Data-Driven Modeling of Batch Processes: Two Methodological Generalizations

Time-Varying Inputs and *Time-Resolved* Outputs

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What I am Going to Tell You?

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- Generalization of the Design of Experiments
  - Design of Dynamic Experiments
    - Georgakis, C. (2013) "Design of Dynamic Experiments: A Data-Driven Methodology for the Optimization of Time-Varying Processes" Ind. & Eng. Chem. Res. **52** (35) pp. 12369-12382
  - Dynamic Response Surface Models
    - Klebanov, N. & C. Georgakis (2016) "Dynamic Response Surface Models: A Data-Driven Approach for the Analysis of Time-Varying Process Outputs" Ind. & Eng. Chem. Res. **55** (14) pp. 4022-4034
- Use DoDE - DRSM to:
  - Model Processes Not Well Understood
    - Mostly Batch but also … Continuous Processes
  - Optimize them
    - Almost as Well as with a Knowledge-Driven Model (KDM)
  - Even … Proceed towards a KDM
- Industrial Applications

The Limitations of DoE

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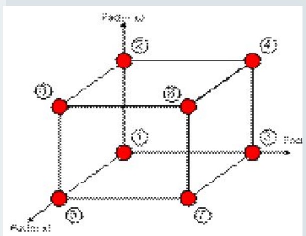
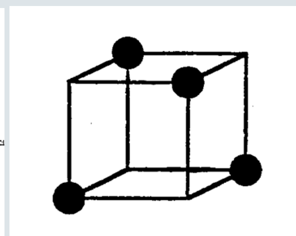
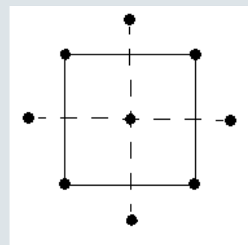
- DoE a Very Powerful Methodology 50 Years Young!
  - Full and Fractional Factorial Designs, ANOVA
  - RSM: Interpolative and Linear and Nonlinear Models
    - Linear in Parameters

The Limitations of DoE

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- DoE a Very Powerful Methodology 50 Years Young!
  - Full and Fractional Factorial Designs, ANOVA
  - RSM: Interpolative and Linear and Nonlinear Models
    - Linear in Parameters
- Two Major Limitations of DoE
  - Inputs Do NOT Vary with Time
    - Why Keep Reaction Temperature Constant?
    - Why Keep Co-reactant Flow Constant?
  - Outputs Measurements at End of Experiment
    - We Take On-Line Spectral and Other Measurement VERY frequently.
- ***Our Answer is DoDE and DRSM***

PART A: The DoDE Approach

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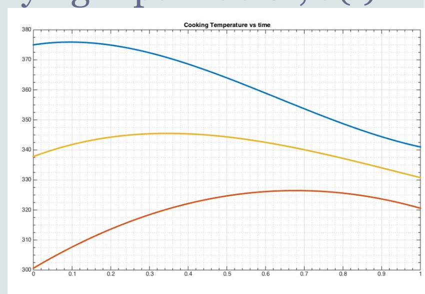
- Applicable to ANY Time-Varying Input Factor, u(t)
  - Define Coded variable, z(τ)

$$u(\tau) \triangleq u_0(\tau) + \Delta u(\tau) z(\tau)$$

$$z(\tau) = \frac{u(\tau) - u_0(\tau)}{\Delta u(\tau)}, \quad \begin{cases} u_0(\tau) = \dfrac{u_{\max}(\tau) + u_{\min}(\tau)}{2} \\ \Delta u(\tau) = \dfrac{u_{\max}(\tau) - u_{\min}(\tau)}{2} \end{cases}$$

$$-1 \le z(\tau) \le +1, \quad \tau = t / t_b$$



- Parameterize Input: z(τ)
  - Using: $P_i(\tau)$=Shifted Legendre Polynomials

$$z(\tau) = \sum_{i=1}^{n} x_i P_{i-1}(\tau).$$

$$P_0(\tau) = 1,\ P_1(\tau) = -1 + 2\tau,\ P_2(\tau) = 1 - 6\tau + 6\tau^2,\ \ldots$$

$$\text{Orthogonality:} \quad \int_0^1 P_i(\tau) P_j(\tau) d\tau = 0 \quad \text{for } i \ne j$$

