CO_2 CONVERSION ENHANCEMENT IN A PERIODICALLY OPERATED SABATIER REACTOR: NONLINEAR FREQUENCY RESPONSE ANALYSIS AND SIMULATION-BASED STUDY

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Introduction

Forced periodic operations

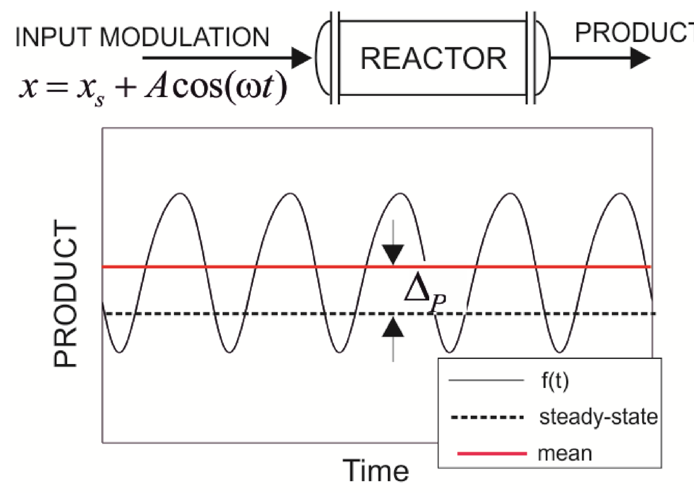
- One aspect of Process Intensification
- In some cases, the process performance can be enhanced by periodic modulation of some inputs around a chosen steady-state

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 ($G_1(\omega)$, $G_2(\omega_1,\omega_2)$, $G_3(\omega_1,\omega_2,\omega_3)$,...)
- The FR consists of indefinite number of harmonics and a non-periodic term

$$y = y_{DC} + B_I\cos(\omega t+\varphi_I) + B_{II}\cos(2\omega t+\varphi_{II}) + B_{III}\cos(3\omega t+\varphi_{III}) + \cdots$$

- y_{DC} – *the non-periodic term* – responsible for average performance of the periodic process – defines the process improvement through periodic operation ($\boldsymbol{\Delta \equiv y_{DC}}$)
- **NFR method: y_{DC} –** *non-periodic term* proportional to $G_2(\omega,-\omega)$ – the asymmetrical second order (ASO) FRF
- Applicable to single and multiple input modulation
- Applicable to any shape of the periodic input



$$\Delta_P \approx 2\left(\frac{A}{2}\right)^2 G_{P2,XX}(\omega,-\omega)$$

THIS WORK: Application to Sabatier reaction

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^o_{298} = -206.1\,\text{kJ/mol}$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^o_{298} = -41.2\,\text{kJ/mol}$$
$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H^o_{298} = -164.9\,\text{kJ/mol}$$

Mathematical model:

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

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

i =CO_2, H_2, CH_4, CO, and H_2O

$$u_i = \frac{c_i}{c_{tf}} \qquad \tau = \frac{t}{L/v_g} \qquad Da = \frac{W_c k_3}{F_{tf}\sqrt{P}}$$

$$\kappa_1 = \frac{k_1}{k_3} = \frac{A_1}{A_3}\exp\left(\frac{E_{a3}-E_{a1}}{R_g T}\right)$$

$$\kappa_2 = \frac{P^{1.5}k_2}{k_3} = \frac{P^{1.5}A_2}{A_3}\exp\left(\frac{E_{a3}-E_{a2}}{R_g T}\right)$$

CO_2 conversion
In periodic conditions

$$X_{av,CO_2} = \frac{u_{CO_2,f}F_{tf,ss} - \left(u_{CO_2}F_{tf}\right)^m}{u_{CO_2,f}F_{tf,ss}}$$

Kinetic model

(addapted from J. Xu, G. F. Froment, *AIChE J.* **1989**, *35*, 88-96.)

$$f_1 = \frac{1}{\sqrt{\delta}}\frac{u_{CH_4}u_{H_2O}}{u_{H_2}^{2.5}} - \delta^{1.5}\frac{u_{H_2}^{0.5}u_{CO}}{k_{1,eq}}$$

$$f_2 = \delta\left(\frac{u_{CO}u_{H_2O}}{u_{H_2}} - \frac{u_{CO_2}}{k_{2,eq}}\right)$$

