

Partial load and transient operation of methane synthesis reactors using sorption-enhanced catalysis

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Abstract:

Sustainable synthetic carbon-based fuels can play a crucial role in the sectors of transportation, heating, and power, which can be challenging to electrify. Many of these synthetic fuels are based on green hydrogen produced by electrolysis. Due to difficulties in the handling and storage of hydrogen, an interesting solution is to convert it into hydrocarbons such as methane, with the advantage of using a well-established infrastructure and having the drop-in capability to substitute fossil natural gas.

In the presented study, the partial load and the transient behavior of a sorption-enhanced catalytic reactor for methane synthesis is analyzed. This kind of reactor can achieve high conversion through adsorption of product water. Its performance is defined and compared to that of a simulated conventional fixed-bed catalytic reactor without sorption-enhancement. In particular, the focus is on investigating the response to partial loads and load transients. These operating conditions are typically met when the hydrogen production system is directly coupled with fluctuating renewable electricity production, and storage is minimized. The results show an excellent partial load behavior, and, unlike traditional reactors, sorption-enhanced catalysis did not show ignition problems.

This article points out the strength of sorption-enhanced catalysis applied to the process of carbon dioxide methanation in transient and partial load operations both from the point of view of synthesized fuel quality and operation stability.

Keywords:

CO₂ methanation; Sorption-enhanced reactor; Synthetic fuels; Transient operation.

1. Introduction

Nowadays, carbon-neutral fuels are considered as an interesting solution for the energy transition in hard-to-abate sectors. An example is the synthesis of methane from hydrogen and carbon dioxide as a substitute for natural gas.

Methane production is carried out through the Sabatier process, which is characterized by the following reaction [1]:



This strongly exothermic reaction can take place using heterogeneous catalysis in fixed-bed reactors. The relevance of this system can be deduced since it has been investigated in many experimental studies [2].

If the hydrogen feeding the process is produced via electrolysis from a fluctuating renewable energy supply, its availability would be discontinuous, and this leads to the need for the storage of either electrical energy or hydrogen. In both cases, high storage costs [1] lead to the need to reduce the battery capacity or the volume and the number of hydrogen tanks as much as possible. For this purpose, the synthesis reactor must be able to withstand continuously changing operating conditions. Therefore, an analysis of the behavior of methane production systems with regard to transient and partial load conditions has been developed by the authors and is presented in this paper.

Investigations of the performance of catalytic reactors for methane synthesis at dynamic load conditions reported in the literature are mainly focused on the thermal stability of the system [3,4]. This is due to the fact that too high temperatures could lead to deactivation and degradation of the catalyst while too low

temperatures could lead to failures in igniting the reaction [5]. Moreover, a decrease in reaction yield at transient and high load conditions is usually highlighted [6].

Many efforts have been made in the scientific community to deal with these problems, and various methods have been used to this end. Fischer et al. [7] and Bremer et al. [8] chose to use an adaptive temperature of the coolant, the former at the design stage and the latter by adopting a steady state “multiplicity” control strategy.

Another option available for managing the temperature distribution is the use of a reactor with recirculation, as investigated in Refs. [9–11]. The recirculation ratio was identified as an additional degree of freedom for thermal control.

With specific reference to the reactor, different approaches, mainly concerning temperature control, were evaluated. Stiegler et al. [6] experimentally analyzed the behavior of a rack-type reactor with a high thermal conductivity metal structure. Sun and Simakov [12] simulated a reactor internally cooled by molten salts and Kreitz et al. [13] numerically studied a microstructured fixed-bed reactor with a periodically oscillating feed composition. Another proposed approach is to dilute the catalyst with an inert material, which was done by means of simulation by Fache et al. [14] and both experimentally and numerically by Herrmann et al. [15].

In order to address these challenges while preserving high product quality, there are grounds for deepening the sorption-enhanced catalysis [16].

Therefore, in this study, the behavior of a methanation reactor of the sorption-enhanced type at an unsteady operating condition is investigated and presented. In order to do so, the reactor was tested experimentally at partial load conditions (i.e. partial inlet flow rates) and during transients (i.e. with single-step or multiple-step changes in inlet flow rates). In addition, a model of a catalytic methanation reactor without sorption-enhancement was set up and its results were compared with the measured data.

