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A New Method to Assess Performance Loss due to Catalyst Deactivation in Fixed- and Fluidized-bed Reactors

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ABSTRACT

A new methodology for the assessment of the performance loss in catalytic reactors due to deactivation was developed and applied to fixed- and fluidized-bed CO methanation, with catalyst subject to coking. The methodology is based on the solution of heat and mass balances, by decoupling the reactor and deactivation dynamics. This is possible by using consecutive 1D, steady-state calculations for the characterization of the reactor performance. In this way, the progressively lower values of catalyst activity along the time on stream are computed with the integration of a dedicated dynamic model. This method has shown promising results in the characterization of the loss of performance of the reactor over time. The model correctly describes a progressive deactivation of the catalyst in fixed-bed reactors, while it shows that the decrease in activity is sudden for the whole reactor volume in fluidized bed reactors and occurs after a critical time-on-stream. Besides, it was observed that the fluidized bed reactor is in general more resistant to deactivation by CO, with the time needed to reach 25% conversion being 1.5 to 2 orders of magnitude higher than for a fixed bed in similar conditions – for example around 250 hours against 50 for a fixed bed at 300°C. This will allow optimizing the reactor with respect to deactivation, hinting the modifications possible in the conditions or in the reactor geometry to maximise the time-on-stream prior to loss in the product quality.

Keywords: Catalyst deactivation, Reactor modelling, Fixed-bed reactors, Fluidized-bed reactors

INTRODUCTION

The increasing amount of anthropogenic greenhouse gases in the atmosphere is a major driver for the development of new technologies that can abate such gas emissions. A widely investigated option to address this challenge is the production of fuels from unconventional and renewable feedstocks, like CO_2 from carbon capture processes, biomass, and green waste. This option shows the advantage of emitting the same amount of CO_2 that was naturally captured during the production of such feedstocks [1–3], making the overall cycle carbon-neutral. However, these carbon-containing streams are usually contaminated by various additional molecules. In particular, the presence of CO and other organic molecules, which are natural constituents of such feedstock, may lead to catalyst deactivation by decomposition of such molecules and consequent coking of the surface. This may strongly hinder the rate of the reactive steps of the process over time [4]. The development of methods that minimize the impact of coking in these reactions is therefore a key to ensure the efficiency of the whole process and its long-term performance and competitiveness. For this scope, it is crucial to model these deactivation phenomena, both in terms of their intrinsic kinetics and of their impact on the reactor performance. These models should target the optimization of the operating conditions in the reactor to reduce the impact of deactivation.

The main difficulty in modelling catalyst deactivation in catalytic reactors is caused by the different characteristic time scales of the phenomena involved: while the reaction has characteristic times below the order of magnitude of seconds, and the same is valid for the transport phenomena in the reactor, the deactivation by coking has

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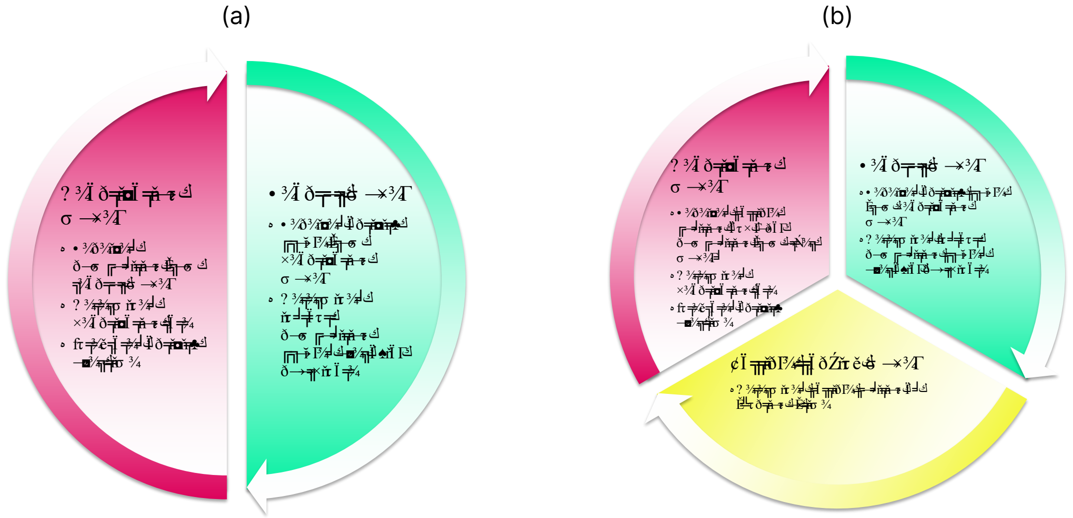

