Title: Model based determination of the optimal reactor concept for Sabatier reaction in small-scale applications over Ru/Al₂O₃

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To be submitted in 'Chemical engineering journal' special issue for CHEMREACTOR 23

This document is the accepted manuscript version of the following article:
Moioli, E., Gallandat, N., & Züttel, A. (2019). Model based determination of the optimal reactor concept for Sabatier reaction in small-scale applications over Ru/Al₂O₃. Chemical Engineering Journal, 375, 121954 (10 pp.).
<https://doi.org/10.1016/j.cej.2019.121954>

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Abstract

The CO₂ methanation is an exothermic reaction controlled by thermodynamic equilibrium. For this reason, the high CO₂ conversion, required by the natural gas grid regulations, can be achieved only with a proper thermal management of the reactor. The model-based optimization of the Sabatier reaction by controlling the heat transfer is developed in this paper. The focus of the study is on small-scale applications, which gives rise to various specific technical limitations for the optimization study. We found that the reactor can be divided into three zones: an initial zone, for reaction activation; a central zone, to remove excess heat; and a final zone, to achieve high conversion reaching the thermodynamic equilibrium curve. The effect of the variation of the heat transfer coefficient along the axial coordinate of the reactor is assessed and the optimal profile is defined. Based on these results, a technical approximation of the optimal reactor is proposed, allowing high CO₂ conversion with a simple manufacturing.

Keywords: CO₂ methanation, reactor design, heat transfer, small scale energy storage

1. Introduction

The exponential growth of the renewable energy production over the last few years has given rise to the problem of energy storage, required by the discontinuous nature of the main renewable energy resources [1]. The energy storage is required to avoid perturbation of the operability of the electric grid related to the intermittent energy production. A promising strategy for energy storage is the power-to-chemicals concept, because it allows the conversion of excess energy into the chemical energy carriers. A promising process in this class is the power-to-gas (PtG) approach, that converts energy into a gaseous fuel such as

hydrogen or methane. A typical example is the Sabatier reaction that utilizes CO₂ and H₂ to produce synthetic natural gas (SNG):

$$\Delta H_R^0(298\text{ K}) = -252 \frac{\text{kJ}}{\text{mol}} \quad \Delta S(298\text{ K}) = 410 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

The reaction is exothermal and characterized by the thermodynamic equilibrium, which limits the CO₂ conversion for high temperature (> 300 °C).

The PtG process is a promising route for energy storage, because it produces an energy carrier that can be used in the existing facilities for natural gas storage, transport and utilisation. Furthermore, the process consumes CO₂, contributing to the reduction of greenhouse gas emissions [2].

The development of an industrial application of the Sabatier reaction dates back to the 1970's, when the oil crisis fostered the research for the production of SNG from biomasses and coal [3]. After a period of lower interest in the technology, resulting from a reduction in the oil price, the Sabatier reaction has again gained high interest from scholars over the last few years [4]. Currently, the research in this area focuses mainly in the elucidation of the reaction mechanism, with an aim to develop highly active and stable catalysts and the reactor design [4,5].

The CO₂ methanation reactors are commonly composed of a series of adiabatic stages with intermediate cooling. This technology is a direct evolution of the CO_x purification systems, used for clean-up of process streams, such as in ammonia synthesis [6]. The intermediate cooling is necessary to achieve high conversion related to the thermodynamic limitation. The adiabatic reactor with intermediate cooling has been discussed by several researches over the last few years. Schaaf et al. [7] considered two different designs of the system: the former

composed of two reactors with intermediate cooling and the latter formed by six reaction stages with four intermediate cooling steps. De Saint Jean et al. [8] discussed the implementation of the adiabatic reactors in a PtG system. The proposed reactor consists of four adiabatic reactors with intermediate cooling. The adiabatic reactors are a simple way to perform the reaction, but they do not approximate well the optimal reaction pathway.

The search for the process intensification strategies involved several examples of cooled reactors, that can adjust the temperature profile inside the reactor and increase the methane productivity. In this sense, Jürgensen et al. [9] described the integration of a counter-current-cooled multi-tubular reactor with a biogas plant providing the necessary CO₂. Kievidt and Thöming [10] used the Semenov number to demonstrate that the adaptation of the cooling inside the reactor strongly improves the methane yield compared to the adiabatic and isothermal operation. El-Sibai et al. [11] described a system that can produce SNG suitable for gas grid injection by using three cooled steps with intermediate water condensation. However, these optimisation studies are of limited applicability in the frame of the small-scale energy storage. In fact, when the target of application of the Sabatier reaction is the storage in remote or non-grid connected systems, the use of complex reactor systems (i.e. including additional unit operations, such as intermediate condensations) is not possible.

