} = K_{p1} \times K_{p2} \]  

And thus: 

\[ \log_{10} K_{p3} = \frac{3666}{T} - 10.592 \]  

### 2.3. Adsorption isotherm and kinetics

The direct DME synthesis catalyst is mixed homogeneously with a LTA zeolite adsorbent. Steam is considered to be the only adsorbed component, due to the high affinity for its adsorption by the zeolite adsorbent. Gabruś et al. derived a Langmuir-Freundlich isotherm model for zeolite 3A from adsorption equilibrium data at elevated temperatures (up to 250 °C) [40], which is shown in Table 5. In these equations

\[
q = \frac{q_s \cdot h^n}{1 + \frac{h^{n+1}}{h_p}} 
\]  

\[
q_s = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} 
\]  

\[
b = \exp\left(\frac{b_0 + \frac{b_1}{T}}{\frac{b_2}{T^2}}\right) 
\]  

\[
n = n_0 + \frac{n_1}{T} 
\]  

\[ q \] is the adsorbent loading (mol kg\(^{-1}\)), \( q_s \) is the saturation loading (mol kg\(^{-1}\)), \( p \) is the partial pressure of the adsorbate (Pa), and \( T \) is the temperature (K). The values for the isotherm constants can be found in Table 6.

### 2.4. Model parameters

The pressure drop in a packed bed with porous particles is given by the Ergun equation [41]. The Ergun parameter \( G \) in Eq. (8) is defined as given in Table 7. As mentioned above, both for the particle concentrations and the adsorbent species concentrations a double linear driving force (LDF) approximation is used. The LDF rate constants are given in Table 2. The effective diffusivities are given by the micropore (intracrystalline) \( D_m \) and macropore (intercrystalline) \( D_p \) respectively. Since the adsorption of gases occurs in the zeolite crystals, where diffusion is slow, intracrystalline diffusion has an important or even rate limiting role in the adsorption and desorption [32]. The molecular gas diffusivity \( D_m \) was calculated using Blan’s law [33] and the binary diffusion coefficients are predicted according to Fuller and Poling [33,42]. Axial dispersion is evaluated according to Wakao (for a rectangular isotherm), which is recommended for strongly adsorbed components under laminar flow conditions [30].

### Table 4

Kinetic, adsorption and equilibrium constants for methanol synthesis and methanol dehydration.

<table>
<thead>
<tr>
<th>( k_i )</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.69 \times 10^{10} \exp\left(\frac{-30000}{RT}\right) )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 7.31 \times 10^{10} \exp\left(\frac{-43000}{RT}\right) )</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>( 4.36 \times 10^{12} \exp\left(\frac{-58200}{RT}\right) )</td>
</tr>
<tr>
<td>( K_{CO} )</td>
<td>( 7.99 \times 10^{-7} \exp\left(\frac{51800}{RT}\right) )</td>
</tr>
<tr>
<td>( K_{CO2} )</td>
<td>( 1.02 \times 10^{-2} \exp\left(\frac{140000}{RT}\right) )</td>
</tr>
</tbody>
</table>

\[ K_{H2/CO2} = 4.13 \times 10^{-1} \exp\left(\frac{20300}{RT}\right) \]

\[ k_1' = 1.09 \times 10^{10} \exp\left(\frac{-41800}{RT}\right) \]

\[ k_2' = 1.65 \times 10^{7} \exp\left(\frac{-38400}{RT}\right) \]

\[ K_a = 3.61 \times 10^{3} \]

\[ K_b = 0.37 \exp\left(\frac{34150}{RT}\right) \]

\[ K_d = 7.14 \times 10^{-1} \exp\left(\frac{124515}{RT}\right) \]

\[ \log_{10} K_{p1} = \frac{3130}{T} - 12.621 \]

\[ \log_{10} K_{p2} = \frac{-37673}{T} + 2.029 \]

\[ k_2 = 3.7 \times 10^{10} \exp\left(\frac{-100000}{RT}\right) \]

\[ K_{CH3OH} = 7.9 \times 10^{-4} \exp\left(\frac{-30500}{RT}\right) \]

\[ K_{H2/CO} = 0.84 \times 10^{-4} \exp\left(\frac{43100}{RT}\right) \]

\[ \ln K_{p4} = \frac{4039}{T} + 3.707 \ln T - 2.783 \times 10^{-5} T + 3.8 \times 10^{-6} T^2 - 6.561 \times 10^{-4} T^2 - 26.64 \]