Figure 1: Model structure for the (a) pseudo-dynamic model in case of a fixed bed and (b) moving observer model in case of fluidized bed.

a visible impact on the reactor performance only after hours to days [5]. In the case of a fluidized-bed reactor, an additional modelling difficulty is originated by the chaotic movement of particles [6], which has a decisive impact on the deactivation, as the position of the particle at each given instant determines the amount of coke precursors in the gas around it. It is, however, too computationally cumbersome to model this motion for the entirety of the particles in a fluidized bed of a commercially usable scale [7]. This study develops a new methodology that unifies in a single model the information on the effects of catalyst deactivation at different scales, resulting in a computationally affordable model. This model can predict the decrease in the activity of the catalyst over time, the effect of particle motion in fluidized bed reactors on catalyst deactivation and the evolution of the concentration profiles over time. Thanks to the prediction of these various indicators, the model can be used to predict the time the reactor can operate before the outlet concentration is not in line anymore with the requirements of the system in which it is installed. To contextualize the methodology in a case of practical interest, the methanation of syngas is considered as case study for this work.

METHODS

This work focuses on the development of a model for the evaluation of the impact of catalyst deactivation on chemical reactors. The time scales of the phenomena determining the operation of the reactor and the deactivation of the catalyst are significantly different and can thus be decoupled. The resulting model characterizes the conversion in the reactor in one spatial dimension, and the activity of the catalyst in time, plus one spatial dimension for the fixed-bed case.

The activity of the catalyst is defined in Equation (1), where r represents the local rate of reaction and r_0 the rate of the same reaction at the same local conditions of pressure, temperature and composition of r, but calculated assuming the catalyst is unaffected by deactivation.

$$a = r/r_0 \tag{1}$$

Figure 1 shows a schematic representation of the workflow leading to the complete deactivation models for the two reactor types (fixed- and fluidized-bed).

The deactivation model for the fixed-bed reactor has been labelled as pseudo-dynamic model due to its constitution as a series of consecutive steady-state calculations to model the performance loss in time. Starting from a time t=0 and an initial activity a=1, the pseudo-dynamic model follows this procedure for each time step:

1. It calls the steady-state model of the reactor, which solves the model equations for the current steady state,
2. it determines the composition profiles and the partial pressures of the two main components involved in deactivation (CO and H_2O),
3. it calculates the deactivation rate from the partial pressures, obtaining the rate of loss of activity as a function of the position in the reactor $da/dt = f(z)$,
4. it integrates the loss of activity and moves to the next step.

The deactivation model for the fluidized bed is referred here as moving observer model because it follows the average catalyst particle through its motions in the bed through a Eulerian-Lagrangian approach. It shows similitudes with the pseudo-dynamic model, with the addition of a model for the position of the particle as a function of time. The activity is therefore no longer calculated as a function of the position, but as a value relative to the single catalyst particle. It is then assumed to be the same throughout the whole reactor due to the very fast mixing inside the system.

Case study

The methanation of CO is used as case study. The fixed-bed model is based on a plate-cooled fixed-bed reactor with 1 m of length, 50 cm of width and 5 cm of spacing between the plates [8]. The channels between the plates are alternatively filled with the catalyst bed and with the cooling medium (boiling water) at the same temperature of the reactor inlet. The reactor is operated with a stoichiometric inlet stream (3:1 H_2/CO) at a pressure of 8 bar and inlet temperatures between 300 and 360°C.

The fluidized-bed model is instead based on a reactor of 2.5 m of length, 22.4 cm diameter and cooled by an inner coil where a cooling oil is circulated. This reactor is also operated with a stoichiometric inlet stream (3:1 H_2/CO), at a pressure of 8 bar and uniform reactor temperatures between 300 and 360°C.

