CO₂ conversion enhancement in a periodically operated Sabatier reactor: Nonlinear frequency response analysis and simulation-based study

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Highlights
- Nonlinear frequency response (NFR) analysis was applied on a Sabatier reactor.  
- A substantial improvement in CO₂ conversion was predicted under certain conditions.  
- The NFR analysis prediction was validated using a kinetic flow reactor model.  
- A comprehensive packed bed model was analyzed using NFR as a guidance.

1. Introduction
The increasing levels of global CO₂ emissions has prompted research in utilizing CO₂ as a feedstock for generating synthetic fuels and chemical [1]. The current industrial usage of CO₂ is limited to processes such as synthesis of urea, salicylic acid and polycarbonates. Conversion of CO₂ into synthetic CH₄ (the Sabatier reaction, accompanied by reverse water gas shift and CO methanation), has recently gained increasing interest as a technologically advantageous route for CO₂ utilization [1]:

\[
\begin{align*}
\text{CO}_2 &+ 4\text{H}_2 \leftrightharpoons \text{CH}_4 + 2\text{H}_2\text{O} & \Delta H_{298K}^e &= -164.9 \text{ kJ/mol} \\
\text{CO}_2 &+ \text{H}_2 \leftrightharpoons \text{CO} + \text{H}_2\text{O} & \Delta H_{298K}^e &= +41.2 \text{ kJ/mol} \\
\text{CO} &+ 3\text{H}_2 \leftrightharpoons \text{CH}_4 + 2\text{H}_2\text{O} & \Delta H_{298K}^e &= -206.1 \text{ kJ/mol}
\end{align*}
\]

Microchannel, monolith, three-phase slurry, and fluidized bed reactors were suggested as design solutions for carrying out CO₂ methanation, as well as the packed bed configuration [2, 3]. Thermal management remains one of the main problems, as the overall process is highly exothermic requiring efficient heat removal to drive the CH₄ formation and, importantly, to prevent catalyst deactivation [2, 3]. It is of crucial importance therefore to increase the CO₂ conversion at low temperatures. Herein, we demonstrate the use of the Nonlinear Frequency Response (NFR) technique to predict the CO₂ conversion enhancement induced by periodic operation.

2. Methods
The nonlinear frequency response (NFR) method is an approximate, analytical method, mathematically based on Volterra series and generalized Fourier transform, which uses the concept of higher order frequency response functions (FRFs) in order to predict whether, at which conditions, and to which extent, a reactor performance can be improved by periodic modulation of one or more input variables [4]. In this work the NFR method was applied to analyze the kinetic flow model of the Sabatier reaction described by a set of five material balances represented by the following dimensionless equation:

\[
\frac{du}{d\tau} = u_i - u + D\alpha \left( \alpha_1\kappa_1 f_1 + \alpha_2\kappa_2 f_2 + \alpha_3 f_3 \right)
\]

In the above equation, \(i\) stands for CO₂, H₂, CH₄, CO, and H₂O, i.e., all species participating, Eqs. (1-3), while \(f_1-f_3\) represent dimensionless reaction terms with stoichiometric coefficients \(\alpha_1-\alpha_3\). \(Da\) stands for the Damköhler number and \(u_i\) is a dimensionless concentration. Guided by the NFR analysis, an isothermal packed bed reactor model was investigated (\(C_i\) stands for the molar concentration of species \(i\)):

\[
\begin{align*}
\varepsilon \frac{\partial C_i}{\partial t} &= D\frac{\partial^2 C_i}{\partial z^2} - \varepsilon v_g \frac{\partial C_i}{\partial z} + \rho_i (1 - \varepsilon) \sum_j \eta_j R_{ij}
\end{align*}
\]
3. Results and discussion

A typical output from the NFR analysis is shown in Fig. 1, where a substantial improvement in CO\textsubscript{2} conversion obtained by the periodic modulation of the inlet flow rate is demonstrated.

This improvement was validated by numerical simulations using a kinetic flow model, Eq. (4), Fig. 2. Interestingly, similar effects were observed in the distributed, packed bed reactor model subject to periodic fluctuations, Fig. 3.

4. Conclusions

For the first time, we have demonstrated that the Nonlinear Frequency Response (NFR) analysis can be used to predict the enhancement of the conversion of CO\textsubscript{2} in the Sabatier reaction at low temperatures. Our findings are of great importance for advancing the field of the thermocatalytic CO\textsubscript{2} conversion.

References


Keywords
Sabatier reactor; periodic operation; nonlinear frequency response.