### Table 5

<table>
<thead>
<tr>
<th>Isotherm model [40].</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( q = \frac{q_s \cdot h^n}{1 + \frac{h^{n+1}}{h_p}} )</td>
<td>(31)</td>
</tr>
<tr>
<td>( q_s = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} )</td>
<td>(32)</td>
</tr>
<tr>
<td>( b = \exp\left(\frac{b_0 + \frac{b_1}{T}}{\frac{b_2}{T^2}}\right) )</td>
<td>(33)</td>
</tr>
<tr>
<td>( n = n_0 + \frac{n_1}{T} )</td>
<td>(34)</td>
</tr>
</tbody>
</table>

### Table 6

Langmuir-Freundlich adsorption isotherm constants according to Gabruś et al. [40].

<table>
<thead>
<tr>
<th>Isotherm parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 ) (mol kg(^{-1}))</td>
<td>0.24486</td>
</tr>
<tr>
<td>( a_1 ) (mol kg(^{-1}) K)</td>
<td>-29.161</td>
</tr>
<tr>
<td>( a_2 ) (mol kg(^{-1}) K(^2))</td>
<td>743.36</td>
</tr>
<tr>
<td>( b_0 ) (Pa(^{-1}))</td>
<td>-10.659</td>
</tr>
<tr>
<td>( b_1 ) (Pa(^{-1}) K)</td>
<td>1969.4</td>
</tr>
<tr>
<td>( b_2 ) (Pa(^{-1}) K(^2))</td>
<td>933.58</td>
</tr>
<tr>
<td>( n_0 ) (-)</td>
<td>-0.09294</td>
</tr>
<tr>
<td>( n_1 ) (K)</td>
<td>340.56</td>
</tr>
</tbody>
</table>

### Table 7

Model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ergun constant</td>
<td>[ G = \frac{1}{q_s} \left(\frac{3901 + \frac{d}{\rho_p}}{\rho_p} + 1.75 \right) ]</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>[ Re_p = \frac{\rho v D_p}{\mu} ]</td>
</tr>
<tr>
<td>Macropore diffusivity</td>
<td>[ D_p = \frac{q_{lm} \pi}{x} ]</td>
</tr>
<tr>
<td>Molecular gas diffusivity</td>
<td>[ D_m = \left(\sum_{j=1}^{\sigma} \frac{n_j}{D_{ij}}\right)^{-1} ]</td>
</tr>
<tr>
<td>Binary diffusion coefficients</td>
<td>[ D_{AB} = \frac{\mu_{AB} \frac{\gamma \mu_{AB}}{\gamma + \mu_{AB}}}{\mu_{AB} \frac{\gamma \mu_{AB}}{\gamma + \mu_{AB}}} ]</td>
</tr>
<tr>
<td>Axial dispersion</td>
<td>[ D_L = \frac{\mu}{\nu} + \frac{\rho v^2}{2} ]</td>
</tr>
</tbody>
</table>
Table 8
Energy balance parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas heat capacity (J K⁻¹)</td>
<td>960</td>
</tr>
<tr>
<td>Particle heat capacity (J kg⁻¹ K⁻¹)</td>
<td>1.25</td>
</tr>
<tr>
<td>Axial thermal conductivity</td>
<td>2.5</td>
</tr>
<tr>
<td>Heat of reaction (kJ mol⁻¹)</td>
<td>-45.95</td>
</tr>
<tr>
<td>Heat of adsorption (kJ mol⁻¹)</td>
<td>-45.95</td>
</tr>
</tbody>
</table>

All parameters in the energy balance (10) can be found in Table 8. The heat capacity of the individual gases and the mixture are calculated according to Poling et al. [33,42]. The heat capacity of the solid phase is calculated according to Westerterp et al. [31]. The heat of reaction is evaluated using Kirschhoff’s law and the heat of adsorption is fixed at −45.95 kJ mol⁻¹ [40].