The kinetic model used is obtained from the work of Kopyscinski et al. [9] for the methanation of CO and Koschany et al. [10] for the methanation of CO_2 (Sabatier reaction), and it consists of three reactions, outlined in **Table 1**.

Table 1: Reactions in the kinetic model for CO methanation [9,10].

Reaction	Equation
CO methanation	$CO + 3H_2 \rightleftharpoons CH_4 + 2H_2O$
CO_2 methanation	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 3H_2O$
Water-gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$

The effect of the Boudouard reaction, i.e., the decomposition of CO to coke (assumed as elemental carbon, C) and CO_2, leading to coking of the catalyst, has not been taken into account in the reaction kinetics due to its low extent in the residence time of the system (few seconds). Future works might explore this aspect further.

Fixed-bed reactor digital twin

The fixed-bed digital twin was developed on a 1D pseudohomogeneous assumption, i.e., the catalyst and the gas were modelled as a single pseudophase and gradients were neglected in any direction other than that of the gas flow. Equations (2) and (3) are the component and energy balance for the reactor, respectively. The activity term $a(t)$ is calculated from the deactivation model, as explained in the dedicated subsection.

Component balance

$$\frac{dF_i}{dz} = \rho_c(1-\varepsilon)A a(t) \sum_{j=1}^{NR} \nu_{ij} r_j \quad (2)$$

Heat balance

$$\frac{dT}{dz} = -\frac{\rho_c(1-\varepsilon)A}{\dot{m}\hat{c}_P} a(t) \sum_{j=1}^{NR} \Delta h_{Rj} r_j - \frac{2W}{\dot{m}\hat{c}_P} U(T-T_e) \quad (3)$$

This digital twin was developed according to state-of-the art models for the calculation of steady-state profiles in fixed beds [11]. The model consists of NC+1 ordinary differential equations, where NC is the number of species considered. The equations were solved in MATLAB via built-in solvers which integrate them in the axial reactor coordinate z.

Fluidized-bed reactor digital twin

For the fluidized bed, a two-phase model was chosen, dividing the reactor in two pseudophases being the bubble and the emulsion or dense phase [4]. The bubble is assumed to contain no catalyst – therefore no reaction happens in it – and to be in a plug-flow regime. The emulsion is instead considered to carry out the reaction since it contains the catalyst, and to be perfectly stirred by the continuous recirculation operated by the bubbles. For the same reason, the reactor is considered isothermal. The component balances for each phase are shown in Equations (4) and (5).

Component balance – bubble phase

$$\frac{dF_i^B}{dz} = -K_i A_B \left(\frac{F_i^B}{Q_B} - \frac{F_i^D}{Q_D}\right) \quad (4)$$

Component balance – dense phase

$$0 = F_i^{D,IN} - F_i^D + \int_0^L K_i A_B \left(\frac{F_i^B}{Q_B} - \frac{F_i^D}{Q_D}\right) dz + V(1-\delta)\left(1-\varepsilon_{mf}\right)\rho_c \sum_{j=1}^{NR} a(t)\nu_{ij} r_j \quad (5)$$

This digital twin was also developed from state-of-the-art models for fluidized-bed systems [12]. Due to the presence of an integral term, the model could not be solved by numerical integration and must instead be converted to a nonlinear algebraic system by discretization of the derivatives. Such system was then solved via built-in solvers in MATLAB for algebraic equations.

Particle motion model

A model for particle motion has been derived from the experimental data obtained by Lefebvre et al. [13], normalized on the dimensions of the reactor studied in this work. The wave of the position of the particle in time has been decomposed according to a Fourier transform in the attempt to divide it into components accounting for gross and local circulation phenomena. The advantage of the Fourier transform over other tested approaches (i.e., artificial neural networks) is that it conserves the periodicity of the function. Wave components with a negligible impact on the particle position have been filtered out to make the function simple. The goal of the function is not to reproduce accurately the data, but more to learn the trend relative to the time an average particle spends at each height in the reactor.

