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Parametric Sensitivity and Thermal Runaway Behavior in Catalytic Fixed-Bed Reactors

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Parametric Sensitivity in Chemical Systems

Effect of wall temperature on

Temperature profiles

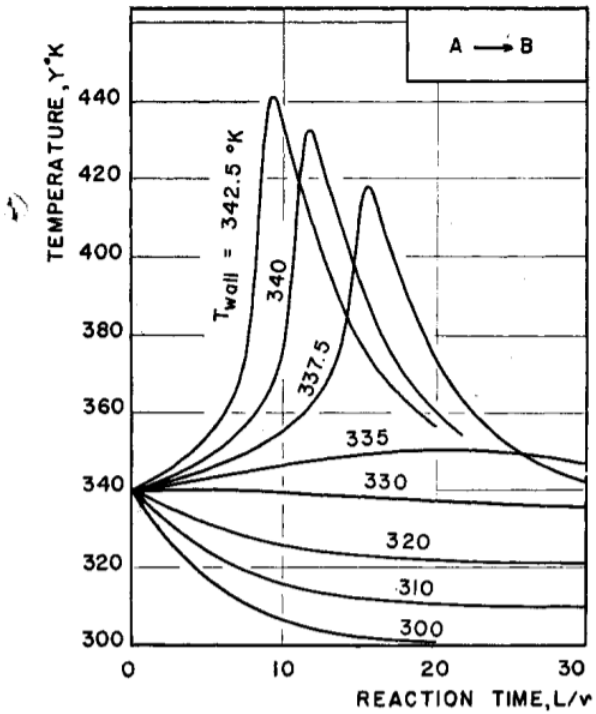


Fig. 2*a*. Temperature profiles in a tubular reactor; effect of wall temperature. E = 22,500, p = 3.94 × 10^{12}, x_i = 0.20, Q = 7,300, K = 0.20, T_i = 340°K.

Concentration profiles

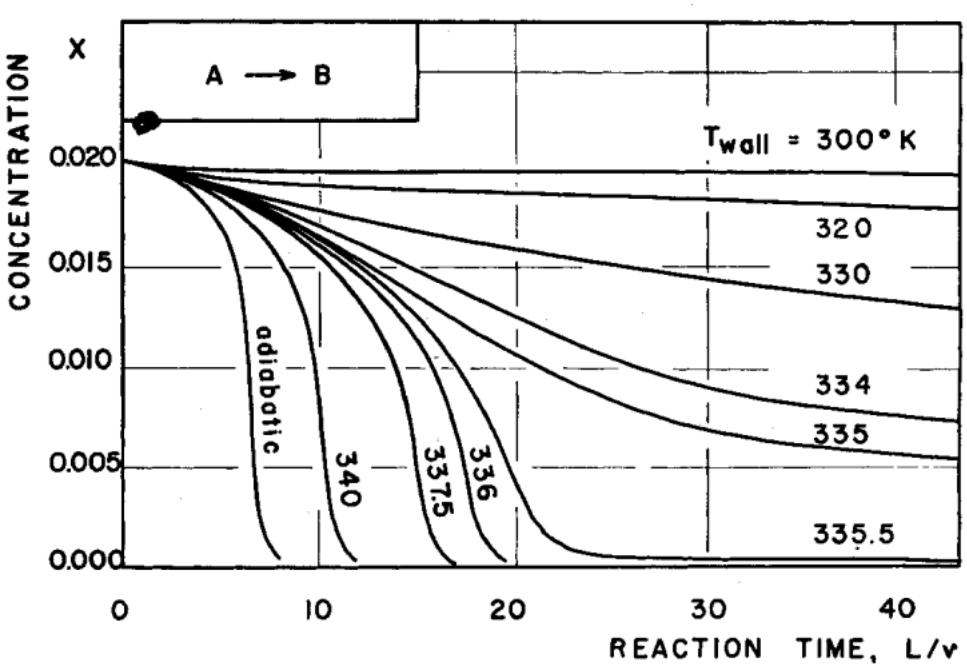


Fig. 2*b*. Concentration profiles in a tubular reactor; effect of wall temperature. Data are the same as in Figure 2*a*.