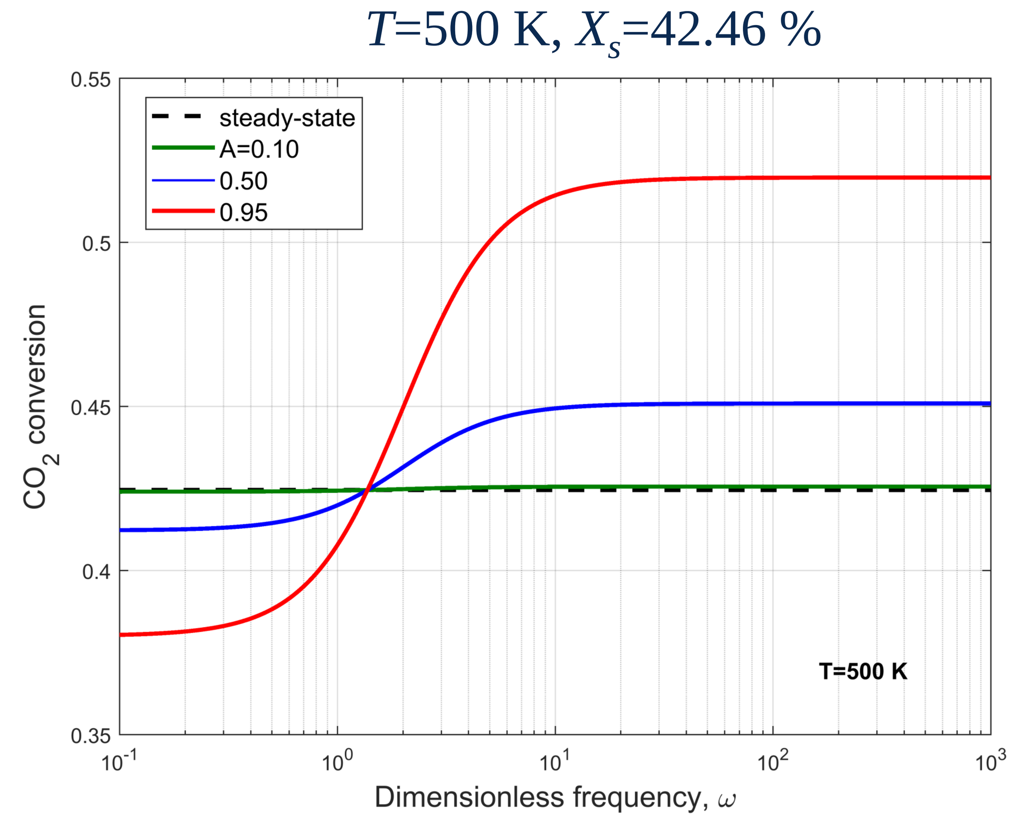
$$f_3 = \frac{1}{\sqrt{\delta}}\frac{u_{CH_4}u_{H_2O}^2}{u_{H_2}^{3.5}} - \delta^{1.5}\frac{u_{H_2}^{0.5}u_{CO_2}}{k_{3,eq}}$$

$$k_{j,eq} = \frac{K_{j,eq}}{P^2}\quad j=1,3; \qquad k_{2,eq} = K_{2,eq}$$

Model parameters from in-house Measurements (Uni. Waterloo)

