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Continuous multi-column sorption-enhanced dimethyl ether synthesis (SEDMES): Dynamic operation

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In this work the continuous production of dimethyl ether (DME) by sorption-enhanced DME synthesis (SEDMES) technology has been demonstrated for the first time with a multi-column test-rig. A continuous single-pass carbon yield up to 95%, higher than ever reported before, has been achieved. The multi-column experiments have also shown that SEDMES can be operated at lower temperatures (220°C) than previously reported. This allows a higher temperature rise, making higher conversions possible while allowing even larger reactor tube diameters. Whereas the anticipated multi-tubular reactor concept is complex and costly, larger reactors could facilitate the economic valorisation. The SEDMES reactor model cannot only describe the transient behaviour of the process during the cyclic steady-state well, but also the dynamic approach towards the cyclic steady-state is adequately captured. Capturing the dynamic operation is of large interest with respect to process flexibility, especially for Power-to-X systems.

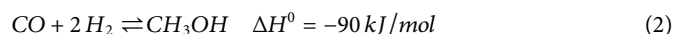
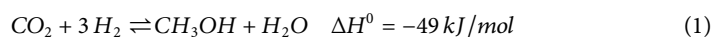
KEYWORDS

CO₂ utilization, continuous cyclic production, dimethyl ether, reactive adsorption, steam separation enhancement

1 Introduction

Dimethyl ether (DME), the simplest ether and the dehydrated form of methanol, is a valuable platform chemical and synthetic fuel. DME, which is gaseous at ambient conditions, can easily and safely be liquefied, transported and stored. In contrast to several other ethers it does not form explosive peroxides. The chemical and physical properties of DME, as well as the combustion characteristics, make that it can be used as fuel in domestic applications replacing LPG, in compression ignition engines (100% DME), in spark ignition engines (30% DME/70% LPG), and in power generation (Semelsberger et al., 2006; Arcoumanis et al., 2008; Azizi et al., 2014). Hence, DME is expected to play an important role in the energy transition, where fossil-based chemicals and fuels have to be replaced by products from renewable feedstocks, including the chemical recycling of carbon dioxide (Centi and Perathoner, 2009). Conventionally, DME is produced from synthesis gas with methanol as intermediate chemical. The following equilibrium reactions are involved in DME synthesis:

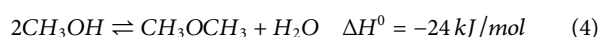
Methanol synthesis:



Water-gas shift:



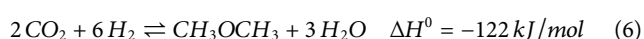
Methanol dehydration:



Direct DME synthesis (from CO):



Sorption-enhanced direct DME synthesis (from CO₂):



The indirect production of DME comprises the production of intermediate methanol, and the subsequent methanol dehydration (Bakhtyari and Rahimpour, 2018). The incomplete methanol and DME yields require extensive separation sections and recycles. The single-step direct DME synthesis process offers a reduction in process steps and increased overall conversion to DME (Ng et al., 1999; Dadgar et al., 2016; Mondal and Yadav, 2019; Liuzzi et al., 2020). Although the direct DME synthesis process outperforms the indirect process in terms of efficiency, separation and recycling are still required. The conventional production methods are considered unattractive, both because of heat management and equilibrium limitations, the latter especially when starting from CO₂ instead of synthesis gas (Detz et al., 2018; Dieterich et al., 2020). Process intensification provides clear opportunities for improving the process performance (Bakhtyari and Rahimpour, 2018). As for many other industrial CO₂ utilisation processes, the main hurdle is the production and efficient handling of steam (Centi and Perathoner, 2009; Kätelhön et al., 2019; van Kampen et al., 2019). Steam separation enhancement is shown to be a promising route for CO₂ conversion; promising results have been reported using membranes and adsorbents (van Kampen et al., 2019; van Kampen et al., 2021a; Bakhtyari et al., 2021). In particular, as the focus of the current work, sorption-enhanced DME synthesis (SEDMES) is a novel process for the production of DME, which is based on *in situ* water removal by a solid adsorbent (Iliuta et al., 2011; Boon et al., 2017; van Kampen et al., 2018). Previous studies focused on the catalysis and adsorption aspects of the process (Boon et al., 2019; Liuzzi et al., 2020; van Kampen et al., 2021b). Experimental investigation into the single column bench-scale sorption-enhanced production of DME, including model validation, demonstrated over 80% single-pass carbon selectivity to DME with pressure swing regeneration using various feed compositions, including relatively CO₂-rich feed. Pressure swing regeneration, rather than the time and energy intensive temperature swing regeneration, allows for a factor four increase in productivity. This is close to the reported direct DME pilot plant productivity for CO to DME, which would strongly deteriorate for CO₂-rich feed, and further optimisation is still possible (van Kampen et al., 2020a; van Kampen et al., 2021c). Inherent to adsorption processes because of the required regeneration of the sorbent (typically a LTA zeolite), sorption-enhanced DME synthesis is a multi-column process (van Kampen et al., 2019; van Kampen et al., 2020b). Traditional single column reactor setups as used previously therefore do not allow demonstration and testing of continuous DME production. In this work, the SEDMES technology is validated experimentally with a multi-column test-rig under industrially relevant conditions. For the larger scale, continuous