O. Bilous and N. R. Amundson, *AIChE J.*, 1 (1955), 513-521 **(CSTR)**
O. Bilous and N. R. Amundson, *AIChE J.*, 2 (1956), 117-126 **(PFR)**

Parametric Sensitivity in CSTRs

Unique steady states

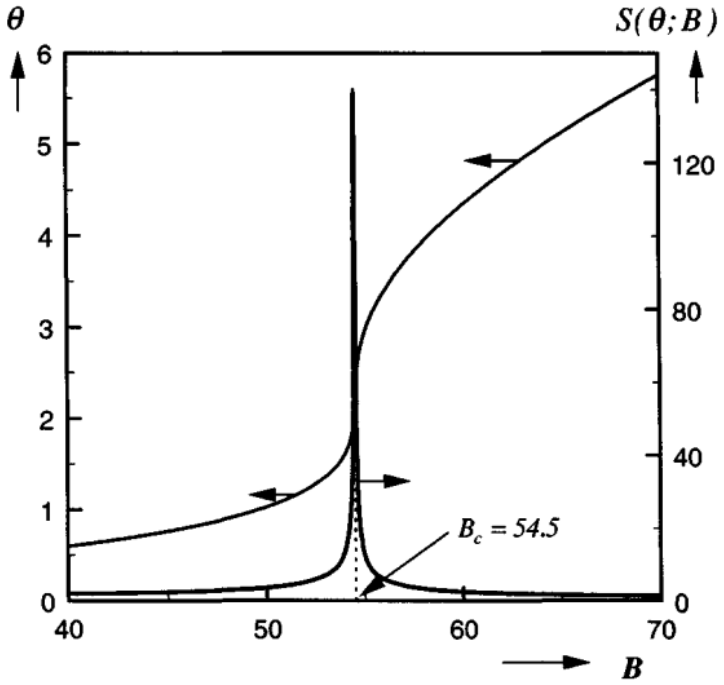


Figure 5.1. Reactor temperature θ and its normalized sensitivity $S(\theta; B)$ as functions of the heat-of-reaction parameter B for a CSTR operating in the region of unique steady states. $Da = 0.11$; $\gamma = 20$; $St = 10$; $n = 1$; $\theta_{co} = 0$. From Chemburkar *et al.* (1986).

Multiple steady states

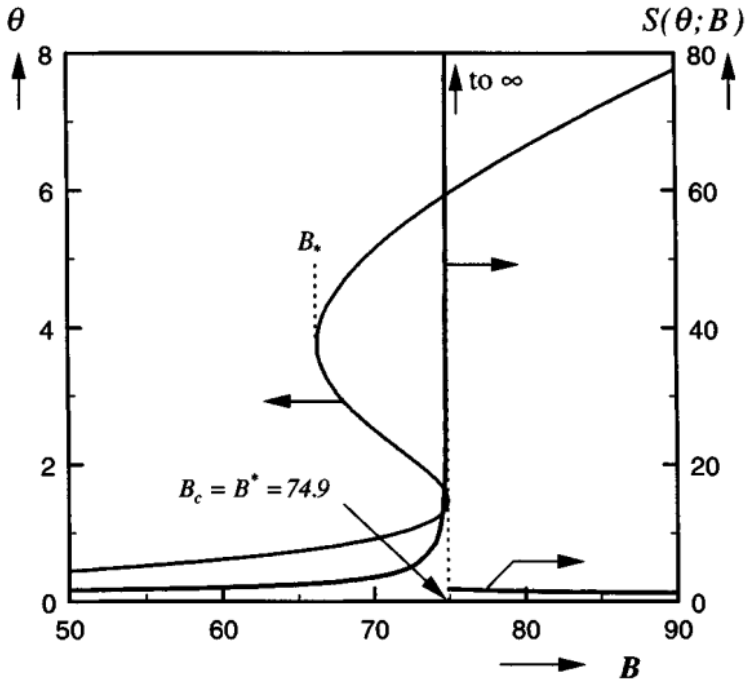
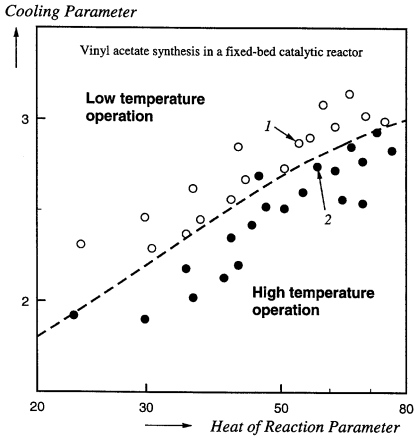