- Dynamic Sub-factors: $x_1, x_2, \ldots, x_n;\ -1 \le x_1 \pm x_2 \pm \ldots \pm x_n \le +1$

DoDE & DRSM: Generalizations of DoE

DoDE with n=2: a 3² Design

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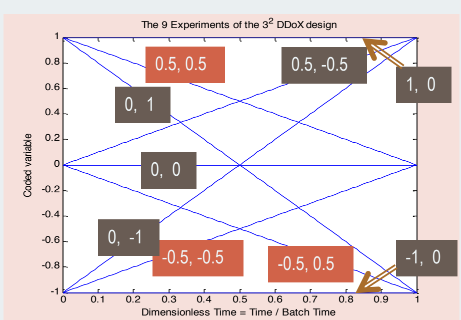
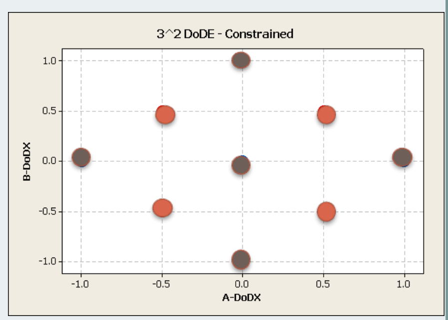
- Dynamic Factor: $z(\tau)$
  - Dynamic Subfactors: x_1 and x_2

$$z(\tau) = x_1 P_0(\tau) + x_2 P_1(\tau) = x_1 + x_2(2\tau - 1); \quad \& \quad -1 \le x_1 \pm x_2 \le +1$$





DoDE & DRSM: Generalizations of DoE

The nine (9) runs within the Region

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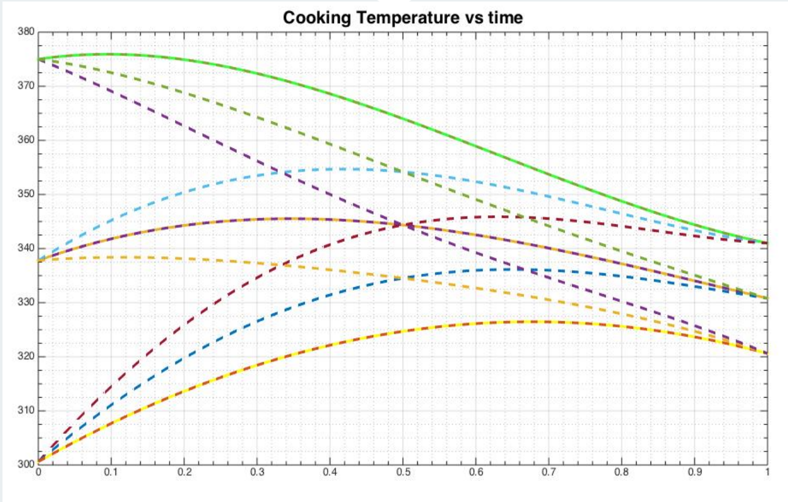

Quadratic Time Profiles

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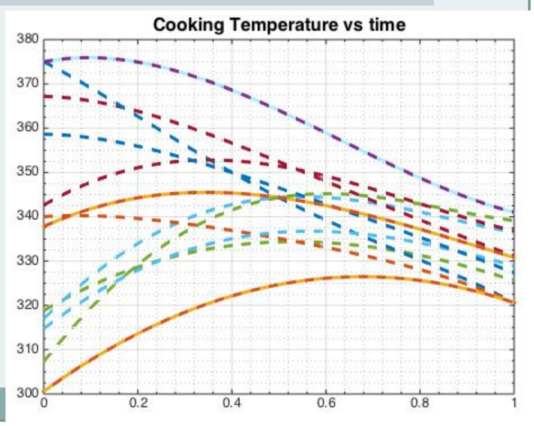
- **The 2^3=*8 Full Factorial DoDE***
- Dynamic Factor: $z(\tau)$
  - Dynamic Subfactors: x_1, x_2 and x_3

$$z(\tau) =$$
$$= x_1 P_0(\tau) + x_2 P_1(\tau) + x_3 P_2(\tau) =$$
$$= x_1 + x_2(2\tau - 1) + x_3(1 - 6\tau + 6\tau^2)$$
&
$$-1 \le x_1 \pm x_2 \pm x_3 \le +1$$
so that
$$-1 \le z(\tau) \le +1$$