Deactivation model

The deactivation model was developed in this work and is based on a reparameterization of a model by Sun et al. [4]. The new parameters were obtained from the catalyst deactivation data during CO methanation reported by Zhang et al. [5], and the resulting model is based on the following equations:

Deactivation rate

$$\frac{da}{dt} = -r_d a \tag{6}$$

Kinetic equation

$$r_d = k_d P_{CO}^{\alpha} f_{H_2O} \tag{7}$$

Temperature dependence (Arrhenius)

$$k_d = k_d^0 \exp\left(-\frac{E_d}{RT}\right) \tag{8}$$

Correction factor for water

$$f_{H_2O} = \frac{x_{H_2O}-1}{(1-c)x_{H_2O}-1} \tag{9}$$

The correction factor is used to account for the hindering effect that a high concentration of water has on the deactivation rate. Water is in fact known to be able to prevent the formation of coke on catalyst particles, slowing down their deactivation [4]. The correction factor in Equation (9) is empirical. The effect of water on deactivation will be studied in more detail in future works.

RESULTS

The results show the prediction of deactivation profiles in the two reactor types by application of the models described in the methods section.

Pseudo-dynamic model – fixed-bed

Figure 2 and **Figure 3** illustrate the results of a simulation of the deactivation effects in the fixed-bed reactor conducted with the pseudo-dynamic model. The evolution of the activity and conversion profiles in time shows that, in the initial moments of the simulation, the activity decreases significantly only at the inlet of the reactor, to then generate a wave of decreasing activity that propagates through the catalyst bed in the axial direction. This is in line with what is expected in fixed bed reactors, where the first layers of catalyst operate as ‘filter’ for the impurities [4]. The deactivation wave reaches the end of the reactor after about 40 h of operation, when the CO conversion at the outlet starts decreasing from an initial value close to 100%. After 50 h, the catalyst has lost most of its activity throughout all the reactor, which leads to a final conversion of 25% and a hotspot temperature of around 420°C (130°C milder compared to the values during effective operation). This decrease in the hotspot temperature is due to the different distribution of the reaction rate on a partially deactivated catalyst. This reduces the reaction rate at the reactor inlet, hence distributing the conversion over a larger area of the reactor than at the operation start.

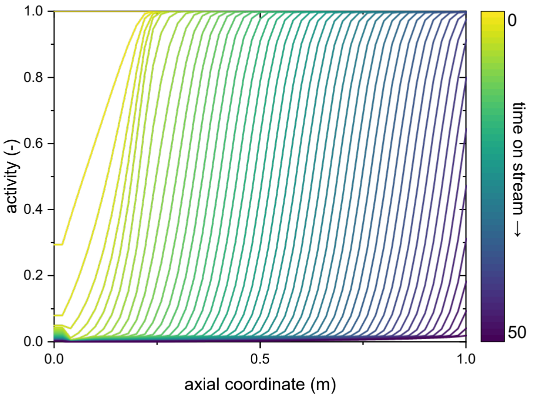

Figure 2: Results of the pseudodynamic model for stoichiometric inlet, T_{in} = 300°C, p = 3 bar – deactivation wave.

The different deactivation velocity appears to be mostly due to the difference in temperature throughout the reactor shown in **Figure 4**: as the deactivation rate strongly depends on the temperature through the Arrhenius equation, the deactivation is much faster in the temperature hotspot. The hotspot itself is moving as a result of the wave of decreasing activity, since the less active catalyst in the initial portions of the bed leads to significantly slower reaction rates and therefore to a less prominent heat release. The reaction rate strongly increases once the reactants reach a portion of the bed where the catalyst is still active, and this leads to the generation of a new hotspot there. Both the decrease in activity and the moving hotspot are coherent with experimental observations for similar systems [4].

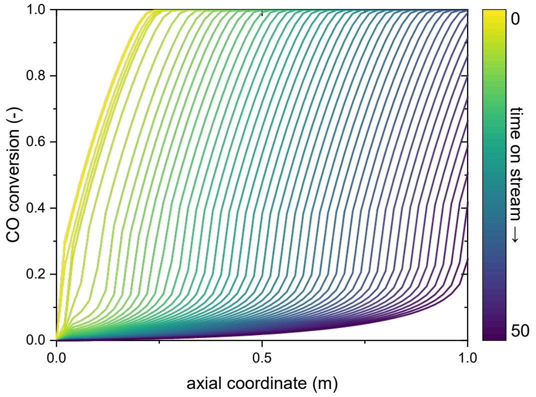

Figure 3: Results of the pseudodynamic model for stoichiometric inlet, T_{in} = 300°C, p = 3 bar – conversion profile.