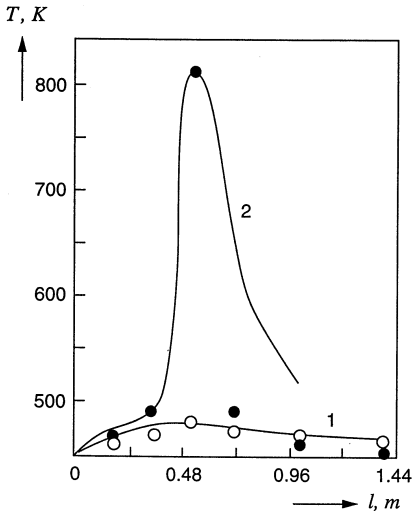
Figure 5.2. Reactor temperature, θ, and its normalized sensitivity, $S(\theta; B)$, as a function of the heat of reaction parameter, B, for a CSTR operating in the region of multiple steady states. $Da = 0.07$; $\gamma = 20$; $St = 10$; $n = 1$; $\theta_{co} = 0$. From Chemburkar, *et al.* (1986).

R. M. Chemburkar, M. Morbidelli, and A. Varma, *Chem. Eng. Sci.*, 41 (1986), 1647-1654

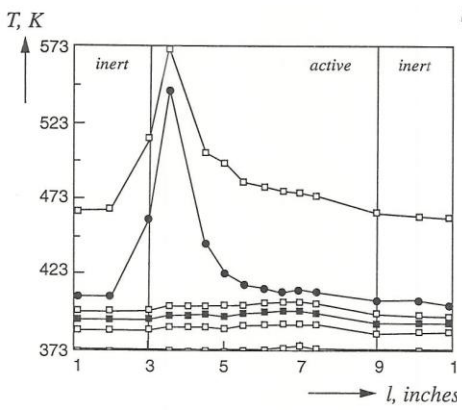
Parametric Sensitivity in Fixed-Bed Reactors

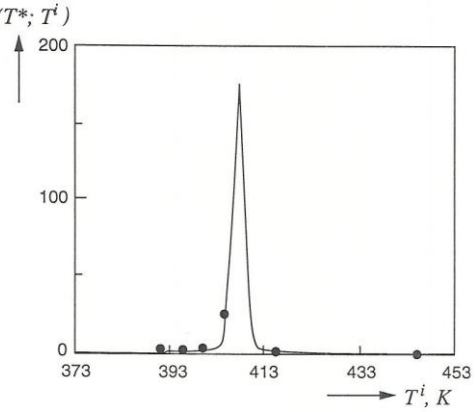
Vinyl Acetate Synthesis





CO Oxidation





G. Emig, H. Hofmann, U. Hoffmann and U. Fiand, *Chem. Eng. Sci.*, 35 (1980), 249-257

A. Varma, M. Morbidelli and H. Wu, *Cambridge University Press,* (1999; 2005)

E. G. Bauman, and A. Varma, *Chem. Eng. Sci.*, 45 (1990), 2133-2139

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Other Topics Investigated

- Selectivity/Yield Issues:
  Parallel or Consecutive Reactions
- Polymerization Reactions
- Sensitivity Analysis in Air Pollution
- Sensitivity Analysis in Metabolic Processes
- Sensitivity Analysis of Combustion Synthesis
- Model Reduction via Sensitivity Analysis

~20 original research papers and monograph:

A. Varma, M. Morbidelli and H. Wu, *Cambridge University Press,* (1999; 2005)

A recent example: Low-temperature oxidation of methanol

40% methanol used for formaldehyde production

Industrial Processes

- **Mo-Fe:**
  250-400 °C, S=95%, X=98%
- **Ag:**
  560-600 °C, S=70%, X=90%
- **Other catalysts:**
  VO_x, Cr-Mo, MoO_3, etc. T=300-500 °C