2.5. Method of solution

The obtained system of partial differential equations is solved in Matlab as a set of ordinary differential equations following the Method of Lines. A method for stiff differential equations is used with Matlab built-in variable-step, variable-order solver ode15s after uniform spatial discretization in 30 finite differences, using a second-order TVD upwind approximation for the convective terms. The feed flow rate and temperature are specified at the reactor inlet, the pressure at the reactor outlet. Danckwerts boundary conditions are used for the heat and mass balances. Simulations are run until cyclic steady state is achieved, meaning that the results for each consecutive cycle are equal in terms of DME yield (relative tolerance 10⁻³).

3. Results and discussion

To investigate the SEDMES process and determine its possible operation window, the effects of various process parameters on the sorption enhanced DME synthesis process were studied first using the developed model. The SEDMES process was considered as a three-column continuous system. While one column is operated in the reactive adsorption step, the other two columns are regenerating. The regeneration steps consist of a blowdown step (for pressure swing), a purge step including heating and cooling for temperature swing operation and a repressurization step (for pressure swing). The base case operating conditions are given in Table 9.

3.1. Sorption enhanced DME synthesis: experimental (breakthrough)

To validate the developed cyclic model, it was initially used to predict the performance of sorption enhanced DME synthesis in a laboratory scale reactor (Table 9). Figs. 5 and 6 show a typical breakthrough experiment for sorption enhanced DME synthesis, as measured by van Kampen et al. [27]. During the first transient period, before steam breakthrough, DME is the major product together with some unconverted CO. After breakthrough of steam (inset Fig. 5), the DME concentration drops combined with a breakthrough of CO₂ and methanol. In the steady state, when the adsorbent is fully saturated, the equilibrium for direct DME synthesis is obtained. As can be seen from Fig. 5, the model with the kinetics taken from Graaf et al. [35] describes this experimentally observed behavior quite reasonable. In contrast to the model predictions with the kinetics from Vanden Bussche and Froment [36], which seem not to be able to describe the SEDMES process adequately (Fig. 6). In the next sections the kinetics from Graaf et al. will therefore be used to investigate the performance of a continuous SEDMES process rather than breakthrough experiments.

3.2. Sorption enhanced DME synthesis: continuous process

A temperature swing (TSA) to 400 °C is considered for the regeneration in the SEDMES process, and a realistic duration of 1 h heating and 2 h of cooling during the purge step is selected. Together with the blowdown/depressurization (30 min) and the repressurization (15 min), this results in a total regeneration time of 3.75 h (225 min). If the adsorption step is operated for half this time, 112.5 min, a three-column system can assure continuous production of DME, where one reactor column produces DME, while the other two columns are regenerating.

To investigate the effect of various process parameters on the performance of the SEDMES process some key parameters have to be indicated. The cyclic process has two input streams, the syngas feed and a purge gas, and three output streams, the DME product stream during the reactive adsorption step, a blowdown stream (containing syngas, some product and initially desorbed steam), and a purge gas stream containing desorbed steam. Time integration of the input and output streams gives an overall yield and selectivity for the cyclic steady state of the SEDMES process.

3.3. Base case

In the reactive adsorption step a syngas stream is fed to the SEDMES system and a DME enriched product stream is produced. In the base case, the syngas feed consists of a stoichiometric amount of H₂ to COₓ (M = [(H₂) + (COₓ)²] = 2) and a CO₂ to CO ratio of 2. The DME product stream contains, besides DME, unreacted syngas and small amounts of methanol, inert gas (originating from the purge step), and steam slip (Fig. 7). Although the conversion is already 64 % (where the thermodynamic equilibrium without adsorption would yield 26 % conversion for the current feed gas composition), a significant fraction of the product stream remains unconverted syngas due to the net moles consuming reaction. The yield towards DME is limited by the slip level of steam in the system. This remaining amount of steam can be affected by various process parameters, as discussed below.