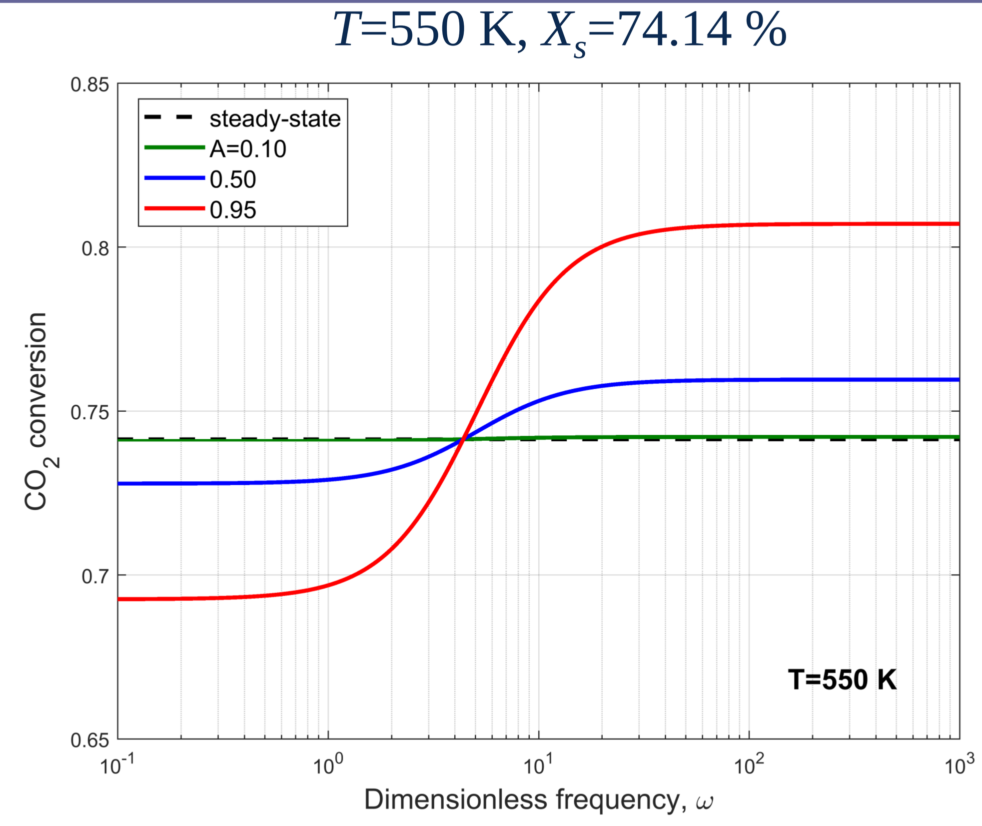
RESULTS – CO_2 conversion for flow-rate modulation

T=500 K, X_s=42.46 %



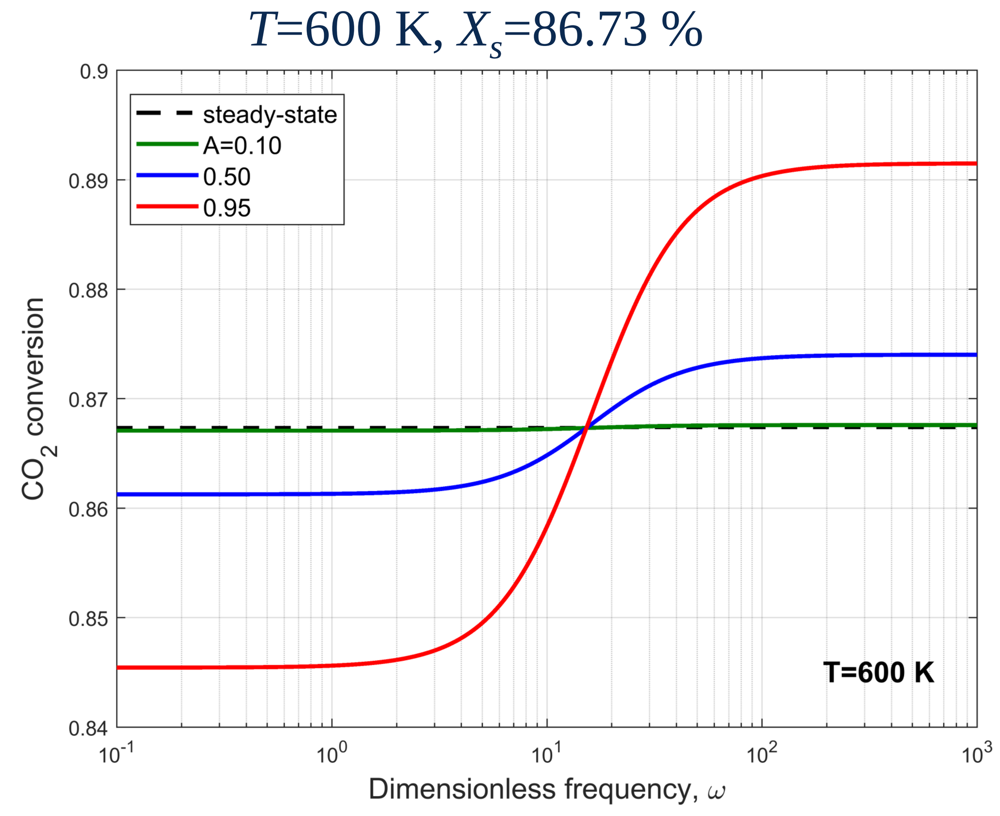
	Forcing amplitudes								
	0.10			0.50			0.95		
ω	X_{CO_2} (%) *num*	X_{CO_2} (%) *NFR*	σ (%)	X_{CO_2} (%) *num*	X_{CO_2} (%) *NFR*	σ (%)	X_{CO_2} (%) *num*	X_{CO_2} (%) *NFR*	σ (%)
0.1	42.41	42.41	0	41.21	41.23	0.05	37.12	38.04	2.5
10	42.56	42.56	0	45.46	44.94	-1.1	63.42	51.43	-18.9