Several additional studies focused on the dynamic operation of the cooled Sabatier reactors. Matthischke et al. [12] showed the existence of an optimal recycle ratio for the optimisation of the reactor operation and output. Sun et al. [13,14] worked on the determination of the dynamic behaviour and analysed the activation of the reactor in several conditions. Bremer et al. [15] presented an optimization of the start-up of the CO₂ methanation reactor, showing the potential of controlling the cooling temperature of the reactor.

Besides the adiabatic and the tubular reactors, other reactor types were developed. For example, three phase reactors are considered for their ability in dissipating heat. Lefebvre et al. [16] experimentally investigated a slurry reactor to assess the response to the rapid variations in the gas load. Ohya et al. [17] reported the performance improvement obtained using a membrane reactor. Schildhauer et al. [18] described the development of a fluidized bed reactor for homogenizing the reaction mixture. Finally, some examples of the microchannel reactors are provided by Holladay et al. [19] and Brooks et al. [20]. These special reactors optimize the heat transfer in the reactor, but they are sometimes complicated to operate, making them not suitable for small scale applications.

In this study, we present an optimisation study of the Sabatier reactor with the target of small-scale application. The reactor must fulfil several special conditions, described as follows:

- No external energy can be provided, i.e. the reaction must be self-sufficient and the heat of reaction must be efficiently used for the various requirements of the system. This constraint is linked to the need of the off-grid operation.
- No external unit operations can be performed. The existence of additional steps, such as intermediate condensation requires a complex process integration that, in principle, is not possible in small-scale applications.
- The reactor should consist of a single unit to facilitate the installation and periodic maintenance.

Furthermore, the gas produced must fulfil the requirements for injection in the gas distribution network and the design should enable an affordable, simple manufacturing. The regulation developed by the Swiss Gas and Water Industry Association for this purpose was

employed in this case [21,22]. The requirements in terms of molar fractions of H₂ and CO₂, and the lower heating value are reported in Table 1.

According to all the above-mentioned specifications and constraints, it is necessary to design a reactor that can convert 99.5% of the CO₂ fed in a reactor, operating with the stoichiometric CO₂:H₂ ratio of 1:4. At the best of our knowledge, this is possible only using ruthenium (Ru) as catalyst [23]. For this reason, the selected catalyst for this study is a 0.5% Ru/Al₂O₃. The optimisation was performed based on the first step of the methodology developed by Peschel et al. [24]. This methodology design the optimal reactor following the single fluid element during its permanence in the reactor, manipulating point by point the fluxes into the element itself. After describing the target line for the optimisation of the reaction (section 3.1), we demonstrated that the cooling is the most important parameter for the operation of the Sabatier reaction, and that the heat requirements completely change according to the various reactor zones (section 3.2). According to the results of section 3.2, we defined the optimal reactor concept (section 3.3), and we designed a piece of equipment that can satisfactorily approximate the optimal reactor towards small-scale applications of the Sabatier reaction.

Table 1 The specifications required for gas injection

Specification	Value
x _{H2} (-)	<0.02
x _{CO2} (-)	<0.06
LHV (kWh/m ³)	>10.6

2. Computational methods

2.1 Kinetics

For the determination of the optimal reactor concept, the kinetic model of Falbo et al.[25] was used. This model was developed based on the power law-type equation from Lunde et al. [26]. The parameters of the kinetic model are reported in Table 2. These parameters have been selected because they refer to the dataset which best fit to the conditions object of this study. Since the selected catalyst is very active in the RWGS/WGS reaction, the reaction is modelled as an equilibrium reaction. This assumption was also verified experimentally in our previous studies [23,27–29], where no CO was detected at the reactor outlet below 300 °C and the CO concentration follows the thermodynamic equilibrium at higher temperature [30].

The CO₂ conversion is defined as:

$$\chi_{CO_2} = \frac{n_{CO_2,IN} - n_{CO_2,OUT}}{n_{CO_2,IN}} \quad (1)$$

The methane yield is defined as:

$$\eta_{CH_4} = \frac{n_{CH_4,OUT}}{n_{CO_2,IN}} \quad (2)$$

Table 2 The parameters of the kinetic model from Falbo et al. [25]

Equation rate	Reaction order (n)	k_0 [mol/(s · gcat · at ⁵ⁿ)]	E_A [kJ/mol]
$r_{CO_2} = k \left\{ [P_{CO_2}]^n [P_{H_2}]^{4n} - \frac{[P_{CH_4}]^n [P_{H_2O}]^{2n}}{K_{eq}(T)^n} \right\}$	0.076	18.26	65.2