DoE & DoDE - Response Surface Models

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❖ The DoE Steps

Design of Experiments → Data → Multilinear Regression → Response Surface Model → Optimization

❖ Response Surface Model (RSM)

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j>i}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2$$

❖ Design of ***Dynamic*** Experiments: **The Same!**

Parameterize Time-Varying Input $z(\tau)$; $(\tau = t/t_b)$

$z(\tau) = \sum_{i=0}^{n} x_i P_i(\tau)$; $P_i(\tau)$ = Shifted Legendre Polynomials

PARAMETERIZE, DoDE experiments, RSM, OPTIMIZE

Georgakis, C., (2009) ADCHEM Proceedings, Istanbul, July 2009.
Georgakis, C. (2013). Ind. Eng. Chem. Res. **52** (35): 12369-12382.

DoDE & DRSM: Generalizations of DoE

DoDE Example: Batch Reactor

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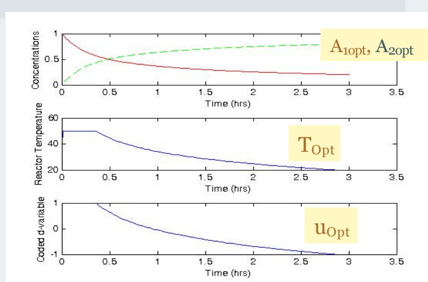
- Batch Reversible Reaction [15 < T < 50 °C]
  - ◆ $A_1 \rightleftarrows A_2$ $k_i = k_{io}\exp(-E_i/RT)$ with $E_2 > E_1$

Model-based Optimum: Decreasing Temperature Profile
Optimum Conversion=74.57% at t_b=2.0 hr

DoE
or
DoDE
???



DoDE & DRSM: Generalizations of DoE

Reactor Optimization via DoE & DoDE

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- Single Factor: Reactor Temperature
  - Data: Conversion at 2hr + Error (±3%)
  - Five **DoE** Experiments at T=15, 32.5 (3), and 50 °C
    - **T constant with time!**
  - Nine **DoDE** Experiment (T(t) linear in Time)
    - Between 15 and 50°C
- Optimization: Maximum Conversion
  - DoE Optimum: x=71.44 at T*= 36.25 °C
  - DoDE Optimum: **x=74.32,** T* from 50 to 28°C
  - Model-Based (True) Optimum = ***74.57%***

DoDE on Isothermal Semi-Batch Reactor

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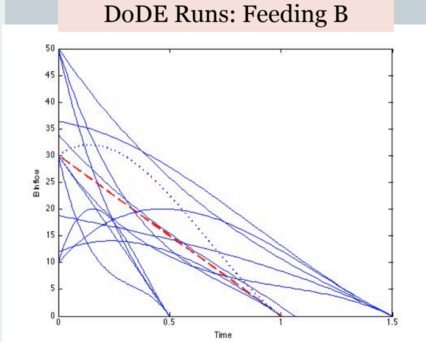
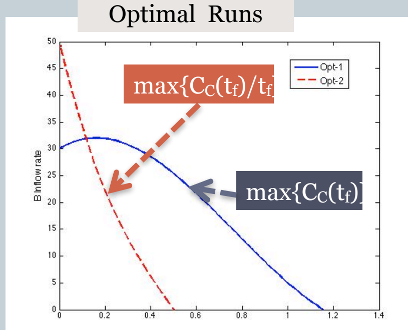
- Reaction Example:

$$Rxn1: \ A + B \rightarrow C, \ r_1 = k_1 C_A C_B, \ k_1 = 2\,l\,mol^{-1}h^{-1}$$
$$Rxn2: \ 2B \rightarrow D, \ r_2 = k_2 C_B^2, \ k_2 = 1\,l\,mol^{-1}h^{-1}$$
$$Rxn2: \ C \rightarrow E, \ r_2 = k_3 C_C, \ k_3 = 1\,h^{-1}$$

DoDE Runs: Feeding B



Optimal Runs



Sepracor Pharmaceutical Reaction System

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Asymmetric Catalytic Hydrogenation