production of DME by sorption enhancement will be demonstrated for the first time in the open literature. Confirmation of the improvements by pressure-swing regeneration, as shown previously (van Kampen et al., 2020a; van Kampen et al., 2021c), is sought. The multi-column experiment allows to evaluate the system operating as an ensemble of columns, instead of earlier work focusing on adsorption and regeneration separately. Sorption-enhancement results in transient and dynamic processes in multiple columns (Carvill et al., 1996; Boon et al., 2015; Abanades et al., 2017; Rodrigues et al., 2017). In contrast to conventional processes operating at steady-state, there is a cyclic steady-state (CSS). The transient behaviour at cyclic steady-state is often investigated in detail. However, process flexibility for systems where the feedstock and operating conditions change, such as for Power-to-X (PtX) systems, could require dynamic operation (Miguel et al., 2017; Detz et al., 2018; Dieterich et al., 2020; Skorikova et al., 2020). Therefore, the dynamic operation is of particular interest for the multi-column experiments. As an ensemble, it is possible for the first time to study the transient behaviour of the system in between two cyclic steady states.

In this article the results of an experimental investigation on the multi-column sorption-enhanced production of DME are discussed, including the SEDMES reactor model for data interpretation. Attention is paid to the confirmation of pressure swing regeneration during the continuous production of DME. Additionally, the dynamic operation is studied in more detail, including operation at lower temperatures than previously reported for SEDMES.

In the next section, the used materials, the multi-column reactor setup and experimental procedures, and model interpretation are reported. In the results and discussion section, the experimental validation of continuous DME production is shown, results of the investigation into lower temperature operation are reported and the process dynamics are discussed. Finally, the main conclusions for the continuous multi-column sorption-enhanced dimethyl ether synthesis are summarized.

2 Experimental

2.1 Materials

Experimental validation of sorption-enhanced DME synthesis was performed using a homogeneous physical mixture of commercially available catalyst and adsorbent: copper-zinc oxide-alumina (CZA) catalyst, γ -Al₂O₃ (assay>98%, Riogen NJ, USA), obtained as 3 mm pellets, and molecular sieve type 3A, purchased as 1.6 mm pellets (UOP Molecular Sieves, Obermeier, DE).

Nitrogen adsorption on the purchased γ -Al₂O₃ resulted in a Brunauer-Emmett-Teller (BET) specific surface area of 192 m²g⁻¹ with an average pore diameter of 8.98 nm, which are within typical ranges reported for this type of material (Boon et al., 2019). The pore size of the molecular sieve type 3A is too small to characterize by nitrogen adsorption, however the adsorption capacity (max 25.5 wt% for the zeolite crystals) and mass transfer rate have been measured in more detail (van Kampen et al., 2021b).

2.2 Methods

A combination of commercially obtained CZA catalyst, γ -Al₂O₃ catalyst and zeolite 3A adsorbent was used for the experimental

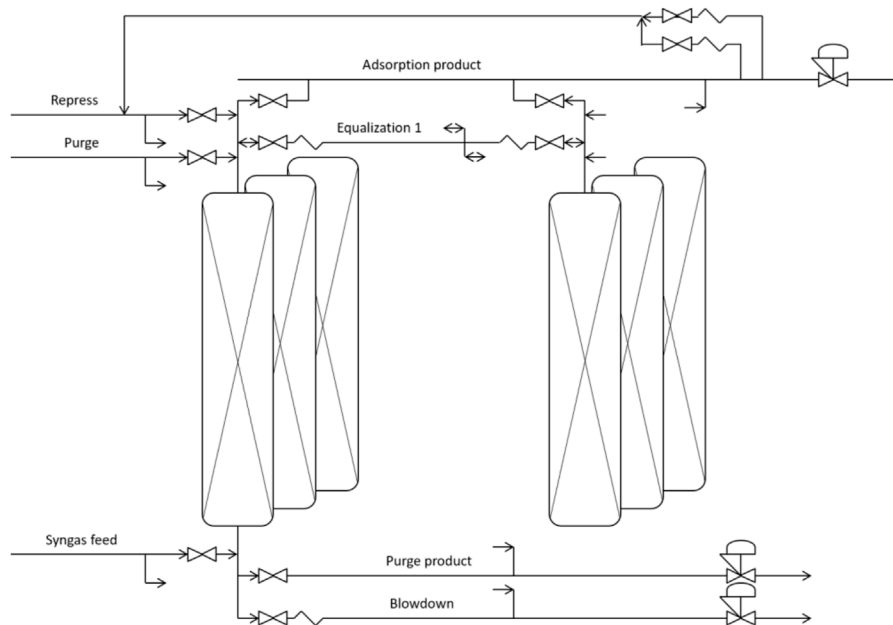


FIGURE 1

Schematic of 2 interconnect reactor columns, including the various feed and product streams. The connections shown for one reactor column are identical for all six columns in the multi-column test-rig.