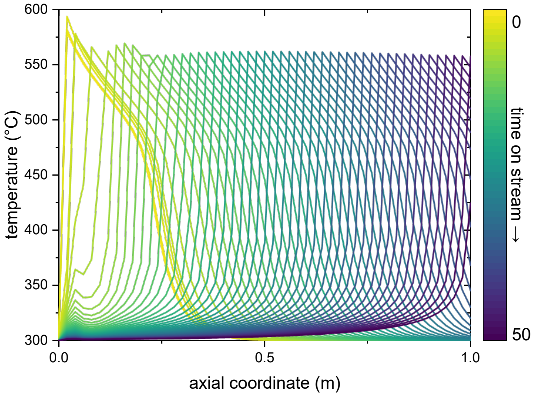

Figure 4: Results of the pseudodynamic model for stoichiometric inlet, T_{in} = 300°C, p = 3 bar – moving hotspot.

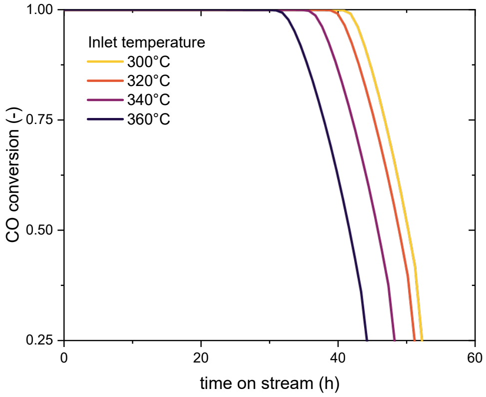

Figure 5: Results of the pseudodynamic model for stoichiometric inlet, p = 3 bar – effect of inlet temperature.

Figure 5 shows the CO conversion at the reactor outlet over time. As expected in fixed-bed reactors operating the CO_x hydrogenation, the conversion remains high until the deactivation wave reaches the terminal part of the reactor (see **Figure 2**). The figure also shows the effect of an increasing inlet temperature on the time required for significant loss of performance of the reactor. A higher inlet temperature leads to higher temperatures throughout the whole reactor, which increase the rate of deactivation as per Equation (8). This leads to a faster propagation of the deactivation wave and consequently to an earlier loss of performance.

Moving observer model – fluidized-bed

The results of the integration of the moving observer model are shown here. **Figure 6** reports the decrease in conversion over time. In the fluidized-bed reactor, the conversion loss does not follow a wave form, but it is uniform over the axial coordinate. This is an effect of the assumption of perfect mixing for the dense phase. The deactivation is limited to a small portion of the reactor, in the initial section, prior to the full consumption of CO. However, the constant and quick motion of the particles throughout the bed ensures that the particles can be assumed to deactivate all at the same rate. The effect of the zones at low CO concentration is, in turn, prevalent due to their significant size compared to the CO-rich ones, which results in an overall slower deactivation. The time on stream required for a significant loss of performance is therefore longer and the CO conversion curve over time takes a different shape than in the fixed-bed reactor.

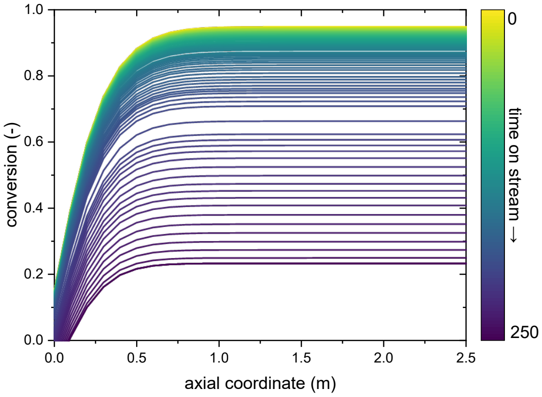

Figure 6: Results of the moving observer model for stoichiometric inlet, T = 300°C, p = 8 bar – conversion profile.

