# $CO_2$ Adsorption Kinetic Modeling for Power-to-Methane Simulations

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## Summary

Empirical TGA data of $CO_2$ adsorption on various solids were used to fit adsorption kinetic models, notably polynomial and nonlinear. Model adequacy was evaluated against laboratory experimental data using statistical parameters. This research aims to deepen detailed understanding of methanation mechanisms to produce synthetic natural gas (SNG) from renewable hydrogen.

## Introduction

In last years, the energy transition no longer focuses exclusively on replacing fossil fuels with renewable generation sources, but extends its integration across all sectors through the so-called "*sector coupling*" [1].

For such sectoral coupling to be effective, it is essential to counteract the intermittency of supply from renewable energies. By taking advantage of production surpluses, it is possible to generate energy vectors such as hydrogen or methane, which allow energy storage and guarantee the desired supply.

One of the technologies that has demonstrated the potencial for large-scale implementation in recent years is known as *Power to Methane* (P2M) [2]. In this process, the energy vector, methane, is obtained by combining $CO_2$ and renewable hydrogen (from electrolysis processes) through the *Sabatier* reaction (r.1).

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \text{(r.1)}$$

However, scaling up an integrated P2M scheme faces economic and technical challenges that hinder significant investment as well as non-negligible CAPEX costs. Electrolyzers still remain costly and with room for improvement. Moreover, the volatility of the $CO_2$ emission consts (20–80 €/t in just a few years) [3] and fluctuations in renewable electricity tariffs add further uncertainty. To mitigate these risks, it is essential to have a comprehensive simulator that covers $CO_2$ adsorption, accurately models catalytic methanation kinetics, and evaluates possible economic scenarios.

Thanks to this tool, different sorbents, column configurations, and reactor conditions could be virtually explored. On this way, the simulator shortens development timelines and provides reliable data for decision making before deploying any pilot or commercial plant with a significantly reduced financial risk.

## Experimental

To describe the kinetics of $CO_2$ adsorption on the different materials, the *Linear Driving Force* (LDF) model (Eq.1) has been initially chosen in its simplest form, assuming first-order behavior [4]. This choice stems from the desire to work with a linear differential equation, whose analytical solution simplifies the initial data fitting and the interpretation of kinetic parameters. The resulting expression is formulated as follows (Eq.1):

$$\frac{dq(t)}{dt} = k_{LDF} \cdot [q_{eq} - q(t)] \qquad \text{(Eq.1)}$$

Where, $q(t)$ is the amount of $CO_2$ adsorbed on the particle at time t, $q_{eq}$ is the equilibrium value at a given $CO_2$ partial pressure, and $k_{LDF}$ is the apparent kinetic constant. Under this hypothesis, the solution is immediate, which allows extracting $k_{LDF}$ by performing a linear fit of $ln[q_{eq} - q(t)]$ versus t.

Although the first-order LDF model is useful as an initial approximation, in practice $CO_2$ adsorption deviates significantly from this simplified model. Therefore, a nonlinear model has been explored in which the rate dependence is generalized to an order $n \neq 1$. In this formulation, the equation is written as follows (Eq.2).

$$\frac{dq(t)}{dt} = k_n * [q_{eq} - q(t)]^n \qquad \text{(Eq.2)}$$

In this formulation, $k_n$ represents a kinetic constant that is determined by nonlinear fitting. For such purpose, a *MATLAB*® script has been developed for minimizing the squared error. Likewise, the same procedure has been applied to fit the parameters of other fitting theoretical models such as *Avrami* or *Veneman* [5].

After the initial experimental phase, focused on comparing different kinetic models of $CO_2$ adsorption on the selected materials, methanation has been included in the same simulation scheme. On this way, a complete model has been developed that describes both adsorption and chemical reaction, allowing analysis of the spatial distribution of concentrations and temperatures within the reactor.

# Results and conclusions

The comparison between the linear fit (first-order LDF model) and the nonlinear fit (free exponent) shows that the latter describes the experimental $CO_2$ adsorption kinetics with greater accuracy, a fact corroborated both by the results presented in **Figure 1**, and the statistical parameters shown in **Table 1**.

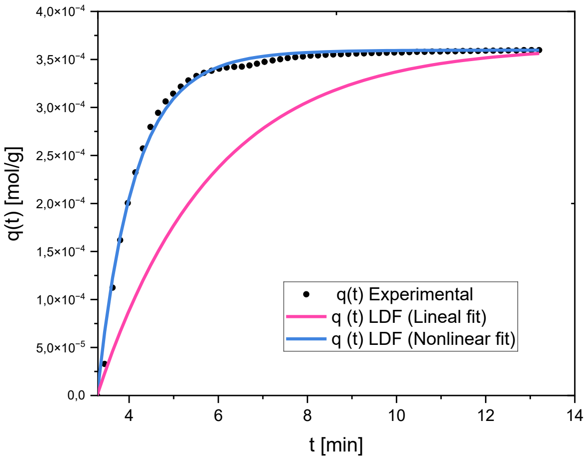

***Figure 1. Experimental adsorption data, q(t), and modeled values using a linear and nonlinear LDF fit versus time, t. Total flow 150 mL/min; Temperature 400 °C; Adsorbent solid $Na_2O$; Catalyst NiFe supported on $Al_2O_3$.***

**Table 1.- Statistical data (Root Mean Square Error, RMSE; Mean Absolute Error, MAE; Coefficient of determination, $R^2$) comparing the LDF model with linear and nonlinear fitting**

| Model | RMSE | MAE | $R^2$ |
|---|---|---|---|
| LDF (Lineal fit) | 0.00007 | 0.00005 | 0.10 |
| LDF (Nonlinear fit) | 0.000006 | 0.000004 | 0.99 |

Moreover, **Figure 2** presents the residuals for the optimal model identified in **Figure 1** (the nonlinear LDF fit) plotted against time. These residuals remain small in magnitude and are scattered randomly around zero throughout the entire adsorption period, with no discernible trend or systematic deviation at any period of time.

The random, uniformly distributed residuals demonstrate that the nonlinear fit accurately represents $CO_2$ adsorption kinetics across all time points. This confirms that the free-exponent LDF model remains precise and unbiased under the specified conditions.

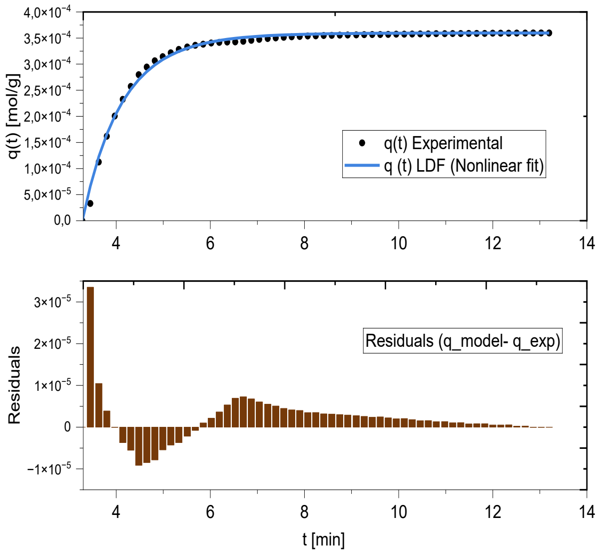

***Figure 2. Residuals of the nonlinear LDF fit (free-exponent model) plotted against time for $CO_2$ adsorption on $Na_2O/NiFe\text{-}Al_2O_3$ at 400 °C and 150 mL/min***

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