demonstration of the direct DME synthesis from CO_2 with stoichiometric H_2 . The experimental runs were conducted on a multi-column high-pressure reactor setup (Figure 1) allowing continuous production with 36 L (divided over six columns of 6 m in length, 1.5" internal diameter) of sample, consisting of a 1:4 ratio (weight basis) catalyst (1:1 CZA: $\gamma\text{-Al}_2\text{O}_3$) to sorbent. The ratio between catalyst and sorbent was selected based on earlier investigations (van Kampen et al., 2020b) and not further optimised in this work. Adsorption was performed at 25 bar(a) in a temperature range of 220°C–250°C with argon as tracer. The inert balance was used to keep the overall pressure stable, considering the net mole consumption by the reaction and the adsorption of water. Regeneration was done by depressurisation to 1–3bar(a) and switching to dry, inert gas (nitrogen) for the purge step. Finally, either the inert purge gas or the reactive feed gas was used for repressurisation. During depressurization and repressurization two columns can be physically connected, resulting in partial repressurization of one column by the depressurization gas from another column, called pressure equalization. Transient gas analysis was performed by Agilent CP490 micro-GC (with Thermal Conductivity Detectors (TCD); three channels: molsieve 5A 20 m, Poraplot PPU 10 m, CP-wax-52CB, all 0.25 mm id, 0.25 μm film; oven 80°C isotherm; carrier helium for the measurement of methane, CO, CO_2 , nitrogen, argon, methanol and DME) and mass spectrometry measuring hydrogen ($m/z = 2$), methane ($m/z = 15$), water ($m/z = 18$), carbon monoxide/nitrogen ($m/z = 28$), methanol ($m/z = 31$), carbon dioxide ($m/z = 44$) and DME ($m/z = 45$) for the outlet gas stream from reactor column 6.

2.3 Data interpretation

In order to facilitate data interpretation, several key metrics have been defined to be able to quantify the SEDMES performance. The

most important metric, the carbon selectivity $S(i)$, used here is defined as follows, (van Kampen et al., 2020b)

$$S(i) = \frac{ny(C_nH_mO_p)}{\sum_i n_i y(i)} \quad (7)$$

The carbon selectivities were calculated as molar concentration-based selectivities for each of the carbon containing species, $y(i)$. For example, the selectivity towards DME can be calculated as

$$S(\text{DME}) = \frac{2y(\text{DME})}{y(\text{CO}) + y(\text{CO}_2) + 2y(\text{DME}) + y(\text{MeOH}) + y(\text{CH}_4)} \quad (8)$$

Considering CO_2 as the carbon feed, the carbon selectivity to DME is also directly a measure of the product yield, whereas the carbon selectivity to CO_2 is a measure of its conversion. Time integration (over the duration of a step) of the streams gives an overall yield and selectivity for the cyclic (steady state) performance of the SEDMES process.

2.4 Model

A one-dimensional pseudo-homogeneous dynamic reactor model was developed in Matlab, verified and validated (van Kampen et al., 2020b; van Kampen et al., 2021c). For the description of the fluid flow, heat and mass transfer, the 1D non-steady differential mass, energy and momentum balances are solved. The total mass, momentum, component mass and overall energy balances are given in Table 1. The reaction rate equations are shown in Table 2. The reaction kinetics have been determined and validated under relevant conditions for the used catalyst materials by fitting the parameters in the kinetic models

TABLE 1 Reactor model equations.

Overall mass balance	$\frac{\partial \rho}{\partial t} = -\frac{\partial \rho v}{\partial z} - \frac{1-\epsilon_b}{\epsilon_b} a_p \sum M_i N_i$	(9)
Momentum balance	$\frac{\partial \rho v}{\partial t} = -\frac{\partial \rho v^2}{\partial z} - \frac{\partial p}{\partial z} - G \frac{\rho v v}{d_p}$	(10)
Species mass balance	$\frac{\partial \rho \omega_i}{\partial t} = -\frac{\partial \rho v \omega_i}{\partial z} + \frac{\partial}{\partial z} (D_z \rho \frac{\partial \omega_i}{\partial z}) - \frac{1-\epsilon_b}{\epsilon_b} a_p M_i N_i$	(11)
Overall energy balance	$(\epsilon_b \rho C_p + (1-\epsilon_b) \rho_p C_p) \frac{\partial T}{\partial t} = -\rho C_p v \frac{\partial T}{\partial z} + \frac{\partial}{\partial z} (\lambda \frac{\partial T}{\partial z}) + \frac{4U(T_w - T)}{d_t} + (1-\epsilon_b) \rho_p (\sum -\Delta H_{r,i} r_i + \sum -\Delta H_{ads,i} \frac{\partial q_i}{\partial t})$	(12)
Equation of state	$PM = \rho RT$	(13)

TABLE 2 Reaction rate equations.