1.1. Sorption-enhanced CO₂ methanation

In the literature, sorption-enhanced methane synthesis reactors have been reported to achieve very high conversion yields through the removal of water (which is one of the two reaction products) due to in-situ adsorption [16]. Generally, the catalyst bed is composed of a bi-functional material with catalytic and adsorption properties. An important difference with respect to systems without sorption-enhancement is the way in which the reaction takes place. As shown by Borgschulte et al. in [17], sorption-enhanced methanation reactors differ from conventional plug flow reactors in that there is a moving coupled reaction and adsorption front. The propagation velocity of the reaction front (which separates the water saturated section of the reactor from the unsaturated one) depends on the adsorption capacity of the bed and the amount of water that is produced and adsorbed. The greater the amount of water that will interact with a section of the bed, the sooner it will be saturated and the faster the reaction front will move on [18]. From an engineering point of view, this means that a reactor saturated with water must be regenerated. Consequently, at least two reactors operating alternately are needed for continuous methane production.

As regards chemical kinetics, it should be noted that the removal of water leads to a significant increase in the partial pressure of the reactants and especially a decrease in water partial pressure, which leads to improved reaction rates.

In the zone of the reaction front, additional heat is released due to the adsorption process [19] which further promotes the conversion. The water adsorption capacity is inversely proportional to the temperature and directly proportional to the pressure. This behavior leads to a self-stabilizing effect since the greater the amount of adsorbed water, the greater the heat released, but if the temperature rises the bed will be saturated faster and the front will proceed [18].

2. Materials and methods

2.1. Experimental setup

The experimental apparatus involved a fixed-bed oil-cooled catalytic reactor consisting of four reactors arranged in parallel (Fig. 1). The bed consisted of pellets of adsorbent material impregnated with catalyst. In more detail, it was constituted by zeolite 13X pellets with a diameter of 1.6 mm to 2.6 mm impregnated with 5 % nickel on a mass basis [18]. In the inlet sectors of the reactors, these pellets were mixed with aluminum beads to improve heat transfer in that zone and partially absorb the released heat. This approach was used to deal with the problem of the continuous heat release in the inlet sector as reported by Kiefer et al. [18].

Each of the four reactors contained a pellet bed with a height of 1 m and a diameter of 32 mm. The reactors were cooled by thermal oil flowing into an external jacket in each reactor tube. The temperature was adjusted and kept constant with a PID controller (Julabo HT60 thermostat).

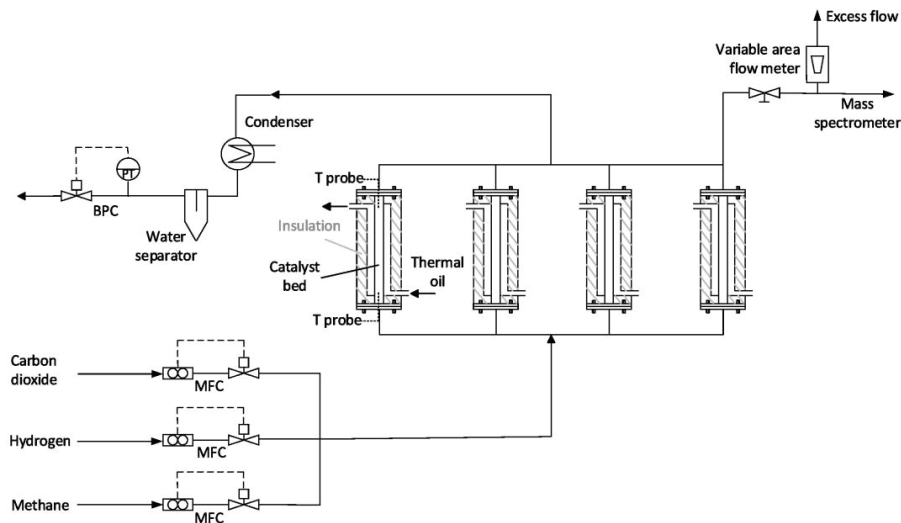


Figure 1. Schematic representation of the sorption-enhanced methanation test rig.

At the inlet and outlet sectors of each reactor duct the temperatures were measured by thermocouples (Type K class A, 1.5 mm jacket diameter) with a sampling period of 2 s. The inlet gas flow was controlled by means of mass flow controllers (MFC, Bronkhorst EL-FLOW Prestige) while the pressure was regulated through a back pressure controller (BPC, Bronkhorst EL-PRESS) located downstream of the reactor.