2.2 Model of the fixed bed reactor

The reactor was modelled with a one-dimensional heterogeneous plug flow reactor (PFR) model. According to Schlereth et al. [31], the 1D model is sufficient to correctly describe the methanation reactor in normal conditions. However, the system can suffer of significant diffusional limitations in the hotspot region (especially inside the catalyst pellet [14]); therefore, an heterogeneous model is required for the problem description. The reactor was modelled with the canonical mass and energy balances [32]. The heterogeneous model considers the interfacial and intra-phase heat and mass transfer. For the computation of the intra-phase mass transfer limitations, the effectiveness factor model was used [32,33]. The reactor is modelled as a pipe with the catalyst bed inside and the coolant outside. When multiple cooling sections are present, they are modelled as separate and independent compartments. The model equations for the fluid phase are:

$$\frac{\partial(uc_i)}{\partial z} = k_g a_v (c_i^b - c_i^s) \quad (3)$$

$$(u\rho_f c_{tot} c_p) \frac{\partial T}{\partial z} = h_f a_v (T^s - T) - \frac{4}{d_{tube}} \alpha (T - T_{cf}) \quad (4)$$

The balance equations for the solid are:

$$k_g a_v (c_i^b - c_i^s) = v_{i,wgs} \eta \rho_b r_{wgs} + v_{i,sab} \eta \rho_b r_{sab} \quad (5)$$

$$k_f a_v (T^s - T) = \eta \rho_b (-\Delta H_{wgs}) r_{wgs} + \eta \rho_b (-\Delta H_{sab}) r_{sab} \quad (6)$$

where:

$$r_{sab} = k \left\{ [P_{CO2}]^n [P_{H2}]^{4n} - \frac{[P_{CH4}]^n [P_{H2O}]^{2n}}{K_{eq}(T)^n} \right\} \quad (7)$$

and r_{wgs} is calculated so that the water-gas-shift reaction reaches the thermodynamic equilibrium. The gas density is calculated via the ideal gas law.

The thermodynamic equilibrium constant for the Sabatier reaction is calculated as [25]:

$$K_{eq}(T) = \exp\left(\left(\frac{1}{1.187}\right) * \left(\frac{56000}{T^2} + \frac{34663}{T} - 16.4 \ln(T) + 0.00557 * T\right) + 33.165\right) \quad (8)$$

The thermodynamic equilibrium constant for the water gas shift reaction is calculated as [34]:

$$K_{eq}(T) = 9.01 \times 10^{-6} (T)^{0.968} \exp\left(\frac{\Delta G}{RT}\right) \quad (9)$$

Where $\Delta G = 43.6 \text{ kJ/mol}$.

The balance of the cooling fluid is:

$$(\rho_{cf} u_{cf} c_{p,cf}) \frac{\partial T_{cf}}{\partial z} = - \frac{4}{d_{tube}} \alpha (T_{cf} - T) \quad (10)$$

The superficial velocity of the gas phase was calculated by the continuity equation (Equation 11) and considered as a constant in the integration of equations (3) and (4):

$$u_s(z) = u_{s,0} \frac{\rho_0}{\rho(z)} \quad (11)$$

The effectiveness factor (degree of utilisation of the catalyst) was calculated as:

$$\eta = \frac{3}{\phi^2} (\phi \coth(\phi) - 1) \quad (12)$$

This is the formula for the effectiveness factor in a spherical pellet.

The Thiele modulus was used in its generalized form, as follows:

$$\phi = \frac{V_p}{S_p} \sqrt{\frac{n+1}{2} \frac{k C_{i,s}^{n-1}}{D}} \quad (13)$$

The boundary conditions are:

$$c_i = c_i^0 \quad (14)$$

$$T = T^0 \quad (15)$$

$$T_{cf} \Big|^{x=L} = T_{cf}^0 \quad (16)$$

The boundary conditions were selected as the industrially relevant. The CO₂ and H₂ were fed in stoichiometric amount (1:4) and without dilution. The inlet temperature was selected according to our previous study [35] and fixed to 230 °C. As a cooling medium, high pressure saturated steam was considered.

The pressure drop along the axial coordinate of the reactor was neglected and the partial pressures of the components were computed using the ideal gas equation. The heat exchange towards external environment was neglected and the reactor was considered insulated. α is the overall effective heat transfer coefficient, calculated with the analogy of a series of resistances. The resistances are the effective heat transfer coefficient for the tube inside and outside and the conductivity of the tube wall. The resulting formula is:

$$\frac{1}{\alpha} = \frac{1}{k_i} + \frac{k_c}{\ln\left(\frac{r_i}{r_e}\right)} + \frac{1}{k_e} \quad (17)$$

The values of k are calculated according to de Wasch and Froment [33]. The effective heat transfer coefficient of packed beds can be divided into a stagnant and a dynamic contribution. The k value is calculated as:

$$k = k_0 + 0.024 \frac{l^* Re}{d_p} \quad (18)$$

The thermal properties of the gases are approximated by polynomials according to the VDI-Wärmeatlas. Heat and mass transfer coefficients for the particle-to-fluid transfer are approximated by Wakao's correlation [36]

$$Sh = 2 + 1.1 Sc^{\frac{1}{3}} Re^{0.6} \quad (19)$$

$$Nu = 2 + 1.1 Pr^{\frac{1}{3}} Re^{0.6} \quad (20)$$

In our case, we used α as a design parameter to define the optimal reactor.