Methanol synthesis from CO Graaf et al. (1988)	$r_{CH_3OH,1} = \frac{k_1 K_{CO} [\varphi_{CO} \varphi_{H_2}^{3/2} - \varphi_{CH_3OH} / (\varphi_{H_2}^2 K_{p1})]}{(1+K_{CO} \varphi_{CO} + K_{CO_2} \varphi_{CO_2}) [\varphi_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) \varphi_{H_2O}]}$	(14)
Water-gas shift Graaf et al. (1988)	$r_{CO} = \frac{k_2 K_{CO} [\varphi_{CO_2} \varphi_{H_2} - \varphi_{H_2O} \varphi_{CO} / K_{p2}]}{(1+K_{CO} \varphi_{CO} + K_{CO_2} \varphi_{CO_2}) [\varphi_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) \varphi_{H_2O}]}$	(15)
Methanol synthesis from CO ₂ Graaf et al. (1988)	$r_{CH_3OH,2} = \frac{k_3 K_{CO_2} [\varphi_{CO_2} \varphi_{H_2}^{3/2} - \varphi_{CH_3OH} \varphi_{H_2O} / (\varphi_{H_2}^2 K_{p3})]}{(1+K_{CO} \varphi_{CO} + K_{CO_2} \varphi_{CO_2}) [\varphi_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) \varphi_{H_2O}]}$	(16)
Methanol dehydration Berčič and Levec, (1992)	$r_{DME} = \frac{k_4 K_{CH_3OH}^2 [C_{CH_3OH}^2 - C_{H_2O} C_{DME} / K_{p4}]}{[1+2(K_{CH_3OH} C_{CH_3OH})^{1/2} + K_{H_2O} C_{H_2O}]^4}$	(17)

TABLE 3 Reaction rate parameters for methanol synthesis and dehydration reaction kinetics (van Kampen et al., 2021c).

Parameter	Value (kJ mol ⁻¹)
<i>E_a</i> (k1)	68.1
<i>E_a</i> (k2)	107
<i>E_a</i> (k3)	54.3
ΔH (<i>K_{CO}</i>)	-15.7
ΔH (<i>K_{CO2}</i>)	-56.0
ΔH (<i>K_{H2O}</i> / <i>K_{H2}</i> ^{1/2})	-107
<i>E_a</i> (k4)	109
ΔH (<i>K_{CH3OH}</i>)	-69.6
ΔH (<i>K_{H2O}</i>)	-39.3

by Graaf et al. (1988) and Berčič et al. (1992) for the methanol synthesis, starting from CO, CO₂ and mixtures thereof, and methanol dehydration respectively (Graaf et al., 1988; Berčič and Levec, 1992; Ng et al., 1999; Boon et al., 2019). Although not derived for sorption-enhanced DME synthesis, it has been shown previously that the relations provide a suitable means to describe kinetics in sorption-enhanced conditions (Boon et al., 2017; Liuzzi et al., 2020; van Kampen et al., 2021c). These reaction rate parameters are given in Table 3. The steam adsorption isotherm of the LTA zeolite adsorbent is determined under the high pressure and temperature working conditions of the SEDMES process (van Kampen et al., 2021b). Numerically, a single reactor column is simulated in time following the consecutive steps in the cycle. 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 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. Full details of the different aspects of the model can be found in previous work (van Kampen et al., 2020b).

3 Results and discussion

In the development of the sorption-enhanced DME synthesis process, for the first time the SEDMES technology is validated under industrially relevant conditions on a multi-column test-rig, allowing for continuous DME production. The previously developed model is used for data interpretation. Finally, learnings can be drawn from the multi-column experiments and improvements are suggested as the way forward to enhance the productivity and carbon selectivity.

3.1 Continuous production

The demonstration of the SEDMES technology on a multi-column test rig allows for continuous production of DME by sorption enhancement, for the first time in the open literature. Figure 2 shows the continuous concentration profiles (balance unconverted H₂), collected as product during the reactive adsorption step which shifts to the subsequent reactor column. In Figure 3 the corresponding continuous DME outlet flowrate is shown for the multi-column test-rig compared to the discontinuous single column operation. Whereas only the outlet concentrations of reactor column 6 are continuously monitored, these concentrations are extrapolated to the other reactor columns which show very similar behaviour for the same step in the full cycle. In these experiments the nitrogen purge gas is used for repressurisation, therefore initially nitrogen is flushed out. After this flush, a representative breakthrough profile of sorption-enhanced DME synthesis is apparent from Figure 2. Prior to steam breakthrough, DME and unconverted CO are the primary products. After steam breakthrough the concentration of DME drops, accompanied by the breakthrough of CO₂ and methanol