T=550 K, X_s=74.14 %



	Forcing amplitude								
	0.10			0.50			0.95		
ω	X_{CO_2} (%) num	X_{CO_2} (%) NFR	σ (%)	X_{CO_2} (%) num	X_{CO_2} (%) NFR	σ (%)	X_{CO_2} (%)		σ (%)
1	74.11	74.10	-0.01	73.24	72.91	-0.45	70.57	69.69	-1.25
30	74.22	74.21	-0.01	76.14	75.88	-0.34	86.30	80.40	-6.84

T=600 K, X_s=86.73 %

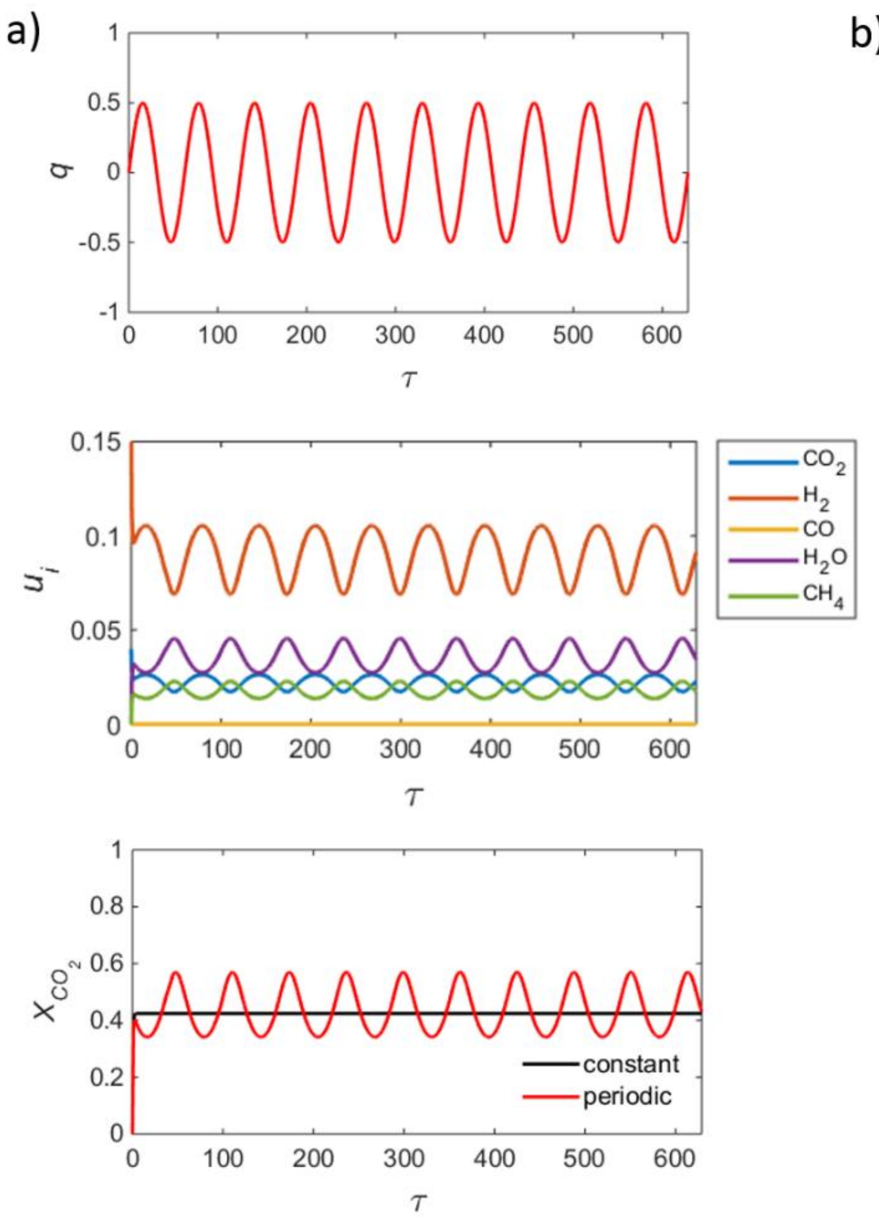


	Forcing amplitude								
	0.10			0.50			0.95		
ω	X_{CO_2} (%) num	X_{CO_2} (%) NFR	σ (%)	X_{CO_2} (%) num	X_{CO_2} (%) NFR	σ (%)	X_{CO_2} (%) num	X_{CO_2} (%) NFR	σ (%)
1	86.71	86.71	0	86.14	86.13	-0.01	84.61	84.56	-0.06
100	86.76	86.76	0	87.45	87.37	-0.09	90.25	89.03	-1.35

Some numerical examples

T = 500 K, ω = 0.1, of A = 50 % (a) and A = 95 % (b)

a)