A sample of the produced syngas mixture was taken at the outlet of one of the four reactors and then directed to a mass spectrometer (Hiden Analytical RGA) to measure the mole fractions of the different gaseous species.

2.2. Testing procedure

Before each experiment, the reactors were heated to the operating temperature of 300 °C via the thermal oil and were purged with a stream of inert gas (i.e. nitrogen). After reaching the desired temperature, the reactors were purged with methane and the absolute pressure was increased to an operating point of 10 bar. Once stable conditions were reached, the reaction was started by flushing a defined mixture of the reactants. A carbon dioxide mole flux of 0.4 mol m⁻² s⁻¹ was set as the reference condition. The reactant ratio, for the full and the partial load tests, was then tuned to be close to stoichiometric conditions with a minimal excess of H₂ to overcome the inaccuracy of the control instrumentation. A small percentage of hydrogen was considered acceptable assuming that the produced syngas would be fed into the natural gas pipeline infrastructures.

The reaction phase of an experiment was terminated when the temperature values measured at the reactor outlet showed that the front had reached the end of the reactor. Afterwards, the reactor drying phase was initiated and the bed was purged with hydrogen to reach the initial state as regards the water content.

The partial load behavior of the system was investigated at loads of 25 %, 50 % and 75 % of the reference inlet mole flow of carbon dioxide.

The reaction time is inversely proportional to the load since the less the water is produced, the longer it takes to saturate the bed. In each case, the reaction time was not fixed a priori but it was determined through temperature and product gas measurements. On this basis, the step variations defined to characterize the considered transients were included in these time frames.

2.3. Mathematical model

A dynamic model based on Ref. [20] and implemented in Matlab®/Simulink® for catalytic methane synthesis reactors was used as a reference for reactors without sorption-enhancement.

The model was based on the equations of chemical kinetics of the process and on mass and energy balances. A one-dimensional approach has been used, discretizing the reactor bed with cylindrical sections in series assuming homogeneous properties of the gas mixture in each of them. While the gas flow is assumed as one-dimensional, the heat exchange with the coolant is estimated with reference to the cylindrical wall surface of each section. Changes in pressure, temperature and mole composition are calculated for each section using the aforementioned equations, written in differential form and solved using the stiff solver ode15s.

The kinetic model considered the Sabatier reaction (R1), methanation of carbon monoxide (R2), and reverse water gas shift (R3) [1]:



Reaction rates were modelled as proposed by Xu and Froment [21], using the following equations:

$$r_{R1} = \frac{k_{R1}}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{R1}} \right) / (DEN)^2 \quad (1)$$

$$r_{R2} = \frac{k_{R2}}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{R2}} \right) / (DEN)^2 \quad (2)$$

$$r_{R3} = \frac{k_{R3}}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{R3}} \right) / (DEN)^2 \quad (3)$$

$$DEN = 1 + A_{CO} p_{CO} + A_{H_2} p_{H_2} + A_{CH_4} p_{CH_4} + A_{H_2O} p_{H_2O} / p_{H_2}, \quad (4)$$

where k , K , and A are terms of the Arrhenius-type temperature functions.

The pressure drop in the reactor was calculated using the Ergun correlation [22].

Regarding heat exchange, the model of heat and mass transfer in packed beds with fluid flow, as described by Tsotsas in [23], was taken as the reference.

The radial heat flux has been estimated using the global heat transfer coefficient, evaluating the transfer coefficient at the reactor inner wall (α_w) as follows:

$$Nu_w = \alpha_w \frac{d}{\lambda_f} \quad (5)$$

$$Nu_w = \left(1.3 + \frac{5}{D/d} \right) \frac{\lambda_{bed}}{\lambda_f} + 0.19 Re^{0.75} Pr^{1/3} \quad (6)$$

The characteristic length of the Reynolds number is, in this case, equal to the pellet diameter.

Fluid properties were calculated according to Ref. [24]. In particular, for the calculation of the thermal conductivity, the correlation of Mason and Saxena was used, while for the viscosity, the correlation of Wilke was applied.