The transient behavior of the system can be explained by the
moving concentration fronts through the reactor bed, as shown in Fig. 8. These figures show the gas phase concentration (wt%) as a function of the axial coordinate in the reactor at the end of the repressurization, adsorption, blowdown and purge steps. For the reactive adsorption step and the purge step, profiles during the steps are shown as well. Fig. 8a clearly shows the reaction front present in the reactor column, characterized by a high conversion towards DME. It can also be observed that nitrogen is present at the end of the reactor, which is a remainder of the purge step. During the first period of the adsorption step this leftover nitrogen is flushed out of the column, in Fig. 8b the nitrogen is therefore totally gone. While undesirable for the SEDMES process, this inert N₂ purge clearly shows the effect that the purge gas has on the adsorption step. This leftover N₂ can be prevented by the choice of a different purge gas and/or the addition of an extra step to the process. In the meantime, it can be observed that the water content starts to increase in the upstream half of the reactor, which results mainly in an increase in the CO₂ concentration and a decrease in the DME concentration (Fig. 8b). This behavior continues until the end of the adsorption step. The nearly flat axial profile at the end of the adsorption step (Fig. 8c) also confirms that the feed flow rate during the adsorption step is rather high, leading to water breakthrough. Hence, the column is not able to maintain sorption enhancement during the entire step. After the adsorption step the column is depressurized in the blowdown step. Fig. 7 shows that the product from this step mainly consists of unconverted syngas and an initial part (about 2 %) of the desorbed water. This initial desorption of water can also be observed from the axial profiles at the end of the adsorption, and therefore beginning of the blowdown step and at the end of the blowdown step (Fig. 8c and d). As the blowdown product consists mainly of syngas, it could be considered to recycle this stream to the feed of the adsorption step (after repressurization and possibly drying). During the purge the remaining water (98 %) is desorbed to regenerate the adsorptive capacity of the adsorbent material. In Fig. 7 it can be seen that the purge product primarily consists of the purge gas and desorbed steam. This high purge product purity allows knocking out H₂O from the purge stream and recycling the N₂ as purge gas. Fig. 8e and f show that at the end of the three-hour purge period almost no water is removed from the reactor column, Fig. 9 also shows that the adsorbent is regenerated almost completely after the purge. The axial loading profile at the end of the purge step shows a small linear decrease due to the countercurrent operation of the regeneration. At the end of the adsorption step the loading is in equilibrium with the water content in the gas phase (Fig. 8c), defined by the adsorption isotherm.

### 3.4. Working capacity

The key parameter in the development of sorption enhanced processes is the cyclic working capacity of the adsorbent that can be reached for the given reactor and operating conditions. The working capacity is defined as the difference in average loading of the adsorbent bed at the end of the regeneration and the end of the adsorption steps. From Fig. 9, the working capacity for the base case can be determined at 2.83 mol kg⁻¹. Complete conversion, in which all produced steam is adsorbed, would require an almost 37 % higher working capacity. However, as discussed below, a trade-off exists between the yield and the productivity, defined as the amount of DME produced per unit of time per unit of bed volume. This clearly indicates that optimizing the working capacity together with the productivity of the system is crucial for the systems performance.

The working capacity can be influenced by many parameters, both during the reactive adsorption step and during the inherent regeneration of the system. These are discussed in the next sections.
3.5. Adsorption

3.5.1. Catalyst to adsorbent ratio

For all reactive adsorption processes an optimum catalyst to sorbent ratio exists, balancing the reaction rate and the steam or other (by-) product adsorption. This ratio defines the fraction of the direct DME synthesis catalyst and the adsorbent material, which are homogeneously mixed and distributed along the reactor. Fig. 10 shows the carbon selectivity in the product stream for four different catalyst to adsorbent ratios, varying from 1:16 to 1:2. Going from 1:2 down to 1:8, the lower ratios clearly result in the highest percentage of DME and the least amount of CO₂ in the product. Conversely, a ratio of 1:2 results in the highest maximum DME concentration.

For the chosen adsorption time and feed flow rate, an increasing amount of adsorbent will benefit the overall DME production rate during the adsorption step due to the limiting adsorption capacity in this scenario. However, to increase the amount of adsorbent, the amount of catalyst cannot be reduced without a cost. For a ratio of 1:16 the amount of catalyst becomes limiting and both the DME selectivity and the maximum DME concentration decrease. For the investigated scenario, the optimal ratio of catalyst to adsorbent appears to be between 1:8 and 1:4 (Fig. 10).

3.5.2. Syngas feed rate

By lowering the gas hourly space velocity (GHSV) the residence time of the reactants in the SEDMES reactor increases, and vice versa. Additionally, the amount of water, produced in a given period, relative to the amount of adsorbent changes. Fig. 11 shows that a lower GHSV...
during the reactive adsorption step leads to a higher conversion towards DME. As mentioned in Section 3.4, considering the base case working capacity of the adsorbent, not enough material is present to adsorb steam produced for 100% conversion to DME. Lowering the space velocity, although the conversion is increased, leads to a decrease in the amount of steam produced. Therefore, a larger part of the steam produced can be adsorbed, resulting in less steam slip at the end of the reactor and therefore in an enhanced conversion.