S = *selectivity to formaldehyde*
X = *methanol conversion*

Target

- ***High selectivity (S > 90-95%) at low temp (< b.p.).***
- ***Long catalyst lifetime***

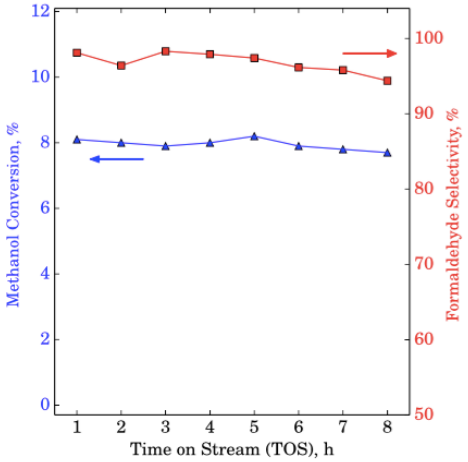
Initial test

Table 5
Representative product compositions of methanol low-temperature oxidation under standard operating conditions.

Product, wt%	1% Pt	1% Pt–0.5% Bi	2% Bi
Methanol	89.6	91.9	99.4
Formaldehyde	0.01	7.95	0.06
Methyl formate	2.44	0.03	0.21
Dimethoxymethane	1.08	0.01	0.12
Formic acid	2.39	0.06	0.16
CO_2	4.48	0.05	0.05

70°C, 1 atm, 0.02 g catalyst, methanol feed rate 0.6 mL/h (liquid, at room temperature), preheated at 70 °C before entering the reactor, total gas flow rate 100 mL/min
methanol b.p.= 65 °C

Stability



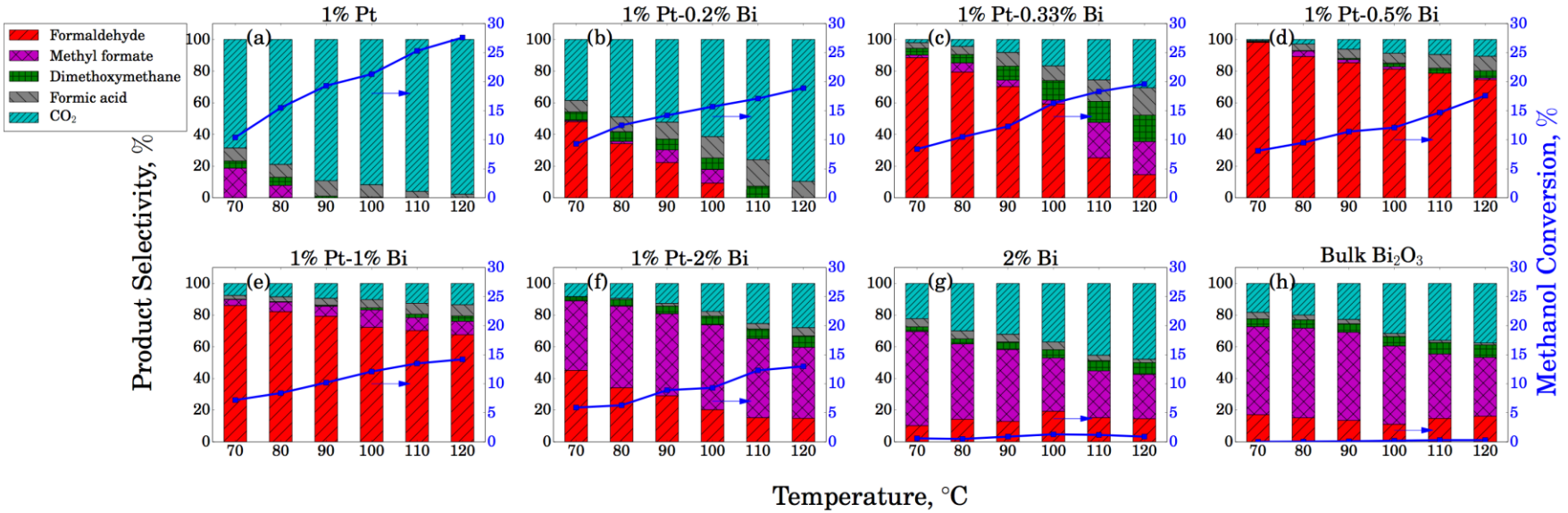
Y. Xiao, Y. Wang and A. Varma, *J. Catal., 363* (2018), 144