3. Results and discussion

As a reference for partial load and transient experiments, a single experiment is analyzed to illustrate the operation of a sorption-enhanced catalytic reactor. To this extent, Fig. 2 shows plots of changes in the outlet mole fractions of the most relevant gases in the mixture and the temperatures measured respectively in the inlet and outlet sectors of the reactor. This experiment has been carried out with a CO_2 set flux of $0.3 \text{ mol m}^{-2} \text{ s}^{-1}$ and a CO_2/H_2 ratio as determined in the sorption-enhanced reaction experiments (see Table 1). The data reported ranges from the test initial condition (i.e. when no water is adsorbed in the bed) to the final condition (i.e. when the bed is completely saturated with water and the conversion process stops).

In Fig. 2 (a) the composition of the gas mixture at the reactor outlet is reported. The methane content at the beginning refers to the gas initially contained in the reactor after increasing the pressure of the system (see Section 2.2). The decline in CH_4 content corresponds to the point when the produced methane reached the reactor outlet.

It should be noted that when the first synthesized methane reached the reactor outlet, its mole fraction undergoes a slight downward peak. This is due to an overshooting of the hydrogen flow rate at the time when the reactant input was set through the flow controllers.

The decrease in methane mole fraction at the end of the test corresponds to the moment when the sorption front reached the outlet, which means that a mixture of reactants and products arrived at the outlet due to the lack of water removal capability (i.e. there is not sufficient sorption-enhancement taking place anymore). In the last part of the measuring period, the behavior of the reactor clearly shows that the synthesis phase has ended (usually in real operations the reaction is stopped, and the bed drying phase starts before reaching that point). During the sorption-enhanced phase, the content of carbon dioxide was always below 1 %. Moreover, ethane and propane were measured below 0.5 % and water below 0.2 % as adjusted during the regeneration phase. The temperatures shown in Fig. 2 (b) follow a trend determined by the displacement of the reaction front and the heat removal from the catalyst bed. Considering the temperature changes measured in the inlet sector of the reactor, it can be concluded that the peak is due to the front traveling through the temperature sensor at that point. Afterwards, in the inlet sector of the bed, the reaction takes place without sorption-enhancement because it is completely saturated with water. The heat released due to the exothermic reaction causes the temperature to stabilize at a value higher than that of the coolant.

The maximum temperature in the inlet sector is lower than that measured close to the outlet due to the mixing of the catalyst bed with aluminum beads.

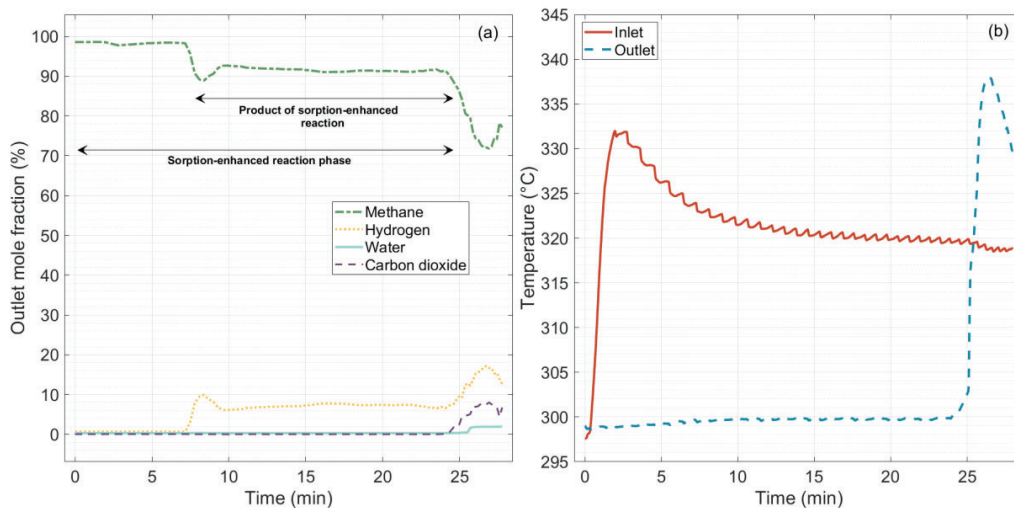


Figure 2. Outlet mole fractions measured by the mass spectrometer (a) and temperatures measured in the inlet and outlet sectors of the reactor (b) using a constant CO₂ set flux of 0.3 mol m⁻² s⁻¹, and reaction absolute pressure of 10 bar.