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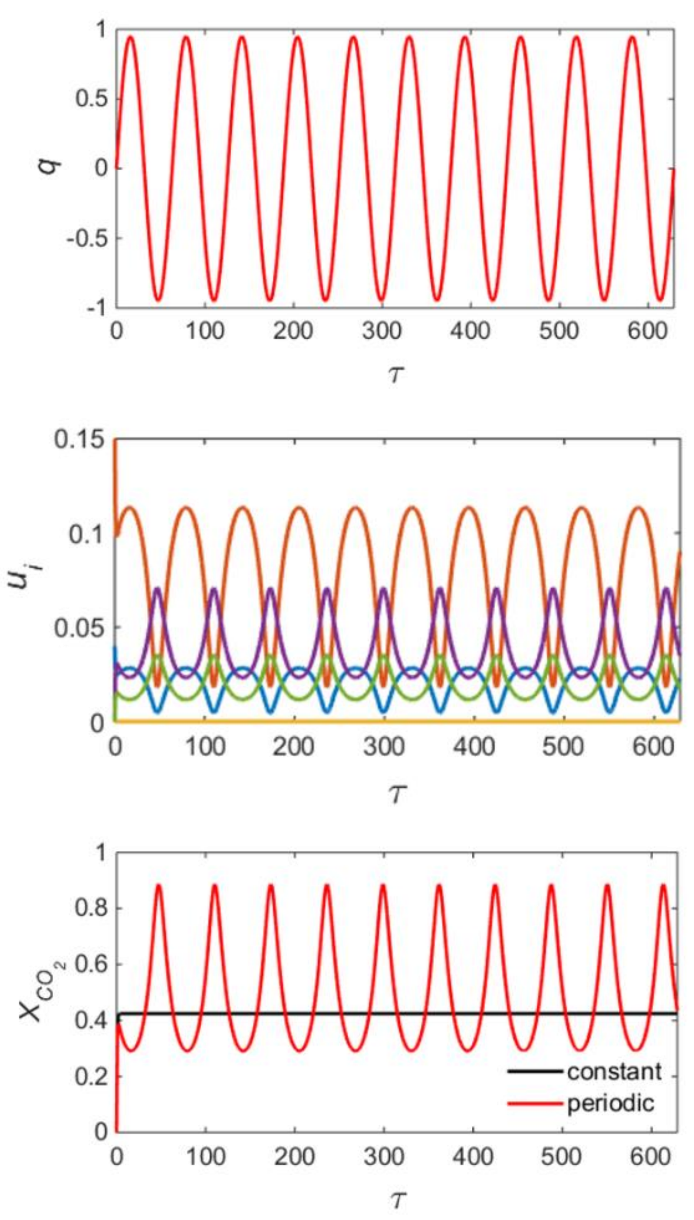