These conversion terms are shown in **Figure 7**. The general behaviour is the same as for the fixed-bed case, but the effect of the temperature is reversed: higher temperatures lead here to slower deactivation and loss of performance. Additionally, the drop in CO conversion occurs more suddenly in the fluidized bed reactor, because deactivation is distributed over the catalyst volume, so that when the critical activity of the catalyst dropping the CO conversion is reached, this is reflected by the entire dense phase. This is challenging for the operation of a fluidized-bed reactor, as the conversion drop is sudden and more difficult to predict than in the fixed-bed reactor.

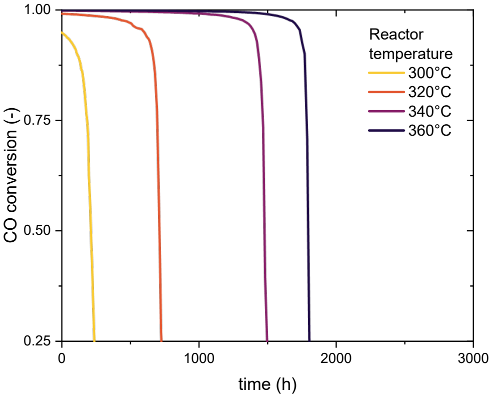

Figure 7: Results of the moving observer model for stoichiometric inlet, p = 8 bar – effect of reactor temperature on conversion.

Figure 8 shows instead the evolution of the catalyst activity over time. The slower deactivation at higher temperatures is due to the faster consumption of CO, which reduces the length of bed in which a significant amount of CO is present and leaves the rest of the bed with low amounts of CO and high amounts of water. This results in a shorter contact time between the particle and a CO-rich gas, therefore a slower deactivation.

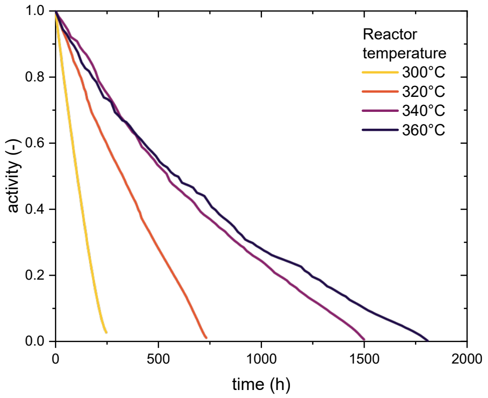

Figure 8: Results of the moving observer model for stoichiometric inlet, p = 8 bar – effect of reactor temperature on activity.

The higher temperature also leads to a stronger impact of the position of the particle on the deactivation rate, as shown by the profile at 360°C being less smooth than that at 300°C. This is due to the sharper variations in composition throughout the reactor at higher temperatures, which amplify the variation of the deactivation rate with the particle position.

CONCLUSIONS

This paper developed a new methodology to describe the reactor deactivation due to coking in fixed- and fluidized-bed reactors. Deactivation can be modelled in fixed-bed reactors by coupling a reliable steady-state model for the calculation of the composition profiles in given conditions, with a model for the deactivation of the catalyst as a function of the local operating conditions (temperature, gas phase composition). The same is possible for fluidized-bed reactors with the addition of a particle tracking model that can express the position of the average catalyst particle as a function of time. Such models are effective in characterizing the loss of performance along the time on stream as a function of key operating conditions of the reactor like the inlet composition, the inlet/operating temperature, pressure etc., and therefore provide the possibility for optimization of such conditions with respect to productivity and minimizing the effect of deactivation. The impact of the operating conditions can in fact be studied in detail with the help of this model, which allows the selection of those sets of conditions that minimize the long-term impact of deactivation on reactor performance.

In the specific case analyzed we observed the behavior of both reactor types at the four temperature values of 300, 320, 340, and 360°C. We considered the catalyst deactivated when a conversion of CO of 25% was reached at the outlet, at which point the simulation was stopped. The most relevant result is the slower deactivation for the fluidized bed, by 1.5 to 2 orders of magnitude.