Regarding this, the optimal GHSV would be as low as possible from a selectivity point-of-view. However, the low GHSV (in combination with the limited size of a lab-scale reactor) results in a large impact of dispersive transport in the behavior of a process. With a maximum Péclet number, defined as the ratio of convective transport over dispersive transport, of 11 for the base case, clearly dispersive transport has a large contribution compared to convective transport for the lab-scale SEDMES process. For lower GHSV this contribution becomes dominant, eventually effecting the selectivity as well. In contrast to the selectivity, the productivity drops significantly for lower space velocities (Fig. 11). Process design for a specific case therefore needs to balance selectivity and productivity.

3.5.3. Temperature and pressure

Other parameters affecting the total adsorption capacity of the system are the temperature and pressure during the reactive adsorption step. The choice of total pressure in the adsorption step has three important implications for the performance of the SEDMES cycle: (1) the thermodynamic equilibrium (excluding the effect of water adsorption) changes, (2) an increase in steam partial pressure increases the equilibrium amount of water adsorbed, and (3) more gas is required for column repressurization.

Whereas the methanol synthesis reactions (1) and (2) are shrinking reactions, increasing the reaction pressure enhances the production of methanol and its subsequent conversion towards DME. As can be observed in Fig. 12 a higher adsorption pressure results indeed in a higher methanol and especially DME yield for the SEDMES process. Interestingly, the conversion of CO increases more with increasing pressure than the conversion of CO2. At an adsorption pressure of 10 bar even more CO is formed due to the reverse-WGS than is converted towards methanol and DME. The conversion of CO to methanol does not result in H2O by-product formation and is therefore not directly enhanced by steam adsorption. As a result, the pressure (due to negative gas expansion coefficient) affects the CO conversion more than the conversion of CO2. However, the conversion of CO2 is enhanced as well. This is caused by the higher working capacity of the adsorbent. Although the adsorbent is less dry at the start of the adsorption step for higher pressures, due to more reaction and adsorption during the repressurization step, the final loading increases with increasing pressure. Whereas the loading after regeneration is similar for all pressures, the working capacity increases with increasing pressure (Fig. 12). Even though operation at elevated pressure results in a higher conversion and therefore a higher steam content, the improved loading (due to the higher steam partial pressure) results in an increased sorption enhancement. Due to the repressurization with syngas, more syngas is fed to the system at 50 bar adsorption pressure compared to 10 bar adsorption pressure. The effective GHSV (considering both repressurization and adsorption steps) is therefore respectively 16% more for 50 bar, and 15% lower for 10 bar than the base case scenario (30 bar). Although an increased GHSV results in a lower conversion and therefore a higher steam content, the improved loading (due to the higher steam partial pressure) results in an increased sorption enhancement.

Fig. 9. Adsorbent loading over the length of the reactor during the adsorption step (start: solid line, one third: long dashed, two third: long dash dot, end: dashed line) and at the end of the purge (dashed black).

Fig. 10. The carbon selectivity of the adsorption product stream, and the maximum DME concentration for four different catalyst to adsorbent ratio’s: 1:16, 1:8, 1:4, and 1:2.

Fig. 11. Carbon selectivity of adsorption product and the DME productivity for three different syngas feed flow rates: 380, 760, and 1520 m³/hr·mcat⁻³.

Fig. 12. Carbon selectivity of adsorption product for various adsorption pressures and the cyclic working capacity of the adsorbent material as a function of the total pressure.
Clearly, operation at elevated pressure has a positive effect on the performance of the SEDMES process, since it improves the thermodynamics of the system, the reaction kinetics and the adsorption capacity. At 30 bar already 64.9 % DME selectivity is achieved, which further improves to 76.7 % at 50 bar operating pressure. Eventually, the optimal pressure has to be determined by a full process techno-economic evaluation in which the benefits (DME yield) and costs (of compression) are determined.