Effect of Bi addition

✈ Bi addition to Pt [1]

Tune selectivity for alcohol oxidation, e.g. glycerol to 1,3-dihydroxyacetone

✈ Effects of Bi loading and Temperature [2]



Methanol conversion and selectivity toward formaldehyde over various catalytic materials, (a)–(f) referring to 1% Pt-y % Bi catalysts, when y = (a) 0, (b) 0.2, (c) 0.33, (d) 0.5, (e) 1, (f)2; (g) for 2% Bi and (h) for bulk Bi_2O_3.

1. Y. Xiao *et al.*, *AIChE J.*, 63 (2017), 705
2. Y. Xiao, Y. Wang and A. Varma, *J. Catal., 363* (2018), 144

Trend to Runway

Kinetics and thermodynamics

Table 2: Kinetic and Thermodynamic Paramaters over the 1% Pt-0.5% Bi Catalyst

step	R_1	R_2	R_3	R_4	R_5
carbon-containing product	CH_2O	$C_2H_4O_2$	CH_2O_2	$C_3H_8O_2$	CO_2
$n_{(i,1)}$	1	1	1	1	1
$n_{(i,2)}$	1	1	1	1	1
Ea_i	15.6×10^3	158.0×10^3	95.6×10^3	164.3×10^3	76.9×10^3
A_i	4.35	8.05×10^{16}	4.83×10^{10}	5.24×10^{18}	1.65×10^8
k_i at 343 K	1.86×10^{-2}	6.93×10^{-8}	1.32×10^{-4}	4.97×10^{-7}	3.24×10^{-4}
k_i at 393 K	3.73×10^{-2}	7.99×10^{-5}	9.38×10^{-3}	7.58×10^{-4}	1.00×10^{-2}
ΔH_{ri}	-179.5×10^3	-217.1×10^3	-419.5×10^3	-76.3×10^3	-676.2×10^3

$$r_i = kP_{CH_3OH}^{n_{(i,1)}} P_{O_2}^{n_{(i,2)}}$$

$$P_j = \frac{P_0}{F_0} F_j$$

$$R_1: CH_3OH + \frac{1}{2}O_2 \longrightarrow CH_2O + H_2O$$

ΔH_1=-180 kJ/mol

$$R_2: CH_3OH + \frac{1}{2}O_2 \longrightarrow \frac{1}{2}C_2H_4O_2 + H_2O$$

$$R_3: CH_3OH + O_2 \longrightarrow CH_2O_2 + H_2O$$

$$R_4: CH_3OH + \frac{1}{6}O_2 \longrightarrow \frac{1}{3}C_3H_8O_2 + \frac{2}{3}H_2O$$

$$R_5: CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$

$$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$

ΔH_5=-676 kJ/mol

Side reaction:

- ***strong exothermic***
- ***runaway trend***

Fits of kinetics

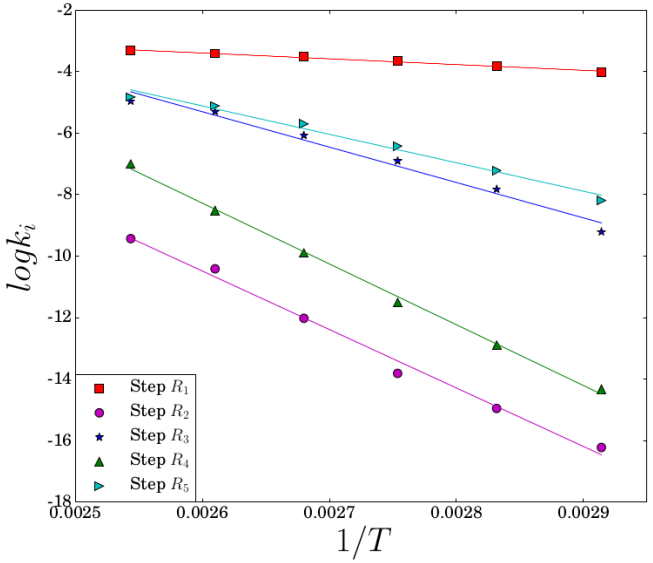
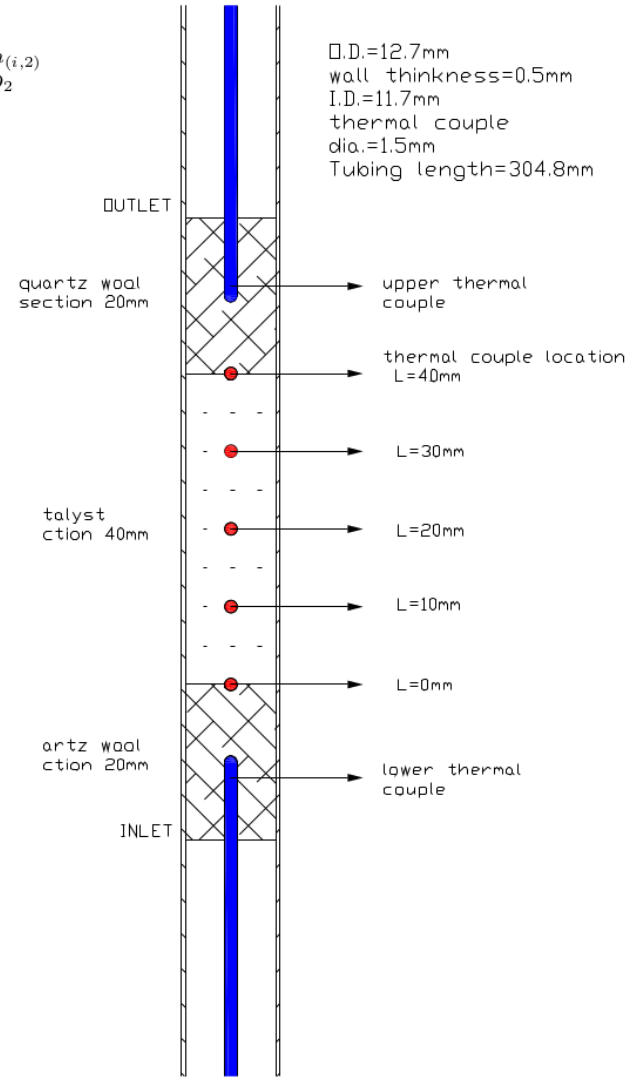


Figure 3: Arrhenius Plots for Rate Constants under Standard Operating Conditions (T_0=343-393 K)