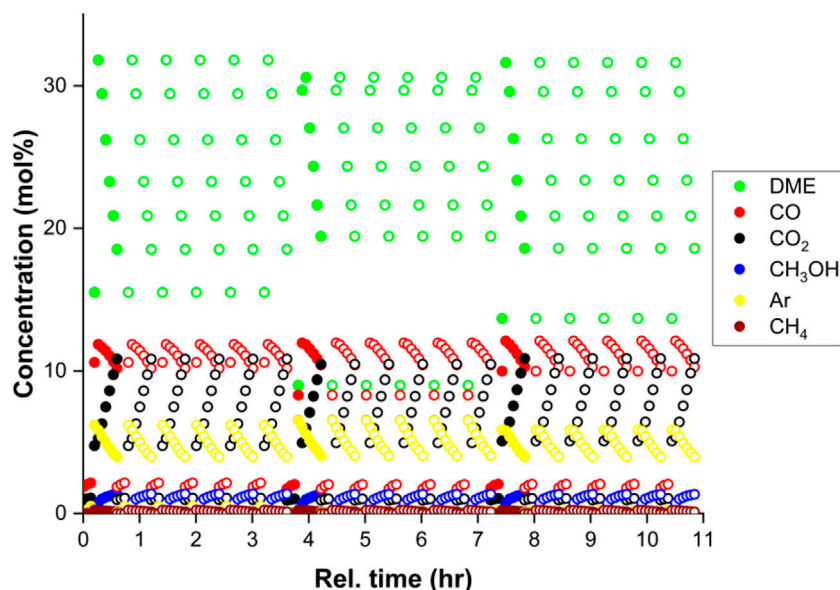


FIGURE 2

Experimental data at 250°C and 25 bar(a) for a CO₂ feed with stoichiometric hydrogen, with argon tracer (24.5% CO₂, 73.6% H₂, 1.9% Ar, GHSV 93 h⁻¹), measured for reactor column 6 (filled dots). For reactor columns 1–5 the data from column 6 is extrapolated (copied, open dots), for the purpose of interpreting the performance of the ensemble of columns.

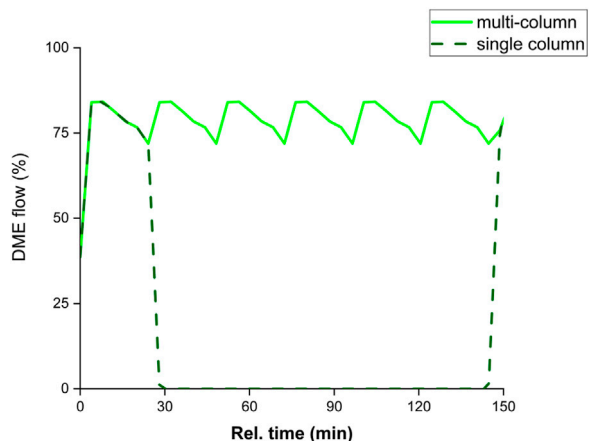


FIGURE 3

Continuous DME outlet flow (after N₂ flush) for the multi-column system and a single column, normalized with respect to the inlet carbon flow (carbon yield).

indicating saturation of the adsorbent. Although the conversion is still far higher than conventional conversion levels (maximum of 1.9% DME), dictated by thermodynamics, the DME concentration drops relatively rapidly. Clearly, the purge times (35 min) used here, which are shorter than the adsorption times (45 min), do not regenerate the system completely and therefore result in a relatively fast steam breakthrough. By improving the regeneration, extending the pressure swing purge time, the theoretical maximum full conversion of CO₂ to DME is approached. A carbon yield of up to 95% towards DME is observed, higher than ever reported before for experimental work on the direct conversion of CO₂ to DME (Figure 4).

However, here the classical trade-off between productivity, affected by the extent of regeneration, and the selectivity occurs (van Kampen et al., 2021c), (Kätelhön et al., 2019). Hence, the other experiments in this work are performed with 65%–90% carbon yield. Typical productivity is in the range of 0.17 kg h⁻¹.

3.2 Lower temperature operation

Sorption-enhanced DME synthesis was initially operated at 275°C (van Kampen et al., 2019; Liuzzi et al., 2020), which was lowered to 250°C with improvements in the performance, provided that both the catalyst activity and regeneration are sufficient (van Kampen et al., 2020a; van Kampen et al., 2021c). Also an initial modelling study indicated temperatures of around 250°C to be optimal for SEDMES (van Kampen et al., 2020b). The direct synthesis of DME is thermodynamically favoured at lower temperatures. However, the catalyst activity requires temperatures around 250°C. In sorption-enhanced synthesis, the temperature also affects the adsorption capacity. As indicated by the study of the adsorbent material, the adsorption capacity benefits from operation at lower temperatures (van Kampen et al., 2021b). Although with a pressure swing regeneration, the operating temperature must be balanced for both good adsorption and desorption properties, maximizing the cyclic working capacity.