Not only the pressure affects the reaction and adsorption behavior, also the temperature has a significant effect. Methanol synthesis is
thermodynamically favored at lower temperatures, yet high catalyst activity requires temperatures of around 250 °C. Despite the fact that the temperature for methanol dehydration is generally higher, around 300 °C [38], direct DME synthesis is often performed at temperatures of around 250 °C [7,10,14–16], not only because the methanol synthesis is considered to be the rate determining step in direct DME synthesis, but also to prevent deactivation of the CZA catalyst at temperatures above 300 °C. Fig. 13 shows this behavior for the kinetically determined carbon selectivity in direct DME synthesis based on the kinetics used in this study, Eqs. (16)–(38). Although the thermodynamic equilibrium is favored at lower temperatures, the faster reaction kinetics at higher temperatures result in an optimum DME yield between 250 and 275 °C.

From the adsorption isotherm (Eqs. 41–44) it can be seen that the equilibrium loading on the zeolite material decreases at higher temperatures. This effect is also exploited in temperature swing regeneration. During the adsorption however, a lower temperature results in a higher working capacity of the material. Whereas the system is limited by the adsorption capacity, the SEDMES process benefits from operation at lower temperatures due to an increased adsorption capacity. Fig. 14 shows the DME carbon selectivity as a function of the working capacities for the studied temperatures. When decreasing the operating temperature from 300 to 250 °C the working capacity is increased, corresponding to the higher isotherm capacity and DME yield with decreasing temperature. At 225 °C the working capacity is lower than at 250 °C, despite the higher isotherm capacity. The catalytic activity limits the conversion at 225 °C and therefore a lower working capacity is obtained, resulting in the V-shaped curve (Fig. 14).

Although the adsorption capacity benefits from operation at lower temperatures, lower temperatures decrease the catalyst activity. For the case studied, clearly an optimum is found at a temperature of around 250 °C. At this temperature a DME yield of more than 79 % is obtained, a 14 % increase compared to the base case scenario.

3.6. Regeneration

Besides tuning the parameters of the reactive adsorption step, the...
conditions for the regeneration step can be optimized as well. The regeneration step is particularly important, because it mainly determines the working capacity of the adsorbent. In the next sections the influence of the regeneration conditions on the performance of the SEDMES process are discussed.

3.6.1. Regeneration mode

In the base case scenario the columns are regenerated by a combined temperature and pressure swing (TPSA), according to experimental practice [27]. Alternative possibilities for the regeneration procedure would be a temperature swing or a pressure swing only. With only a temperature swing the system would not be exposed to alternating pressures (at elevated temperature), relieving some design constraints on such a system and allowing for recovery of purge gas at higher pressure. If a pressure swing system is feasible, no relatively time-consuming heating and cooling is required during the regeneration step, making the regeneration (and therefore total cycle) time possibly shorter and the productivity potentially higher.

Fig. 15 shows the carbon selectivity for the product stream during the adsorption step. The syngas feed is adjusted in the TSA case to account for the repressurization with syngas in the case of (T)PSA. In Section 3.5.2 it is discussed that a higher space velocity results in a decreased carbon selectivity (Fig. 11). From Fig. 15 it can be seen that either a TSA or PSA does not perform as well as the base case TPSA regeneration. As a result, TPSA gives the highest DME yield and productivity due to the better regeneration of the adsorbent material (Fig. 16).

In Fig. 16 the effect of the pressure swing and the temperature swing on the working capacity of the adsorbent material is shown. The studied cases are operated at the same base case conditions, such as adsorption at 275 °C and 30 bar(a). Moreover, all cycle times are kept the same, only the extent of pressure reduction and/or temperature increase is varied. The GHSV is adjusted, so each case has the same amount of syngas fed during the combined repressurization and adsorption steps. A first aspect to be noticed is the regeneration by purging alone: without temperature increase or depressurization a working capacity of 0.72 mol kg⁻¹ is already obtained. Increasing the temperature or reducing the pressure during regeneration increases the working capacity. However, with increasing temperature swing the gained extra working capacity becomes less compared to increasing the pressure with a pressure swing, where the working capacity is still improved significantly between 27 and 29 bar pressure difference. This behavior can be related to the shape of the isotherm, which is steep for low partial pressures and flattens for higher partial pressures of steam.

Although a combined temperature and pressure swing regeneration results in the highest working capacity, and also the current experimental work on sorption enhanced DME synthesis shows the best performance with a TPSA, the studied regeneration response behavior indicates that both TSA and PSA alone could be an option in the SEDMES process development. This is generally preferred in the design of a process and the possibly shorter regeneration (and therefore total cycle) times could potentially increase the productivity.