Future works will be focused on improving the model. Aging experiments will be run on the catalyst, with the goal to gather more deactivation data and improve the model parameters and structure to better characterize the catalyst deactivation and its dependence on temperature and composition. A deeper investigation will also be conducted on particle behavior in the fluidized bed, with the aim of refining the existing model, for example by adding a term accounting for stochasticity.

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REFERENCES

1. Pearson RJ, Eisaman MD, Turner JWG, Edwards PP, Jiang Z, Kuznetsov VL, et al. Energy storage via carbon-neutral fuels made from CO2, Water, and Renewable Energy. Proceedings of the IEEE. 2012;100(2):440–60.
2. Choi YH, Jang YJ, Park H, Kim WY, Lee YH, Choi

SH, et al. Carbon dioxide Fischer-Tropsch synthesis: A new path to carbon-neutral fuels. Appl Catal B [Internet]. 2017;202:605–10. Available from: http://dx.doi.org/10.1016/j.apcatb.2016.09.072

3. Moioli E, Schildhauer T. Negative CO2 emissions from flexible biofuel synthesis: Concepts, potentials, technologies. Vol. 158, Renewable and Sustainable Energy Reviews. Elsevier Ltd; 2022.
4. Sun D, Khan FM, Simakov DSA. Heat removal and catalyst deactivation in a Sabatier reactor for chemical fixation of CO2: Simulation-based analysis. Chemical Engineering Journal [Internet]. 2017;329:165–77. Available from: http://dx.doi.org/10.1016/j.cej.2017.06.160
5. Zhang J, Fatah N, Capela S, Kara Y, Guerrini O, Khodakov AY. Kinetic investigation of carbon monoxide hydrogenation under realistic conditions of methanation of biomass derived syngas. Fuel [Internet]. 2013;111:845–54. Available from: http://dx.doi.org/10.1016/j.fuel.2013.04.057
6. Lefebvre S, Chaouki J, Guy C. Solid Phase Hydrodynamics of Three-Phase Fluidized Bed Reactors – A Convective / Dispersive Phenomena Solid Phase Hydrodynamics of Three-Phase Fluidized Bed Reactors – A Convective / Dispersive Phenomena. International Journal of Chemical Reactor Engineering. 2007;5.
7. Uglietti R, Bracconi M, Maestri M. Development and assessment of speed-up algorithms for the reactive CFD-DEM simulation of fluidized bed reactors. React Chem Eng. 2020 Feb 1;5(2):278–88.
8. Moioli E, Senn P, Østrup S, Hütter C. Results from the operation of an efficient and flexible large-scale biogas methanation system. Energy Advances. 2023;3(1):131–42.
9. Kopyscinski J, Schildhauer TJ, Vogel F, Biollaz SMA, Wokaun A. Applying spatially resolved concentration and temperature measurements in a catalytic plate reactor for the kinetic study of CO methanation. J Catal. 2010 May 4;271(2):262–79.
10. Koschany F, Schlereth D, Hinrichsen O. On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)x. Appl Catal B [Internet]. 2016;181:504–16. Available from: http://dx.doi.org/10.1016/j.apcatb.2015.07.026
11. Chemical Reaction Engineering - Octave Levenspiel - Google Libri [Internet]. [cited 2025 Mar 5]. Available from: https://books.google.ch/books?hl=it&lr&id=vw48EAAAQBAJ&oi=fnd&pg=PP1&dq=chemical+reaction+engineering+levenspiel&ots=5y-Zju7O2B&sig=YlACK-vHrI0cYXzPPt9B0wjeS6ww&redir_esc=y#v=onepage&q=chemical%20reaction%20engineering%20levenspiel&f=false
12. Abashar MEE, Al-Rabiah AA. Investigation of the efficiency of sorption-enhanced methanol synthesis process in circulating fast fluidized bed reactors. Fuel Processing Technology [Internet]. 2018;179(July):387–98. Available from: https://doi.org/10.1016/j.fuproc.2018.07.028
13. Lefebvre S, Guy C, Chaouki J. A convective/dispersive solid phase mixing model for three-phase fluidized bed reactors: Effect of dimensionless numbers. Chem Eng Sci. 2007;62(18–20):4954–62.