As shown in Figure 5, the multi-column testing demonstrates SEDMES at temperatures as low as 220°C with very similar performance to the original higher temperature operation. As mentioned before, after an initial nitrogen flush (grey line), a representative SEDMES breakthrough profile can be seen. Prior to steam breakthrough, DME and unconverted CO are the primary products. After steam breakthrough the concentration of DME drops, accompanied by an increase of CO₂ and methanol

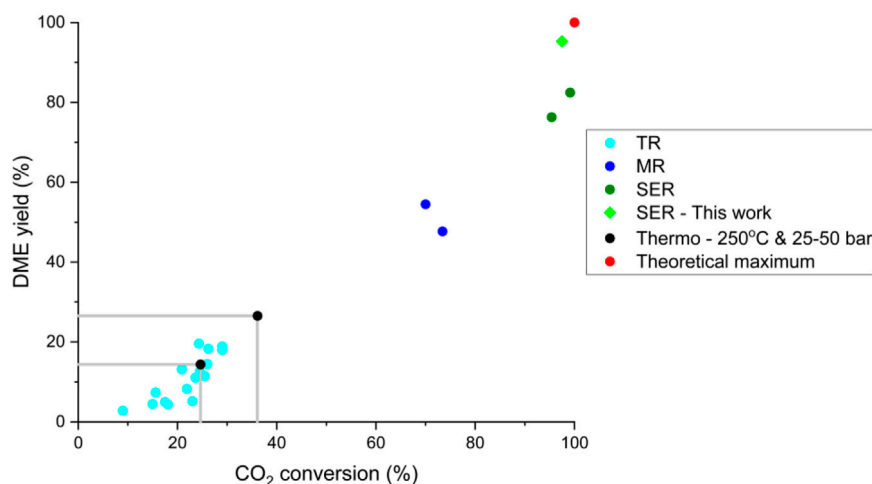


FIGURE 4

Comparison of experimental CO₂ conversion and DME yield for sorption enhanced reactors (SER; green) and membrane reactors (MR; dark blue) with results for traditional reactors (TR; light blue), reported in the open literature. Adapted from (van Kampen et al., 2021a).

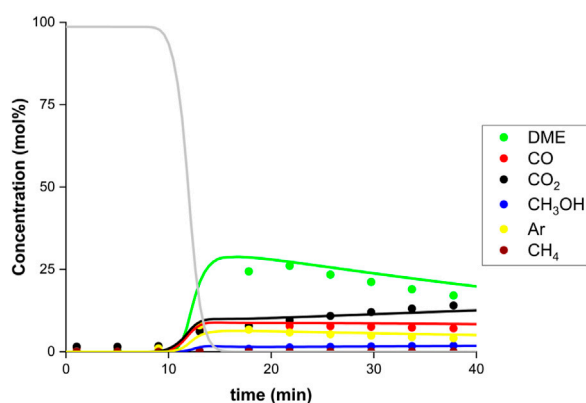


FIGURE 5

Breakthrough experiment at 220°C and 25 bar(a) for a CO₂ feed with stoichiometric hydrogen, with argon tracer (24.5% CO₂, 73.6% H₂, 1.9% Ar, GHSV 93 h⁻¹), (dots: DME (green), CO (red), CO₂ (black), methanol (blue), argon (yellow), methane (brown), nitrogen (grey)) and model prediction (lines).

indicating the increasing adsorbent saturation. This temperature of 220°C is on the low side, especially for the methanol dehydration over an alumina catalyst. However, it has been observed that periodic regeneration can have a positive effect on catalyst activity and can even restore lost activity (van Kampen et al., 2018; Boon et al., 2019). This result seems very promising with respect to the heat management of the system. Both methanol synthesis and direct DME synthesis are exothermic reactions, limiting the conversion and deactivating the methanol catalyst by hydrothermal sintering, and therefore require a cooled reactor, such as a multi-tubular reactor concept (Song et al., 2008; Guffanti et al., 2021a; Guffanti et al., 2021b). In sorption-enhanced DME synthesis, the exothermic adsorption is added to the already exothermic reaction system. SEDMES temperature control appears not to be an issue in a multi-tubular cooled reactor. Larger tube diameters can be adopted compared to

conventional direct DME synthesis. However, operation at lower temperatures would allow a higher maximum temperature rise, and therefore makes higher conversions possible and it allows even larger diameters of the tubes in the multi-tubular reactor (Guffanti et al., 2021a). Where a multi-tubular reactor concept is also a costly part of the DME synthesis process, larger reactors would benefit the economic valorisation of CO₂ conversion (Skorikova et al., 2020).