Furthermore, a comparison of the behavior of the methanation reactors with and without sorption-enhancement that demonstrates the underlying differences of the two systems is shown.

For this purpose, Fig. 3. shows the simulated steady state temperature profile along the reactor axis of a conventional fixed-bed catalytic reactor considering the bed geometry and the operating conditions as introduced above for the sorption-enhanced case. More specifically, a CO₂ flux of 0.3 mol m⁻² s⁻¹, a CO₂/H₂ ratio as determined in the sorption-enhanced reaction experiments (see Table 1), an initial reactor temperature and temperature control setpoint of 300 °C, and a reaction absolute pressure of 10 bar. Since a discretized lumped parameter approach was used, the profile is depicted by steps.

In the conventional reactor, the temperature profile reaches a steady state as shown in Fig. 3 (it should be considered that the section where maximum temperature is reached depends on the value of the inlet reactant flow rate). In contrast to this behavior, considering Fig. 2 (b), it can be noted that the temperature peak for sorption-enhanced systems is not static, but moves through the reactor together with the reaction front.

In the following, the partial load (Section 3.1) and transient operation of the system (Section 3.2) are presented, while in Section 3.3 the thermal behavior will be discussed.

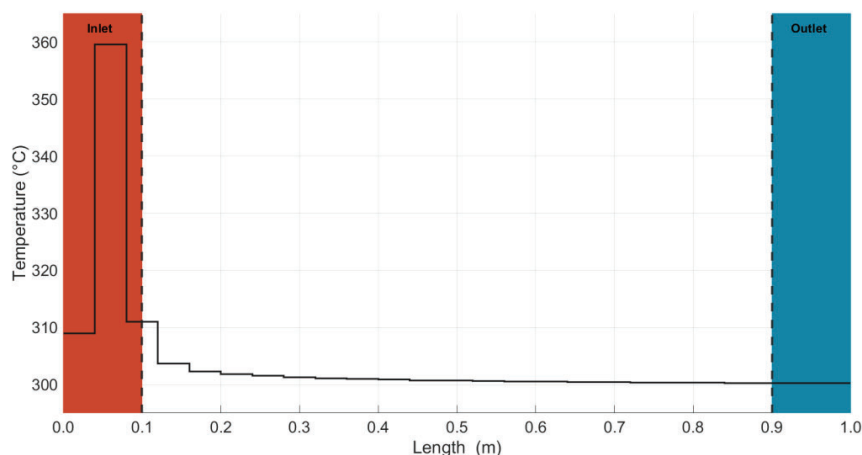


Figure 3. Temperature profile along the length of a simulated non-sorption-enhanced reactor with a constant CO₂ flux of 0.3 mol m⁻² s⁻¹, an initial reactor temperature of 300 °C, and a reaction absolute pressure of 10 bar.

3.1. Partial load behavior

The reactor system was analyzed at partial load conditions by repeating the above-introduced experiment (i.e. 75 % of the reference load) at inlet flow rates of 25 %, 50 %, and 100 % of the reference load.

Table 1 presents the carbon dioxide conversion determined from the measured outlet gas composition. For the sake of comparison, the results are presented for a simulated conventional reactor, an equilibrium conversion calculation at a temperature of 300 °C and the measurements on the sorption-enhanced reactor. The carbon dioxide conversion was calculated by means of the following equation:

$$Conv_{CO_2} = 1 - x_{outlet\ CO_2} / x_{inlet\ CO_2} \quad (7)$$

The measured mole fraction was averaged over the timespan marked in Fig. 2 (a) as "product of sorption-enhanced reaction".

For the simulations and the calculation of equilibrium conversion, the actual flux determined from the experiments was used.

The simulation results for the conventional reactor show a decreasing conversion with increasing load, i.e. increasing inlet mole flux. This is due to a decreased residence time.

Compared to the equilibrium calculations, the gap between the equilibrium conversion and the simulated conversion in the reactor increases with the load. The changes in equilibrium conversion given in the table are due to the changes in the inlet stoichiometry determined for the different load conditions. In contrast to the conventional reactor, the CO₂ conversion determined for the sorption-enhanced reactor experiments does not show a dependency on the load. The conversion is significantly higher than the equilibrium conversion for all cases. This goes hand in hand with the above-introduced shift in the chemical equilibrium through water removal.

