CO_2 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 CO_2 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 CO_2 emissions has prompted research in utilizing CO_2 as a feedstock for generating synthetic fuels and chemical [1]. The current industrial usage of CO_2 is limited to processes such as synthesis of urea, salicylic acid and polycarbonates. Conversion of CO_2 into synthetic CH_4 (the Sabatier reaction, accompanied by reverse water gas shift and CO methanation), has recently gained increasing interest as a technologically advantageous route for CO_2 utilization [1]:

$$\mathrm{CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O} \qquad \Delta H^{\circ}_{298K} = -164.9 \text{ kJ/mol} \tag{1}$$

$$\mathrm{CO_2 + H_2 \rightleftarrows CO + H_2O} \qquad \Delta H^{\circ}_{298K} = +41.2 \text{ kJ/mol} \tag{2}$$

$$\mathrm{CO + 3H_2 \rightleftarrows CH_4 + H_2O} \qquad \Delta H^{\circ}_{298K} = -206.1 \text{ kJ/mol} \tag{3}$$

Microchannel, monolith, three-phase slurry, and fluidized bed reactors were suggested as design solutions for carrying out CO_2 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 CH_4 formation and, importantly, to prevent catalyst deactivation [2, 3]. It is of crucial importance therefore to increase the CO_2 conversion at low temperatures. Herein, we demonstrate the use of the Nonlinear Frequency Response (NFR) technique to predict the CO_2 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:

$$\frac{du_i}{d\tau} = u_{if} - u_i + Da\left(\alpha_{i1}\kappa_1 f_1 + \alpha_{i2}\kappa_2 f_2 + \alpha_{i3} f_3\right) \tag{4}$$

In the above equation, i stands for CO_2, H_2, CH_4, CO, and H_2O, i.e., all species participating, Eqs. (1-3), while f_1-f_3 represent dimensionless reaction terms with stoichiometric coefficients α_1-α_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):

$$\varepsilon \frac{\partial C_i}{\partial t} = D_{ae}\frac{\partial^2 C_i}{\partial z^2} - \varepsilon v_g \frac{\partial C_i}{\partial z} + \rho_s (1-\varepsilon)\sum_j \eta_j R_{ij} \tag{5}$$

3. Results and discussion

A typical output from the NFR analysis is shown in Fig. 1, where a substantial improvement in CO_2 conversion obtained by the periodic modulation of the inlet flow rate is demonstrated.

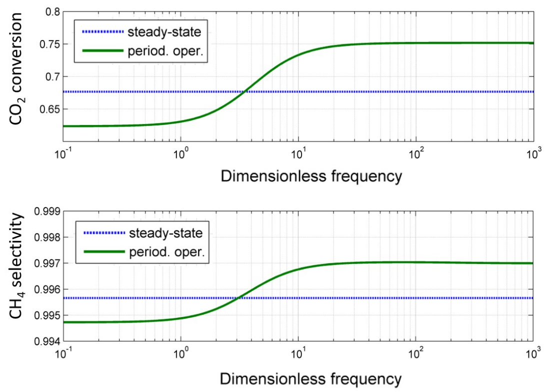

Figure 1. NFR analysis applied on the Sabatier reaction system: blue lines represent steady state conversions obtained with constant input.

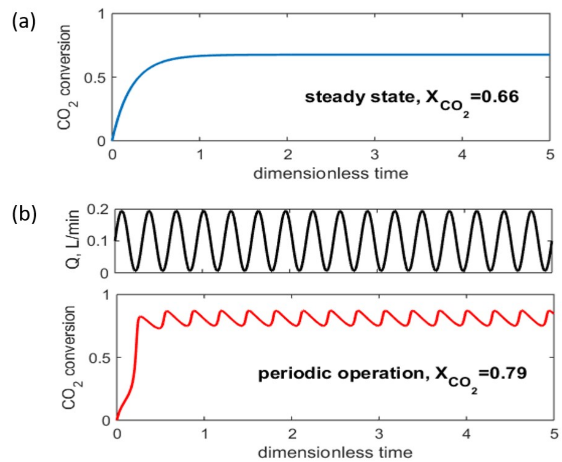

Figure 2. Numerical simulations of the flow model, Eq. (4) with constant and modulated feed rate (same average feed flow rate).

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.

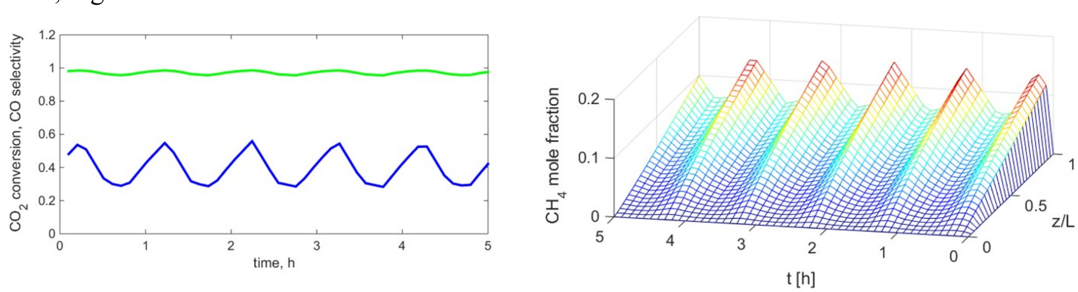

Figure 3. Time evolution of CO_2 conversion (blue line) and CH_4 selectivity (green line) (left panel) and spatio-temporal evolution of CH_4 mole fraction obtained by the periodic modulation of the inlet flow rate (steady state conversion was 0.2).

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_2 in the Sabatier reaction at low temperatures. Our findings are of great importance for advancing the field of the thermocatalytic CO_2 conversion.

References

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Keywords
Sabatier reactor; periodic operation; nonlinear frequency response.