3.3 Process dynamics and cyclic steady-state

Figure 5 also shows the typical transient response after sorbent regeneration and column repressurisation with nitrogen, during the feeding of CO₂, H₂, and Ar. A large DME peak appears, followed by a steady decline due to the gradual saturation of the column with water. The SEDMES reactor model adequately describes the transient concentration profiles at cyclic steady-state, confirming previous model validation. However, not only the behaviour at cyclic steady-state is described by the model. The SEDMES reactor model is a dynamic cycle model, simulating each step of a cycle towards cyclic steady-state. The model predicts the dynamic behaviour of the system, both the various steps in a cycle and consequently the subsequent cycles, very well, as demonstrated in Figure 6 by the approach to CSS observed experimentally and predicted by the model. Initially, in the first cycle shown in Figure 6, the adsorbent material is relatively dry. For the chosen operating conditions and cycle design, more water is adsorbed during the reactive adsorption step than desorbed during the regeneration. This results in an accumulation of water loaded on the adsorbent material, hence a lower working capacity and a decreasing carbon selectivity to DME until a cyclic steady-state is reached, where an equal amount of water is adsorbed and desorbed during a cycle.

The approach to a new cyclic steady-state goes relatively quickly, especially if the CSS values are close to the old values. In Figure 7 it can be seen that the experimental carbon selectivity at 250°C reaches the predicted cyclic steady-state within

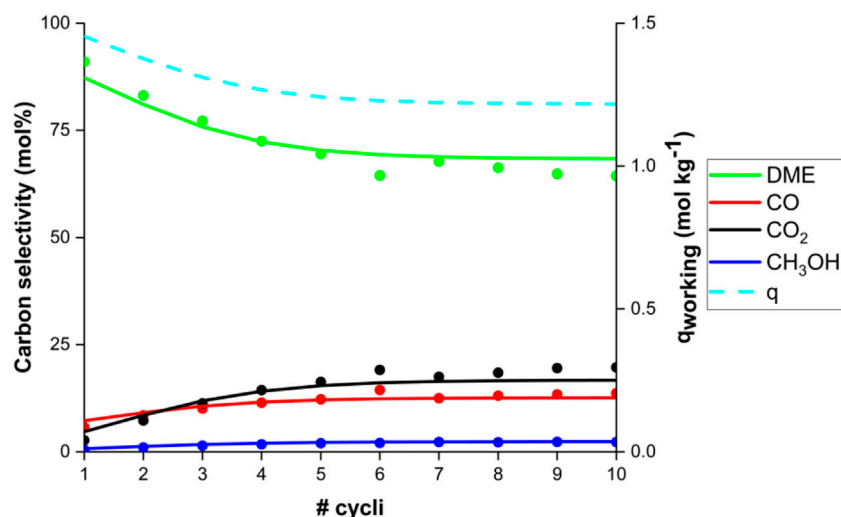


FIGURE 6

Experimental carbon selectivity (dots) to DME (green), CO (red), CO₂ (black) and methanol (blue) and model prediction (lines) as function of the number of subsequent cycles. The model working capacity q (dashed blue line) is shown on the right axis. Conditions: 220°C and 25 bar(a) for a CO₂ feed with stoichiometric hydrogen, with argon tracer.

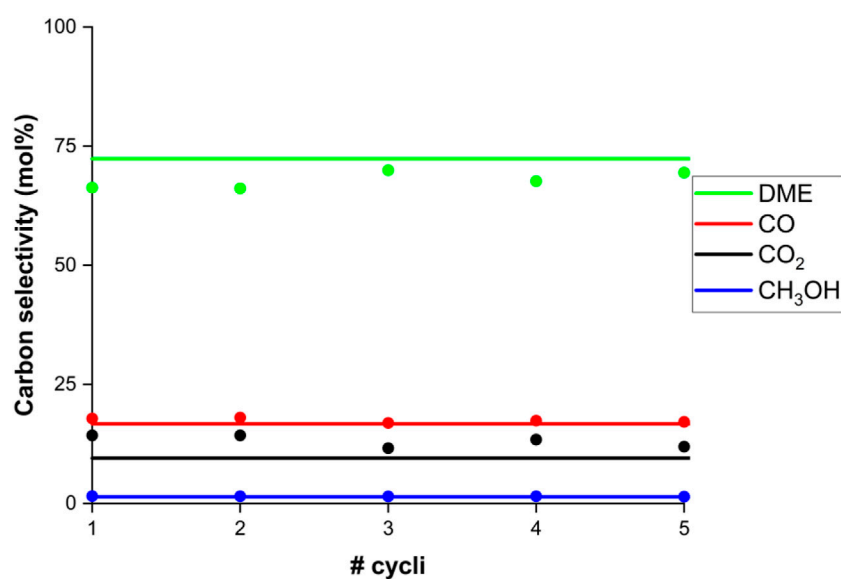


FIGURE 7

Experimental carbon selectivity (dots) to DME (green), CO (red), CO₂ (black) and methanol (blue) as function of the number of subsequent cycles. Model prediction for cyclic steady-state (lines). Conditions: 250°C and 25 bar(a) for a CO₂ feed with stoichiometric hydrogen, with argon tracer.

approximately 5 cycles. Whereas, the working capacity is slightly higher (8.8%) at this elevated temperature, a small increase in the carbon selectivity to DME and a small decrease in the carbon selectivity to CO₂ can be observed during the first cycles.