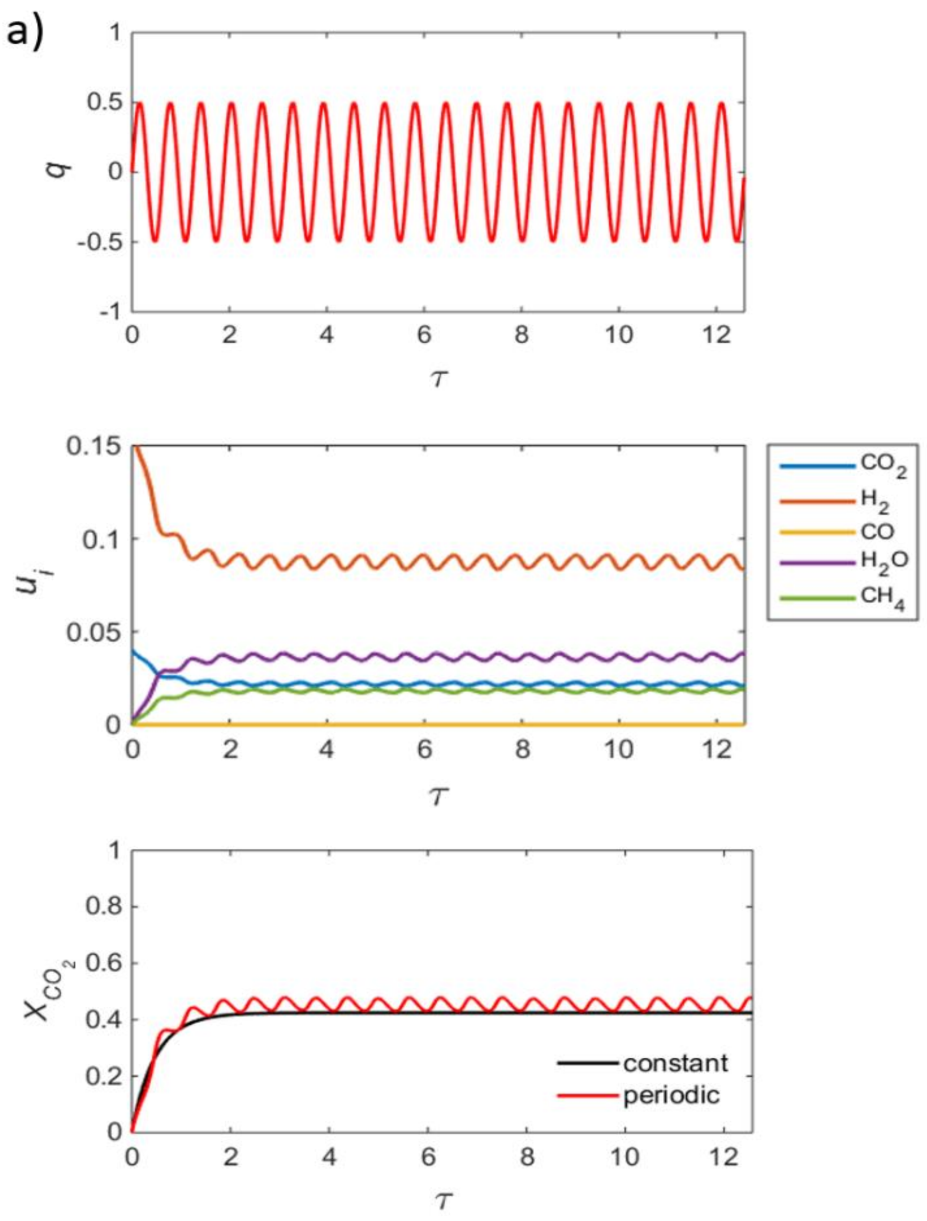


T = 500 K, ω = 10, of A = 50 % (a) and A = 95 % (b)

a)



b)