3.6.2. Purge: composition and flow rate

An important aspect for the SEDMES process is the regeneration during the purge step, in which most of the sorbent regeneration occurs. Fig. 17 shows the direct link between the working capacity of the system and the DME yield. Whereas other performance parameters remain (relatively) unaffected, an increase in the working capacity by increasing the purge flow rate results in a linear increase in the DME yield. However, a limited amount of steam is still desorbed at the end of the purge step as is shown for the base case scenario (Fig. 8f). By increasing the purge gas flow rate even further the regeneration, and therefore the DME yield, is only slightly improved.

As mentioned before (in Section 3.3) for the base case, some purge gas ends up in the DME product, so preferably either reactants or products already present in the process are used as purge gas, viz. syngas, CO₂ or H₂. As shown in Fig. 18, using syngas as purge gas results in a lower DME yield (and productivity) compared to the nitrogen purge. Although no methanol is formed at the regeneration conditions (low pressure, high temperature), and subsequently also no DME is produced, still the reverse-WGS reaction occurs. This is evidenced by the purge product enrichment in CO (compared to CO₂). As a result of the formed and adsorbed H₂O the adsorbent is regenerated to a lesser extent when using syngas as purge gas compared to an inert purge gas (Fig. 19). Therefore, the DME yield in the SEDMES cycle is evidently lower compared to a cycle with an inert N₂ purge. Another possible purge gas would be CO₂. In comparison, for CO₂ adsorption processes, such as the SEWGS process, often steam is used as a purge gas. Although CO₂ purge performs better than the syngas feed in regenerating the adsorptive capacity of the system, it still performs considerably less than an inert (N₂) purge stream (Fig. 18). Finally, H₂ is considered as a purge gas. A H₂ purge performs equally well as the N₂ purge. Due to the slight excess of H₂ remaining after the purge, more reaction occurs during the repressurization. This results in a slightly higher adsorbent loading at the start of the adsorption step itself. This higher adsorbent loading balances the higher conversion during repressurization, resulting in a performance which is similar to the base case.

The purge product composition has to be compared as well. In the case of N₂ purge gas more than 99 % of the purge product consists of N₂ and desorbed H₂O. This would allow reusing this stream as purge feed gas after removal of H₂O, so a limited amount of make-up purge gas is required. For a syngas purge system, the purge product is enriched in CO. After removal of steam and compression the purge product could be used as syngas feed to the adsorption step. Whereas the regeneration is less extensive with syngas as the purge gas, the working capacity of the system is reduced by 13 % compared to N₂ purge (Fig. 19). However, the enrichment in CO of the syngas adsorption feed would also reduce the required working capacity for the system.

3.6.3. Repressurization

Also in the repressurization step of the column several choices can be made for the gas to use. Here, the syngas feed and the DME product have been considered. The reactant stream is available upstream of the reactor and therefore the column can be repressurized co-currently with syngas, avoiding dilution by another stream as seen for N₂ purge. Alternatively, the reactor can be repressurized with the DME-rich product. Product repressurization is done in counter-current operation compared to reactant repressurization and this results in an opposite axial profile compared to syngas repressurization (Fig. 8). An advantage of counter-current repressurization is that the adsorbent is completely dry at the end of the column and the initial product composition is almost pure DME. Consequently, the carbon selectivity for DME in the adsorption product stream is the highest for repressurization with DME product (Fig. 20). Although more DME is present in the product composition for a repressurization with DME, the amount of DME necessary to repressurize has to be subtracted from the adsorption product. This results in less DME formed for DME repressurization compared to syngas repressurization. However, the effective productivity for repressurization with DME is higher, i.e. more DME is produced per amount of syngas fed. Repressurization with product is interesting due to the high purity of the product initially obtained in the adsorption step. Although the loss of product can be costly, a trade-off needs to be found between using syngas feed or DME product as repressurization gas.

3.7. Heat management

Direct DME synthesis is an overall exothermic process (Eqs. 5 and 6), since both methanol synthesis (Eqs. 1 and 2) and its subsequent dehydration are exothermic (Eq. 4). In addition, the adsorption of
steam is also exothermic ($\Delta H_{\text{ads}} \approx -45 \text{kJ mol}^{-1}$). Thus, heat management is an important aspect of the process.