The dynamics of operation are an essential element in the Power-to-X (PtX) context where CO₂ can be converted with intermittently produced green hydrogen from electrolysis (Miguel et al., 2017; Detz et al., 2018; Skorikova et al., 2020; Cloete et al., 2021). Whereas SEDMES is a dynamic process in

nature, it allows for process flexibility and coping with this intermittency. Common process variables for adsorption processes include the cycle time and flowrates for the various process steps, which can be used to control performance parameters such as purity and productivity (de Witte et al., 2021). Here, integrating scheduling, by means of cycle design, and control strategies would result in more efficient and economical operation (Dias and Ierapetritou, 2016). However, the real-time dynamic performance strongly depends on these

decision variables in a non-linear manner, making the modelling, simulation and control challenging (Dowling et al., 2012; Khajuria and Pistikopoulos, 2013). The complex and highly non-linear dynamic behaviour still poses challenges for the control of such intensified processes, but recent advances enable the solution of complex, non-linear problems and the implementation of non-linear controllers (Dias and Ierapetritou, 2019). The detailed investigation of SEDMES operation and control are outside the scope of the current work, but are part of currently ongoing research.

4 Conclusion

In this article, for the first time in the open literature, sorption-enhanced dimethyl ether synthesis (SEDMES) technology is validated experimentally on a multi-column test-rig under industrially relevant conditions. Multi-column operation allowed for the demonstration of continuous DME production by sorption enhancement, for which up to 95% carbon yield is observed. Pressure swing regeneration is confirmed as the preferential mode of regeneration, which is essential for further optimisation of the process.

The multi-column experiments have demonstrated that SEDMES can be operated at 220°C, which is lower than expected based on previous data. Operation at lower temperatures would allow for a higher maximum temperature rise and would ease the heat management of the system. Where the typical multi-tubular reactor concept for DME synthesis is also a costly part of the process, larger reactors would benefit the economic valorisation of the process.

SEDMES is a transient and dynamic process, resulting in more degrees of freedom compared to conventional technologies. The SEDMES reactor model not only describes the transient behaviour during cyclic steady-state well, also the dynamic approach to the cyclic steady-state is modelled well. Dynamic operation is of large interest with respect to process flexibility, especially for Power-to-X (PtX) systems.

In conclusion, the multi-column experiments have demonstrated the continuous production of DME with a high single-pass conversion of CO₂. Experimental evidence, supported by modelling, of the dynamic operation at lower temperatures will allow further optimisation of a PtX SEDMES process.

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Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

JVK: Conceptualization, Methodology, Software, Formal analysis, Validation, Investigation, Visualization, Writing—Original Draft JO: Methodology, Investigation JB: Conceptualization, Writing—Review & Editing, Project administration, Funding acquisition MVS: Writing—Review & Editing, Resources, Supervision.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Nomenclature

a_p Particle interfacial area ($m^2 m^{-3}$)
 c_i Concentration of component i ($mol m^{-3}$)
 C_p Specific heat capacity gas ($J kg^{-1} K^{-1}$)
 $C_{p,p}$ Specific heat capacity particles ($J kg^{-1} K^{-1}$)
 d_p Particle diameter (m)
 D_z Axial dispersion coefficient ($m^2 s^{-1}$)
 G Ergun constant (–)
 ΔH_{ads} Adsorption enthalpy ($J mol^{-1}$)
 $\Delta H_{r,i}$ Reaction enthalpy ($J mol^{-1}$)
 M_i Molecular weight of component i ($kg mol^{-1}$)
 N_i Mole flux of component i ($mol m^{-2} s^{-1}$)
 P Reactor pressure (bara)
 q_i Adsorbent loading ($mol kg^{-1}$)
 r_i Reaction rate of component i ($mol m^{-3} s^{-1}$) or ($mol kg^{-1} s^{-1}$)
 or ($kmol kg^{-1} hr^{-1}$)

R Ideal gas constant ($J mol^{-1} K^{-1}$)
 t Time (s)
 T Temperature (K)
 u Superficial gas velocity ($m s^{-1}$)
 U Overall heat transfer coefficient ($W m^{-2} K^{-1}$)
 v Interstitial gas velocity ($m s^{-1}$)
 z axial coordinate (m)

Greek letters

ϵ_b Bed voidage (–)
 λ Axial thermal conductivity ($W m^{-1} K^{-1}$)
 ρ Density ($kg m^{-3}$)
 ρ_p Particle density ($kg m^{-3}$)
 ω_i Weight fraction of component i (–)