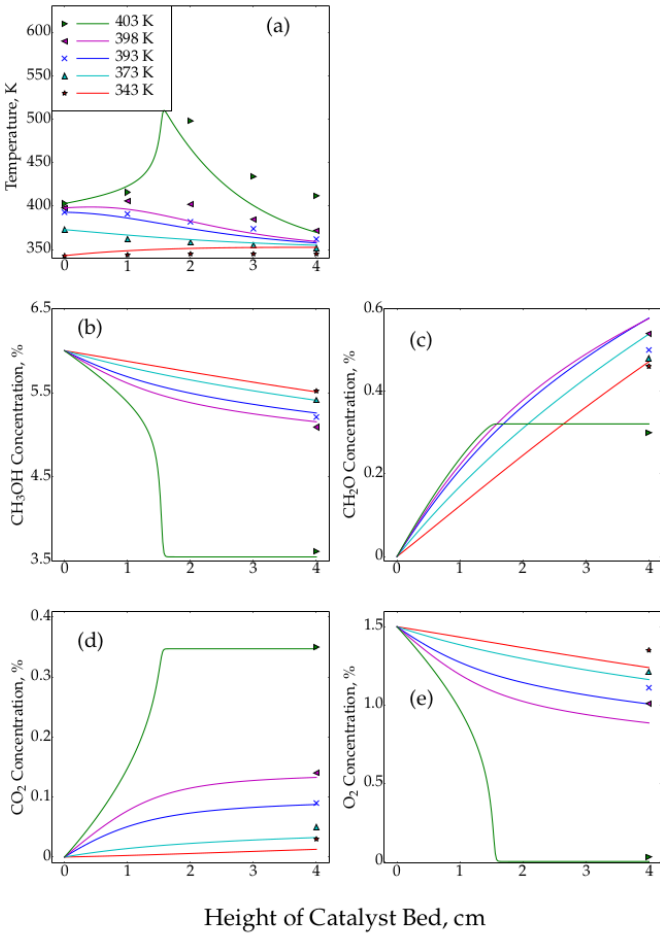
Reactor configuration



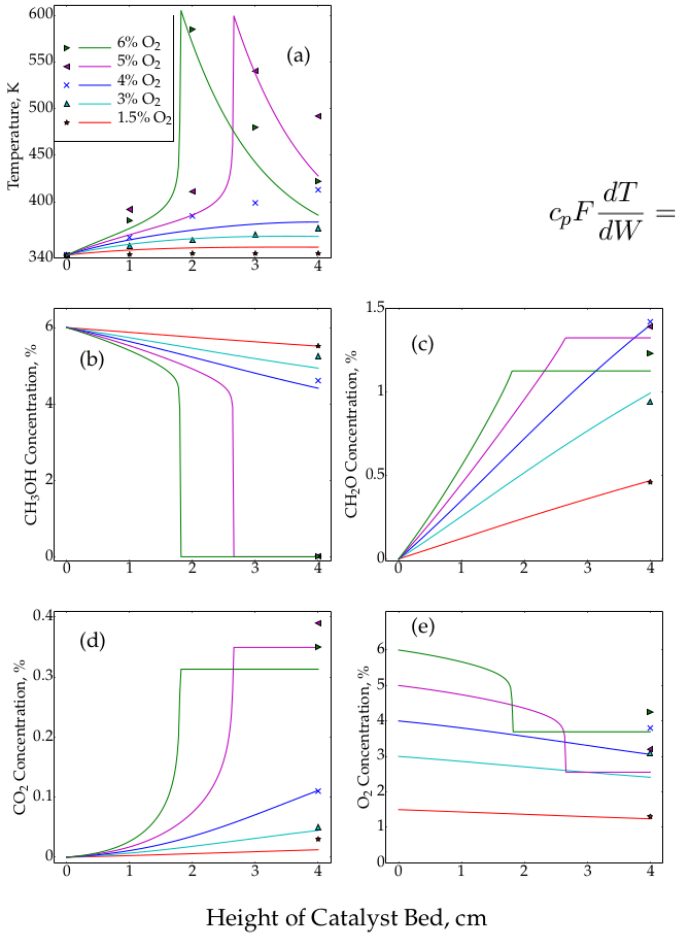
Y. Xiao, and A. Varma, *In preparation*

Runaway: Experiment and Theory

Feed temperature effect



O_2 concentration



One-dimensional model

$$\frac{dF_j}{dW} = \sum_{i,j=1}^{i=5,j=9} \alpha_{(i,j)} r_i$$

$$c_p F \frac{dT}{dW} = \sum_{i=1}^{i=5} (-\Delta H_{ri}) \cdot r_i - \frac{4U}{d_t \rho_{cat}} (T - T_c)$$