2.3 Computational methods

The system of differential equations (Equations 3, 4 and 10) was reduced to one mass balance and two heat balances by substitution of the concentration of the various components (CO_2 , H_2 , CH_4 , H_2O) with CO_2 conversion (Equation 1). The resulting equations constitute a differential-algebraic equations (DAE) system together with the Equations (5) and (6). The DAE system was integrated numerically over the axial reactor coordinate using the MATLAB ode23t solver.

3. Results and discussion

3.1 Maximal rate line

The first step of the optimisation process is the determination of the unconstrained optimal reaction concept. The optimisation function is the residence time required for 99.5% CO_2 conversion, in line with the legal requirements for injection in the natural gas network. The reaction rate depends on the pressure of the system, temperature and the component mole fraction of CO_2 , H_2 , CH_4 and H_2O . Focusing on the small-scale applications, the dosing or the removal of the components is not practical, because no complex equipment can be installed.

Hence, the manipulation of reactant and products will not be considered in this discussion.

The pressure of the system positively influences the reaction, because it shifts the equilibrium CO_2 conversion according to the Le Chatelier's principle. For this reason, the pressure is set at the highest value technically suitable for a PtG system, 10 bar in our case [32]. The influence of temperature on the reaction rate is complex and determined by the interrelationship of kinetic and equilibrium constants. The manipulation of temperature in the reactor is thus the object of the analysis.

The maximal reaction rate is calculated by maximisation of the reaction rate function by fixing the conversion value and finding the temperature corresponding to the maximum value of the reaction rate.

$$MRR = \max_{\bar{\chi}} f(T) \quad (21)$$

Where

$$f(T) = k(T) \left\{ [1 - \bar{\chi}]^n [4(1 - \bar{\chi})]^{4n} - \frac{[\bar{\chi}]^n [2\bar{\chi}]^{2n}}{K_{eq}(T)^n} \right\} \quad (22)$$

The maximal reaction rate curve is shown in Figure 1. The optimal temperature decreases with conversion, according to the thermodynamic limitations. The optimal line is relatively close to the equilibrium line and this distance decreases with the increase of conversion. The small distance between the equilibrium and the maximal rate line is a challenging point for reactor design, because the reaction rate changes dramatically in this interval, between the maximal and the zero rate. The practical aspects for the approximation of this line are discussed in the next sections.

Figure 1: The reaction rate calculated as a function of temperature and conversion

3.2 Effect of cooling in the methanation reaction

As a first step, the performance of a series of adiabatic reactors with intermediate cooling was calculated. This was used as technical reference case, because the adiabatic reactors are employed in several industrial applications [3]. In this typology of reactor, the heat flux was not controlled in a strict manner and the reaction and cooling were decoupled. The trajectory of this reactor system is displayed in Figure S1. Figure S1 is generated by simulating the performance of a series of three adiabatic stages which reach the thermodynamic equilibrium, with intermediate cooling to 180 °C. The cooling temperature (180 °C) is the minimal temperature possible after each stage to ensure the activation of the reaction in the next stage [35]. The intermediate cooling is operated by cooling water. The residence time required to reach 99.5% conversion was 2.25 s and it was reached with 3 adiabatic stages. It is noteworthy that 60% of the residence time was needed for intermediate cooling.

3.2.1 Single step reactor

The first step of the reactor optimization consists of the analysis of the performance of a single cooled reactor. The parameters used in the simulations are reported in table 3.

Table 3 Parameters used in the simulations

Parameter	Value
Pressure (bar)	10
Tube diameter (m)	0.01
Catalyst density (kg/m^3)	1500
$CO_2:H_2$ ratio (-)	1:4
Pellet diameter (mm)	1
Catalyst void ratio (-)	0.6

The inlet temperature of the counter current cooling medium was set to the maximal temperature for 99.5% CO_2 conversion at 10 bar (230 °C). Also, the tube diameter was considered constant and equal to 0.01 m. To efficiently describe the optimization potential, the optimization parameter selected was the heat transfer coefficient (α). The reactor model was integrated varying this value, to assess the effect on the reactor performance. The trajectories in the state space of different reactors simulated are displayed in Figure 2. The temperature of the packed bed with the axial coordinate, together with the temperature of the cooling medium are reported in figure S2. The characteristics of the cooling system used are reported in table 4. The flow rate of the circulating coolant is determining for the outlet temperature; in our case we fixed the mass ratio coolant/gas to 30. In these conditions, the coolant exits the reactor 50 °C hotter than the inlet conditions.