By operating the reactors adiabatically rather than isothermally the heat of reaction and heat of adsorption affect the adsorption step, and the heat of desorption affects the regeneration. Due to the exothermic nature of both the reaction and adsorption, the temperature in the reactor rises significantly (Fig. 22). As a result, the adsorbent loading, limited by the temperature dependent isotherm, almost halves to $1.48 \text{ mol kg}^{-1}$. The reduced working capacity results in a tremendous drop in performance if the reactors are operated adiabatically compared to the isothermal case, as is shown in Fig. 21. Whereas the adsorption of steam is exothermic, its desorption is endothermic. The inherent cooling of the reactor limits the desorption due to the isothermal displacement (Fig. 22). Therefore, in temperature swing regeneration heat is supplied to improve the desorption. The current TPSA conditions require to go towards isothermal operation of the reactive adsorption step, rather than an adiabatic system.

### 3.8. SEDMES vs. direct DME

In direct DME synthesis CO is converted to DME with CO$_2$ as the major by-product. With increasing CO$_2$ content in the feed both the conversion and the selectivity towards DME decrease significantly, as shown in Fig. 23. KOGAS has developed a direct DME synthesis process in which natural gas is reformed (with CO$_2$) to a CO-rich syngas, which is subsequently converted to DME and CO$_2$. With an average DME production of 8 tons per day, a CO conversion of around 80 % is achieved with a maximum DME selectivity of 67 % [13]. A carbon-selectivity of 67 % to DME would mean full (100 %) conversion of CO towards DME and CO$_2$ for a CO feed (Eq. 5). Fig. 23 shows that for an increasing CO$_2$ content in the feed both the conversion of the carbon feed and the selectivity to DME drop to far lower values for the direct DME synthesis. This is, however, not the case for sorption enhanced DME synthesis. One of the major advantages of SEDMES is the highly selective direct conversion of CO$_2$ to DME. As a result, both the carbon conversion and the DME selectivity are far higher for the SEDMES process compared to the direct DME synthesis, especially for a CO$_2$-rich feed (Fig. 23).

### 4. Conclusion

For the first time, sorption enhanced DME synthesis (SEDMES) is studied as a full cyclic process of adsorption and inherent regeneration. Reaction kinetics derived for methanol synthesis and methanol dehydrogenation, and a water adsorption isotherm for LTA zeolite 3A describe experimental data for the SEDMES process reasonably well.

The SEDMES process is a promising process intensification, already achieving over 80 % single-pass CO$_2$ conversion and more than 70 % single-pass DME (carbon) yield for a non-optimized three-reactor column system. The increased single-pass conversion reduces downstream separation units and recycle streams, especially for a CO$_2$-rich feed.

A key parameter for optimizing the SEDMES process is the total adsorption capacity of the system. Improving this capacity could be done by optimizing the reactive adsorption conditions and by optimizing the regeneration method. The results described in this work show, supported by experimental work, that a typical window for the SEDMES process includes adsorption temperatures between 250 and 275 °C and pressures of 20 bar or more.

The regeneration, inherent to a reactive adsorption process, has a large influence on the total adsorption capacity of the system. A combination of temperature and pressure swing regeneration results in the best system performance regarding the DME yield and CO$_2$ conversion, which is also supported by experimental findings in the literature. However, this study indicates that both TSA and PSA alone could be an option in the SEDMES process development, which is generally preferred for its facilitated design and possibly improved productivity.

Finally, under the current TPSA conditions, (near) isothermal operation of the reactive adsorption step is required to achieve high performance of the system.

Because of the mentioned promising aspects of the SEDMES process, such as the extremely high efficiency carbon conversion, it is prone to play an important role in the energy transition in which the carbon conversion will become leading. The development of the process is ongoing by experimental and modelling means, resulting in a demonstration scale continuous DME production (kg per hour scale) within the EU.

CRediT authorship contribution statement

Jasper van Kampen: Conceptualization, Methodology, Software, Validation, Investigation, Data curation, Writing - original draft, Visualization. Jurriaan Boon: Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition. Jaap Vente: Conceptualization, Writing - review & editing, Resources, Funding acquisition. Martin van Sint Annaland: Writing - review & editing, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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