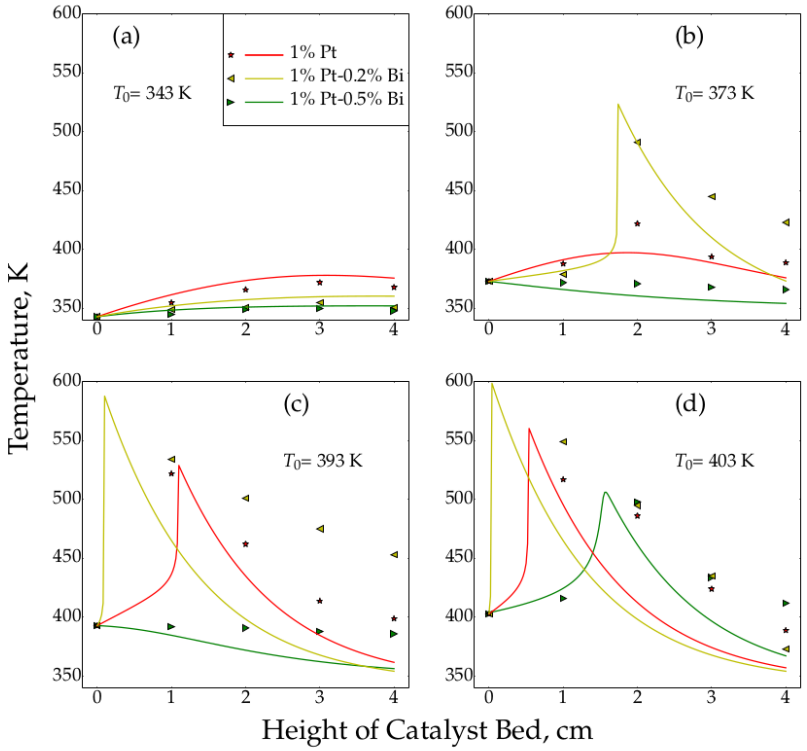
$$\frac{1}{U} = \frac{1}{\alpha_i} + \frac{d}{\lambda} \frac{A_b}{A_m} + \frac{1}{\alpha_u} \frac{A_b}{A_u}$$

Comparison for Experiments and Model Predictions under Standard Operating Conditions over the 1% Pt-0.5% Bi Catalyst for (a) Temperature Profile, (b) CH_3OH Concentration, (c) CH_2O Concentration, (d) CO_2 Concentration (e) O_2 Concentration

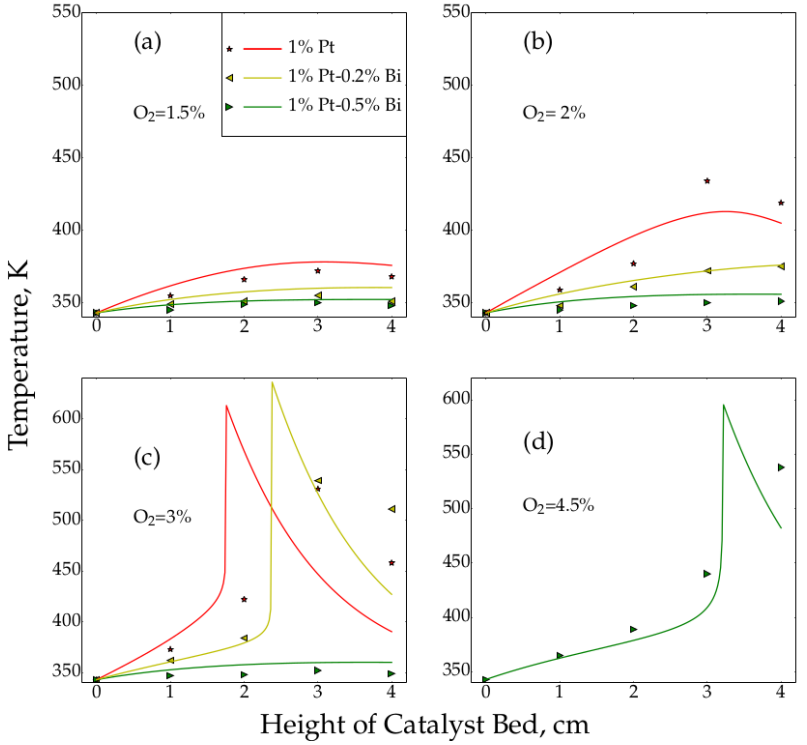
The onset of reactor runaway predicted successfully

Runaway: Caused by catalyst design

Effect of feed temperature



Effect of O_2 concentration



Sensitivity of Catalyst Design: Reactor Thermal Runaway under Standard Operating Conditions

The onset of reactor runaway predicted successfully

Effects of Bi addition:

- ***Tuning selectivity to target product***
- ***influencing reactor thermal behavior***

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Thank You!