In addition to the CO₂ conversion given in Table 1, Table 2 shows the outlet CH₄ content for the simulation of the conventional reactor, the equilibrium value, and the average values measured for the sorption-enhanced reaction. This is the measurement relevant for the application of the product, e.g. feeding into a gas grid. The CH₄ mole fraction of the simulation and that of the calculation for the equilibrium were considered on a dry basis.

In addition, for further considerations on sorption-enhanced reactor measurements, the standard deviation of the averaged data is also presented.

The results for the simulated conventional reactor are in line with the trend observed for the CO₂ conversion. The theoretical maximum CH₄ content given by the equilibrium shows the strong influence of the non-stoichiometric reactant ratio, especially at low partial load. The CH₄ content in the product measured for the sorption-enhanced reactor shows a dependency on the stoichiometry. The quality of the product is limited by the accuracy of the initial mixing and not by the conversion. Furthermore, the low values of the standard deviation of the measured data imply that production is highly stable.

Another major characteristic of the sorption-enhanced reactor system is the duration of the production phase. With the aim of exploring this aspect, Fig. 4 shows the duration at the partial load conditions measured from the start of the feed supply until detecting an increase in CO₂ mole fraction at the reactor outlet above 1 %.

Table 1. Partial load CO₂ conversion with the corresponding inlet mole fluxes.

Inlet mole flux (mol m ⁻² s ⁻¹)	Reactant ratio (-)	Conv _{CO₂} (-)		
		Conventional reactor simulation	Equilibrium* at 300 °C and 10 bar	Sorption-enhanced reactor measurements
CO ₂	H ₂ /CO ₂			
0.1	4.18	0.9622	0.9985	0.9998
0.2	4.14	0.9187	0.9960	0.9998
0.3	4.09	0.8864	0.9902	0.9997
0.4	4.09	0.8657	0.9892	0.9999

* Calculations performed using Cantera [25].

Table 2. Partial load CH₄ outlet content with the corresponding inlet mole fluxes.

Inlet mole flux (mol m ⁻² s ⁻¹)	Reactant ratio (-)	Outlet CH ₄ mole fraction (%)		
		Conventional reactor simulation	Equilibrium* at 300 °C and 10 bar	Sorption-enhanced reactor measurements
CO ₂	H ₂ /CO ₂			
0.1	4.18	82.965	84.116	84.548 (std: 0.625)
0.2	4.14	73.682	87.053	88.063 (std: 0.454)
0.3	4.09	67.476	89.097	91.565 (std: 0.435)
0.4	4.09	63.852	89.269	92.364 (std: 0.460)

* Calculations performed using Cantera [25].

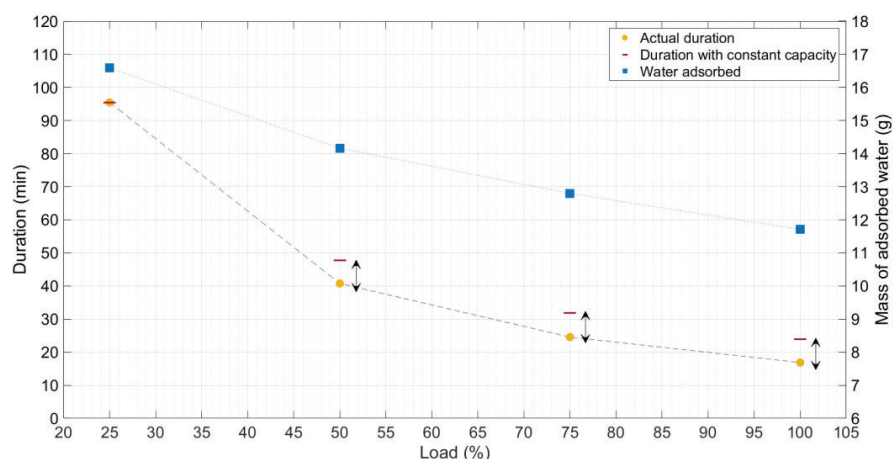


Figure 4. Actual durations of the production phase and calculated durations in the case of constant adsorption capacity at different partial loads with the mass of adsorbed water under the same conditions.