Table 4 properties of the cooling medium

Property	Value
Coolant	Molten salt Dynalene MS-2
Inlet temperature (°C)	200
Specific heat (J/kg/K)	1590
Ratio coolant/gas (kg/kg)	30

In figure 2 α was varied between 30 and 6000 W/m²/K. Figure 2 is plotted by integrating the reactor model and obtaining the axial profile of temperature and methane. On the base of these results, a (x,y) couple of coordinates is generated in order to plot methane yield vs. reactor temperature. At low α , the reactor initially is close to adiabatic (no heat release). The performance followed a straight line from the inlet conditions to the thermodynamic equilibrium. The slope of the line was determined by the value of the heat transfer coefficient. When the equilibrium line is reached, heat must be extracted from the reactor to increase the conversion. For low α , the cooling rate is low and becomes the rate determining step of the process. For this reason, the CO₂ conversion followed the equilibrium line until reaching the final temperature. At first, increase in α does not change the temperature-concentration curve substantially compared to the quasi-adiabatic case. The only differences lie in the increase of the slope of the adiabatic part of the curve and in the increase of the overcooling that provokes the separation of the reactor curve from the equilibrium line for high conversion. At $\alpha = 1000$ W/m²/K, the shape of the curve starts being substantially different than the quasi-adiabatic case. The cooling is sufficient to limit the adherence to the equilibrium curve to a small conversion interval. Furthermore, at high conversion, the overcooling causes to reach the cooling temperature before the complete conversion, so that the final part of the reactor operates in an isothermal way. If the cooling power is further

increased, the trajectory is completely changed. At $\alpha = 3000 \text{ W/m}^2/\text{K}$, the reactor activation is delayed, and only at $T > 300 \text{ }^\circ\text{C}$, it is possible to observe the runaway of the methanation reactor. This is in good agreement with what was observed in our previous study regarding the reactor activation for cooled reactors [35]. In this case, the trajectory does not reach the thermodynamic line and the gases are quickly cooled down to the coolant temperature. The reactor operates in isothermal mode for the last 10% of CO_2 conversion. It is noteworthy that the extent of the hotspot is drastically decreased for this reactor configuration. As a last example, an extremely high cooling rate was considered ($\alpha = 6000 \text{ W/m}^2/\text{K}$). This example is not necessarily referring to a real case, but it wants to represent the asymptotic behaviour for a reactor with extremely good heat transfer. In this case, the reaction went through a limited hotspot (approx. $50 \text{ }^\circ\text{C}$) and afterwards the gases were cooled back to the coolant temperature. The reactor operated then isothermally until reaching the final CO_2 conversion value. In this case, the reaction activation is ensured by the high temperature of the coolant, without the characteristic runaway behaviour of the Sabatier reaction. The results of this section are in line with the observations of Kiewidt and Thöming [10], which are formulated in terms of Semenov number instead of heat exchange coefficient. However, the operation of the reactor with a single heat transfer coefficient limits the optimisation potential, because it does not allow the adaptation of the cooling to the variation of the requirements in the various sections of the reactor.

Figure 2: Single stage reactor: variation of the trajectory in the state space for different values of heat transfer coefficient

The results of Figure 2 must be integrated with the information about the residence time required to reach 99.5% conversion. Figure 3 shows the residence time as a function of heat exchange coefficient. Starting from the large residence time required for low α s, we can observe that the time requirement is drastically reduced by the first time increase in the value of U . This shows that, in this region, the cooling is determining the performance of the reaction, as previously observed. As a practical consequence, it is sufficient to increase the cooling rate (e.g. increasing α from 30 to 100–200 W/m²/K), to realise a large improvement in the overall reactor performance. In this reactor configuration, approximately 50-60% of the conversion (Figure 2) is obtained in the thermal runaway section of the reactor, where the reaction is fast and kinetically controlled. However, only 20% of the residence time is related to the kinetic zone. This is marked in Figure S2a, where the division of the two zones of the reactor (kinetically and cooling controlled) is illustrated. The residence time function reaches

a minimum at $\alpha = 300 \text{ W/m}^2/\text{K}$, after which the required time for 99.5% conversion increases. This increase is because of the overcooling in the final zone of the reactor, that shifts the reaction trajectory below the optimal rate curve. This phenomenon becomes more significant with the increase of α . Interestingly, we can observe a discontinuity in the line for $\alpha > 3000 \text{ W/m}^2/\text{K}$. In this region, the performance of the reactor is affected by the absence of a pronounced hotspot. This difference is explained by the absence of runaway, which causes the reactor to work at low temperature, and thus low reaction rate is observed. Figure S2b shows the conversion profile as a function of residence time for this reactor. It is noteworthy that the residence time of the isothermal reactor is larger than the technical reference (3.2 vs. 2.2 s). The residence time of the optimal single stage reactor is 1.76 s, which is 20% less than the technical reference.

