CO₂ CONVERSION ENHANCEMENT IN A PERIODICALLY OPERATED SABATIER REACTOR: NONLINEAR FREQUENCY RESPONSE ANALYSIS AND SIMULATION-BASED STUDY

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Introduction

**Forced periodic operations**
- One aspect of Process Intensification
- In some cases, the process performance can be enhanced by periodic modulation of some inputs around a chosen steady-state

**Nonlinear Frequency Response Method**
- Frequency response of a stable weakly nonlinear system is defined by a set of Frequency Response Functions (FRFs) of the first, second, third, … order \((G_j(\omega), \ G_j(\omega,\alpha), \ G_j(\omega,\alpha,\beta), \ldots)\)
- The FR consists of infinite number of harmonics and a non-periodic term

\[
\begin{align*}
\gamma &= y_{nc} + B_1 \cos(\omega t) + B_2 \cos(2\omega t) + B_3 \cos(3\omega t) + \ldots,
\end{align*}
\]

- \(y_{nc}\) – the non-periodic term – responsible for average performance of the periodic process – defines the process improvement through periodic operation (\(\Delta \equiv y_{nc}\))

- NFR method: \(y_{nc}\) – non-periodic term proportional to \(G_j(\omega,\alpha)\) – the asymmetrical second order (ASO) FRF
- Applicable to single and multiple input modulation
- Applicable to any shape of the periodic input

**THIS WORK: Application to Sabatier reaction**

\[
\begin{align*}
\text{CO} + 3\text{H}_2 &\rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{\text{f,0}}^{0} = -206.1 \text{kJ/mol} \\
\text{CO} + \text{H}_2 &\rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{\text{f,0}}^{0} = -41.2 \text{kJ/mol} \\
\text{CO} + 4\text{H}_2 &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{\text{f,0}}^{0} = -164.9 \text{kJ/mol}
\end{align*}
\]

**Mathematical model:**
- **Model assumptions:** CSTR, isothermal, diluted reaction system, constant total pressure
- **Model equations (dimensionless):**

\[
\begin{align*}
\frac{dx}{dt} = u_0 + Da (\alpha \Delta k_{f_1} + \alpha \Delta k_{f_2} + \alpha \Delta k_{f_3}) \\
\Delta k_{f_1} = \frac{k_{f_1} \Delta X_{\text{CO}} \Delta t}{k_{f_1} \Delta X_{\text{CO}} \Delta t + k_{f_2} \Delta X_{\text{CO}} \Delta t + k_{f_3} \Delta X_{\text{CO}} \Delta t}
\end{align*}
\]

**Kinetic model** (adapted from J. Xu, G. F. Frontczak, AIChE J. 1988, 35, 95-101)

\[
\begin{align*}
f_1 &= -\frac{k_{f_1} X_{\text{CO}}^a X_{\text{H}_2}^b X_{\text{H}_2}\text{O} c}{k_{f_1} X_{\text{CO}}^a X_{\text{H}_2}^b X_{\text{H}_2}\text{O} c + k_{f_2} X_{\text{CO}}^a X_{\text{H}_2}^b X_{\text{H}_2}\text{O} c + k_{f_3} X_{\text{CO}}^a X_{\text{H}_2}^b X_{\text{H}_2}\text{O} c}
\end{align*}
\]

**RESULTS – CO₂ conversion for flow-rate modulation**

**Some numerical examples**

\[
\begin{align*}
T = 500 K, \ \chi = 42.46 \% \\
T = 550 K, \ \chi = 74.14 \% \\
T = 600 K, \ \chi = 86.73 \%
\end{align*}
\]