In addition, to the measured durations, those that would have been encountered if the adsorption capacity were constant and equal to that found at the lowest load are included in the figure. Furthermore, on the secondary vertical axis, the amount of water adsorbed at the corresponding conditions is presented. The water adsorbed (and consequently the adsorption capacity of the reactor) was estimated by multiplying the duration by the water production calculated from the conversion of the inlet CO₂ flow rate.

In an ideal system, the water adsorption capacity would be constant for the different load conditions. In Fig. 4, however, a decline in this capacity with increasing load can be seen. The measured durations of sorption-enhanced reactions are slightly shorter as the adsorption capacity decreases.

This behavior goes hand in hand with observations reported in Ref. [18], where it was contributed to increased bed temperatures and less distinct reaction fronts caused by kinetic limitations. This is an important aspect to consider when designing similar systems.

3.2. Transient response

The sorption-enhanced reactor system was assessed to load changes by investigating the system response to single and multiple subsequent steps in the feed flow rate. For the single step, the system was operated at 100 % of the load for 6 min, then the load was reduced to 25 % for 6 min and increased again to 100 % afterwards. Figure 5 (a) shows the outlet mole fraction of the species measured in the gas mixture at the outlet with reference to the single step case. As a multiple step case, the procedure was repeated with three steps lasting 3 min each as shown in Fig. 5 (b). Figures 5 (c) and 5 (d) show the respective feed flow rates as set by means of the mass flow controllers.

Figure 5 (a) presents the same characteristic features of methane synthesis that were evaluated in Fig. 2 with respect to the steady state case. In addition, it can be seen that the downward spike in methane fraction relates to the time when the step was imposed by decreasing the inlet flux. The same general behavior can be seen in Fig. 5 (b).

As the transition between one load to the other occurs, the methane content gradually changes to the levels obtained when the steady state is reached in the partial load tests. In fact, as presented in Table 2, the outlet methane mole fraction value changes for different tests at partial load.

The spikes in the hydrogen fraction are related to the change in the H₂/CO₂ ratio used in the corresponding partial load conditions. When considering the carbon dioxide outlet fraction, it can be argued that the steps have no impact on CO₂ conversion.

3.3. Effect on temperature

As a final analysis, the maximum temperature values measured during the different load and transient conditions are analyzed. These temperatures correspond to the peaks of the front measured in the reactor inlet and outlet sectors. In this regard, Table 3 shows that the variation of these peaks is limited for the different load conditions. The values measured at the inlet are lower than those at the outlet because, as mentioned earlier, in the first section of the reactor the catalyst was mixed with aluminum beads.

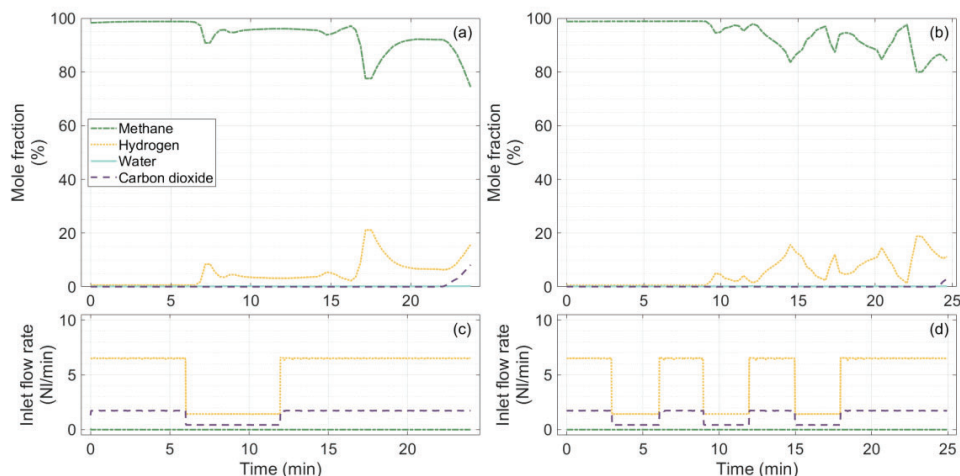


Figure 5. Outlet mole fraction as measured by the mass spectrometer in the case of single step input (a) and multiple step input (b); inlet flow rate of reactants in the case of single step input (c) and multiple step input (d).