Figure 3: Single stage reactor: residence time required for 99.5% methane yield as a function of α

3.2.2 Influence of the final zone in the reactor performance

When approaching the high CO₂ conversion value required for the injection in the gas grid, the reaction rate becomes slow, because of the high concentration of products. For this reason, the optimisation of the last part of the reactor is of capital importance for determining the overall performance of the reactor, limiting the residence time. To analyse this section in detail, we performed a series of simulations changing the heat transfer coefficient of the reactor only for temperature below 310 °C. In this way, the trajectories in the state space can be analysed starting from the same value of conversion and temperature. The results of the simulations are displayed in Figure 4. This figure shows how methane yield changes by decreasing the temperature with different cooling rates (controlled by the heat transfer coefficient). The first curve was analysed at $\alpha = 150 \text{ W/m}^2/\text{K}$. In this case, at first, the cooling is controlling the reaction rate. The conversion increases with a small temperature decrease, reaching the maximum reaction rate. This is possible because of the low cooling rate. When approaching the 99% conversion, the reaction rate reduces and the gases are cooled down until reaching the final temperature and conversion. The trajectory in the state space follows approximately a line between 280 and 230 °C. If the cooling rate is increased ($\alpha = 500 \text{ W/m}^2/\text{K}$), the trajectory is almost linear from the starting point to 240 °C. This is resulting from the difference of cooling and reaction rate, which allows approximately 2% conversion while reducing the temperature of 60–70 °C. The remaining part of required conversion (from 98 to 99.5%) was performed in quasi-isothermal operation. For much higher cooling rate ($\alpha = 2500 \text{ W/m}^2/\text{K}$), the gases are immediately cooled to the final temperature with practically no conversion during this phase. When the coolant temperature is reached, the cooling rate is adapted to the reaction rate and the final conversion is reached

isothermally. The trajectories in state space described above result in different performances in terms of normalized residence time required for 99.5% CO₂ conversion. The influence of the heat transfer coefficient on the performance of the last part of the reactor is shown in Figure 5.

Figure 4: Multiple stage reactor: methane yield vs. Temperature as a function of α in the high conversion area

The results are normalized to the lowest residence time to underline the penalisation related to the operation in non-optimal conditions. The calculated function has an evident minimum, with a large increase of the residence time for lower and higher α s than the optimal point. The origin of this effect follows the previous explanation. At low α ($\alpha < 200$ W/m²/K), the reactor trajectory remains close to the equilibrium line, so that the reaction rate is low and the conversion is determined by the cooling rate. This result in a high value of residence time required to reach the desired conversion. For large cooling power, the large residence time is related to the effect of overcooling; the reaction is not fast enough to compensate the cooling,

with the consequence of a fast decrease of temperature. This results in the operation of the reactor at a lower temperature with a consequent lower reaction rate. The residence time function tends to an asymptote for high α s, because over a certain threshold, an increase of cooling does not have effect on the residence time (the cooling from 310 °C to the final temperature is fast).

As shown in Figure S2, the contribution of this part of the reactor is fundamental for the determination of the performance of the entire reactor. Therefore, the operation of this reactor section, not in optimal conditions, has a strong influence over the entire reactor. It is noteworthy that the variability in the residence time between the optimal point and the values for higher α is larger than in the case depicted in Figure 3. For example, the ratio in residence time between the optimal point and the value $\alpha = 1000 \text{ W/m}^2/\text{K}$ is 1.8 for the last section of the reactor (Figure 5), but only 1.1 for the entire reactor (Figure 3). This is because of the stronger influence of the cooling properties and the low exothermicity (for the low conversion to achieve) in the last part of the reactor. For this reason, the optimisation of this section of the reactor is crucial for the operation of the Sabatier reaction. Additionally, the optimal α for the final section is lower than the value for the entire reactor, showing that a lower cooling is required at the end of the reactor.

Figure 5: Multiple stage reactor: normalized residence time for 99.5% methane yield in the last section of the reactor as a function of α (the residence time is normalized assuming 1 the minimum time required)

3.2.3 Influence of addition of an adiabatic zone

To assess the influence of the cooling properties of the reactor excluding the problems related to the reactor activation, the reactor was divided into two zones: the first part with an adiabatic area to ensure the activation of the reaction and the second part with external cooling. The presence of the first adiabatic zone has a strong impact on the reactor performance, as shown in Figure 6. For $\alpha < 3000$ W/m²/K, division in two zones does not change the general trends already observed in Figure 3. However, the performance of the reactor is worse, because of the less prompt removal of the reaction heat. The main difference of the performance appears for $\alpha > 3000$ W/m²/K. In this case, the discontinuity observed in Figure 3 is disappeared. This is obtained because the activation of the reaction and the presence of the hotspot are guaranteed by the first adiabatic zone. This example underlines that the reactor performance can be greatly improved by dividing the reactor into, at least,

three zones: activation, removal of the reaction heat and moderate cooling to finish the reaction. The realisation of this reactor concept is discussed in the following section.

Figure 6: Multiple stage reactor: residence time required for 99.5% methane yield as a function of α in a 2-step reactor: adiabatic + cooled

3.3 Optimal reactor concept

The optimal reactor concept is defined by freely varying the heat transfer coefficient over the axial coordinate. In this way, it is possible to determine the α , point-by-point, to maximize the overall reactor performance. α is the global heat transfer coefficient of the reactor as in equation (4). The profile of α that minimize the residence time is shown in Figure 7. Initially, the reactor operates adiabatically, to ensure a fast reaction activation. This is in good agreement with what was observed in our previous study [35]. As soon as the reaction is initiated, the reaction rate increases exponentially, causing the release of heat. This is initially positive for the self-sustainability of the reaction, but when approaching the thermodynamic equilibrium, this causes a progressive decrease of the reaction rate. For this reason, the

optimal α increases exponentially. The high α is required to remove sufficient heat to avoid surpassing the maximal rate line and reaching the thermodynamic equilibrium. When the temperature of the gases starts to decrease, the cooling must be reduced, to avoid overcooling with the negative impact described in the previous section. Hence, the cooling rate (controlled by the α) is adapted to the reaction rate to optimise the latter. This is represented by the decreasing α s in Figure 7. When the reaction mixture approaches the full conversion, the reaction rate assumes low values, with a consequent low heat production. For this reason, in the last section of the reactor, α assumes an almost constant optimal value. The results of Figure 7 confirm the qualitative observation concerning the separation of the reactor into three zones, requiring different levels of cooling.

Figure 7: Optimized reactor: the α profile over the axial reactor coordinate

Figure 8 shows the CH_4 yield vs. temperature of the optimal reactor concept. The temperature raises adiabatically in the first part of the reactor, performing in a short residence time with approximately 50% CH_4 yield. It is noteworthy that the temperature of the hotspot is reduced to 100 °C, compared to the adiabatic case, with positive effects on the lifetime of the catalyst.

The effect of the increase of the heat transfer coefficient is traceable in the limitation of the hotspot and in the decrease in the temperature to reach the maximal rate line. The progressive adjustment of α , with the reactor axial coordinate, allows following the optimal rate line, minimizing the residence time requirement to reach the final conversion required.

3.4 Realisation of the optimal reactor

The practical realisation of a reactor following the heat transfer coefficient described in section 3.3 is a complicated task, because this would require a complex design. Furthermore, the concept is difficult to apply to the small-scale applications targeted in this paper, where a single reactor unit is necessary. For this reason, we assessed the possibility of approximating the optimal profile with a limited number of different reactor concepts. As mentioned above, we defined the optimal reactor concept based on the qualitative assumption that the optimal operation can be performed by dividing the reactor in three zones. The scheme of the reactor designed is shown in Figure 9. The first zone was operated adiabatically, generating the temperature rise required to reach the maximal reaction rate. The second zone requires a high cooling rate, realised by the water cooling. In this way it is possible to achieve a high cooling rate—thanks to the large temperature difference between the coolant and the gases. When the temperature reaches the threshold of 300–350 °C, the gases were fed in the last section, operated by molten salts cooling at 230 °C. The pipe diameter is defined according to the desired gas flow rate and the necessary cooling properties of this last section. For ease of manufacturing, the pipe diameter defined in the last section can be maintained on the entire reactor, but the optimal solution would require a lower diameter in the central section, to increase the external heat transfer.

Figure 8: Methane yield vs. temperature curve in the optimal reactor: - Optimal reactor. - - - Methane yield with the max. reaction rate, ---- Equilibrium conversion for a stoichiometric mixture of $\text{CO}_2 + 4\text{H}_2$.

Figure 9: Schematic drawing of the heat flow in the optimal reactor concept. The heat exchange in the high temperature region of the reactor is performed with cooling water, while the final cooling is operated with molten salts used also for the preheat

An important part of the reactor design is the heat integration. The Sabatier reaction is highly exothermic; therefore, a good design of the heat management system is of capital importance for the operation of the reactor. Furthermore, the heat must be efficiently used for the

autothermal operation of the reactor, to guarantee a high energy efficiency of the system, which is a fundamental requirement in small-scale applications. Figure 9 reports the heat management scheme for the optimal reactor designed. The reactive gases must be preheated up to the minimal temperature (approx. 180 °C) for the reaction activation. This operation is performed by heat exchange with the exhaust gases, which have a sufficient enthalpic content for the operation. If the gas-gas exchange is not sufficient, the remaining required heat can be recovered from the molten salts circulating in the last section of the reactor. The main part of the reaction heat (cooling the gas from the hotspot to 300 °C) is removed by the cooling water, which is not integrated in the system. This results in an optimised heat management of the reactor, but this operation produces low temperature heat which can have limited further uses. If the reactor is integrated in a more complex system (e.g. with reuse of the waste heat), the cooling water can be substituted with another fluid, according to the optimal requirement of the global system.