Table 3. Maximum temperatures observed in the cases analyzed.

Partial load/step response	Maximum temperature measured at the inlet sector (°C)	Maximum temperature measured at the outlet sector (°C)
25 % load	323.5	333.8
50 % load	328.3	338.1
75 % load	332.0	338.0
100 % load	331.7	340.8
Single step	326.2	339.4
Multiple step	323.4	339.5

The location where the front is present at any given time experiences maximum conversion and concurrently maximum heat release due to both the exothermic nature of the reaction and that of the adsorption process. The local increase in temperature improves the chemical kinetics of the reaction and increases the conversion of the reactants to the products. The faster the water is produced, the more rapidly the bed will be saturated and consequently the front will move along the reactor axis. Since the temperature peak is not static, the system is able to handle the problem of hot-spot formation. This is not the case in conventional fixed-bed catalytic methanation reactors where, as explained when discussing Fig. 2, the temperature peak at a given flow remains steady.

4. Conclusion

In the perspective of sustainable fuel production from renewable sources, an investigation of methane production at transient and partial load conditions was presented. The potential of sorption-enhanced catalysis applied to the methanation of carbon dioxide has been analyzed for its potential of having high conversions at flexible operation conditions.

To this extent, the behavior of an oil-cooled fixed-bed methanation reactor with a bi-functional catalyst has been experimentally tested and compared to a dynamic model of a fixed-bed reactor without sorption-enhancement.

Partial load conditions were tested in terms of varying reactant flow rates. Furthermore, transient load changes were investigated by evaluating the response to abrupt changes from a partial load to another. These responses were evaluated considering conversion and thermal stability, which is the main issue discussed in the literature for conventional catalytic reactor systems.

The results show exceptional thermal stability of the system in response to transients, despite the exothermic nature of both the methanation reaction and the adsorption phenomenon. The system is able to autonomously manage the temperature so that deactivation of the catalyst by thermal degradation is avoided. Nonetheless, the sorption-enhanced catalyst allows for full conversion without ignition problems.

From the point of view of product quality, the sorption-enhanced reactor shows an excellent CO₂ conversion above 99.97 % independent of the load. In contrast, the simulation results for a conventional catalytic reactor of the same size show a CO₂ conversion ranging from 96.2 % to 86.7 %, which decreases as the feed flow rate increases. Sorption-enhanced reactors achieve higher CO₂ conversions than those calculated for an

equilibrium reactor, due to the continuous water removal. The conventional reactors simulated in this study approach the theoretical equilibrium conversion for low flow rates.

Another characteristic of the sorption-enhanced reaction is the existence of a coupled reaction and adsorption front moving through the reactor. The duration of a sorption-enhanced reaction phase is determined by the water adsorption capacity of the catalyst bed at the given conditions. Consequently, decreasing the load leads to slower movement of the front through the reactor. It was observed that the adsorption capacity of the reactor slightly decreases with the increasing load, which was attributed to transport limitations in the reactor bed. Nonetheless, this allowed the system to operate at low partial loads.

The investigations of step responses to analyze the transient behavior showed that there is no influence on the CO₂ conversion, which stays constantly high throughout the sorption-enhanced production phase, even for abrupt load changes. This is beneficial considering the direct coupling with the fluctuating supply of reactants. The characteristics identified help to design power-to-gas systems and to minimize electricity or gas storage as the system can be operated at very low partial loads during phases with a low wind speed or solar irradiation.

Based on these results, this paper shows the excellent performance of sorption-enhanced catalysis during transient operations or at partial load conditions in the perspective of coupling methane synthesis with renewable energy sources.

Acknowledgments

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Nomenclature

A_j	adsorption constant for species j
d	pellet diameter, m
D	reactor diameter, m
ΔH_r^0	standard reaction enthalpy, kJ/mol
k_i	rate coefficient of reaction i, kmol/(kg _{cat} h bar)
K_i	equilibrium constant of reaction i
Nu	Nusselt number
p_j	partial pressure of the species j, bar
Pr	Prandtl number
r_i	rate of reaction i, kmol/(kg _{cat} h)
Re	Reynolds number
x_j	Mole fraction of species j

Greek symbols

α	heat transfer coefficient, W/(m ² K)
λ	thermal conductivity, W/(m K)

Subscripts and superscripts

f	fluid
w	wall

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