3.5 Comparison of the performance of the reactor concepts

In the previous sections, we analysed the following 5 different reactor concepts:

- Multistage adiabatic reactor
- Single cooled reactor
- 2-stage cooled reactor (adiabatic + cooled)
- 3-stage cooled reactor (adiabatic + 2 cooled stages with different α)
- Reactor with free α manipulation.

The performance of the various reactor types, in terms of normalized residence time, for 99.5% CO₂ conversion is compared in Figure 10. The reference point is the multistage adiabatic reactor. Compared to this, the optimized cooled reactor shows a 22% reduction of the residence time—thanks to the simultaneous operation of cooling and reaction. This is

already a significant reduction compared to the technical reference. The optimization of the cooling system provides a further improvement of the performance of the reactor, providing 26% and 31% reduction of the residence time from the reference point for the two and three stages reactors, respectively. The optimal reactor with free α manipulation results in a reduction of the residence time of 34%. These results confirm that the key point of the optimisation of the Sabatier reactor is the good management of the cooling system. Furthermore, it is noteworthy that the main savings appear in the simple application of an integrated reaction-cooling system. However, the adaptation of the cooling system, point-by-point to the reaction conditions, generates a potential for further optimization. The optimal reactor depends on the specific application and on the possibilities in terms of reactor manufacturing. For our specific case, we assume that the three stages reactor can be the best solution, because it couples a good efficiency with a relative ease in manufacturing.

Figure 10: Comparison of residence time for 99.5% methane yield in various reactor configurations (the normalisation is performed using the adiabatic reactor as reference)

4. Conclusions

This paper described the design of the optimal reactor for the Sabatier reaction for small-scale applications. We observed that the critical factor for reaction optimization is the heat management. The reaction being a strong exothermal one, the removal of the reaction heat is crucial to achieve the highest reaction rate possible. On the one hand, the heat must be efficiently removed to achieve high conversion, according to the thermodynamic limitations; while on the other hand, an excess in the cooling provokes the operation at low reaction rate. We demonstrated that the isothermal operation is disadvantageous for the conditions studied, because it requires a higher residence time than the adiabatic reactor with intermediate cooling. This is a clear example of the negative effect of excessive cooling. Afterwards, we observed that the Sabatier reactor can be divided into three zones with different cooling requirements:

- The activation area, favoured by the adiabatic operation;
- The hotspot region, which requires high cooling to reduce the temperature;
- The final zone, where the cooling must be adapted to maximize the reaction rate.

The final zone has an important effect on the performance of the entire reactor, because the reaction rate is low and the optimization of this section is of capital importance.

The optimal reactor can be designed by point-by-point manipulation of the cooling properties of the reactor. However, it was demonstrated that the definition of a reactor, only with three different zones, already provides a good improvement from the reference adiabatic reactor, because the reduction of the residence time for this solution is 31%, compared to the 34% of the global optimum.

The results of this paper open new perspectives in the small-scale application of the Sabatier reaction, because it allows the manufacturing of a single unit capable of high CO₂ conversion

in a small volume. Indeed, the reduction of the dimensions of the reactor and the elimination of unit operations in the downstream are two elements of capital importance for small-scale applications, where no auxiliary fluids are available and low maintenance is required.

Acknowledgement

The collaboration with Gaznat and the financial support by the KTI/CTI, project no. 6441.1 PFIW-IW “Development of a Novel, Highly Efficient Energy System for Natural Gas Metering and Regulating Stations Based on Waste Heat Recovery and Synthetic Methane Production” are greatly acknowledged.

Nomenclature

α = global heat transfer coefficient (W/(m²K))

c_i^b = bulk concentration of the species i (mol/L)

c_i^s = surface concentration of the species i (mol/L)

d_{tube} = diameter of the reactor tube (m)

$h_f a_v$ = local heat transfer coefficient (W/(m²K))

$k_g a_v$ = material transfer coefficient (mol/m²)

k = kinetic constant (mol / (s * *gcat* * *ata*^{5 n}))

n = reaction order

n_i = number of moles of the component I (mol)

r_A = reaction rate (mol/m³s)

u = speed of the gases (m/s)

D = diffusion coefficient (m²/s)

K_{eq} = equilibrium constant

P_i = partial pressure of the component I (Pa)

S_p = surface of the particle (m^2)

T = temperature (K)

T_{cf} = temperature of the cooling fluid (K)

V_p = volume of the particle (m^3)

χ = conversion

ρ_f = density of the fluid

η = effectiveness factor of the catalyst pellet

ϕ = Thiele modulus

ν_i = stoichiometric coefficient of the component i

ΔH = reaction enthalpy (J/mol)

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