Reactant —Catalytic Hydrogenation→ trans-Product

Reactant —Catalytic Hydrogenation→ cis-Product

Project Specific Goals:

- Optimize Reaction Conditions
  - Selectivity of Asymmetric Hydrogenation
  - Minimize Catalyst Loading
- Performance Criterion
  - Profit = Value of Product- Cost of Reactants

Experiments and Analysis performed by Fenia Makrydaki, PhD candidate

DoDE & DRSM: Generalizations of DoE

Sepracor Experimental System

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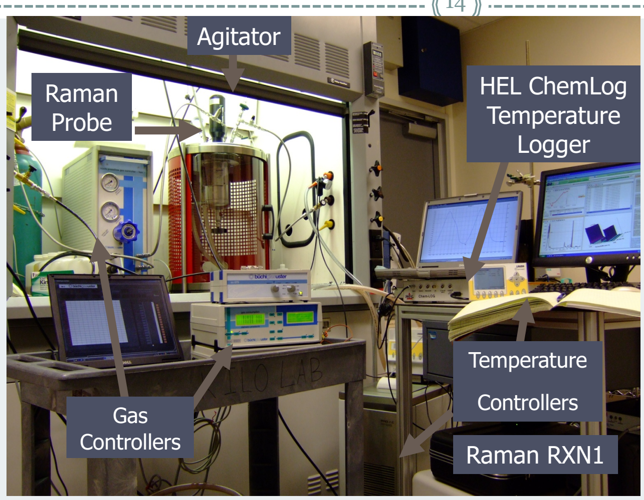

Advantages

- ✓ Accurate Measurements
- ✓ Precise Pressure Control
- ✓ H2 Consumption Monitoring
- ✓ Minimize Mass Transfer Limitations

DoDE & DRSM: Generalizations of DoE

Design of Dynamic Experiments – DoDE

$8=2^3$ experiments with 2 Levels & 3 (2+1dynamic) Factors Full Factorial

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- ❑ ***Time Variant Experiments: Temperature Profile***
- ❑ ***Advantages: Additional degrees of freedom***

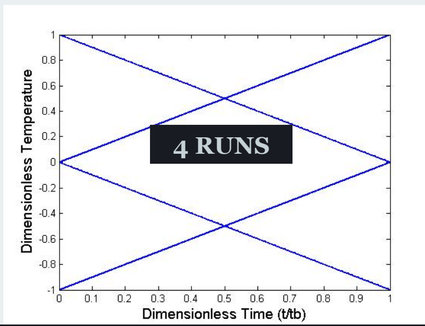

Figure A: 2 level, 2 factor, full factorial case

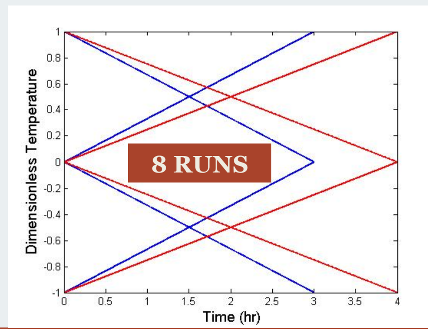

Figure B: 2 level, 2 factor, full factorial case for two time horizons.

Makrydaki, F., Georgakis, C., & Saranteas, K.: DYCOPS 2010, Leuven, Belgium, July 5-7, 2010

DoE Design Table & Responses

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- D-Optimal Experimental Design -17 Runs
  - ❖ with 3 Center Points

Run	x_1 (T)	x_2 (RE)	x_3 (CL)	x_4 (BT)	DE (%)	Y (%)	PI ($/l)
1	-1	1.67	0	-1	97.4	85.5	562.2
2	1	1.67	-1	1	93.7	75.7	897.7
3	-1	-1	-1	-1	97.7	98.6	155.7
4	-1	1.67	1	-2.25	97.3	96.1	668
5	1	1.67	-1	-1	90	39.7	-16.2
6	-1	-1	-1	-1	97.7	98.6	155.7
BEST DoE Run							
7	**-1**	**1.67**	**-1**	**0**	**96.8**	**95.4**	**726.1**
12	1	1.67	1	0	93.8	94.6	1242.9
13	0	1.67	1	-1	95.7	85.7	714.1
14	1	-1	-1	-2	94	74.7	174.7
15	0	0	0	-2.33	94.9	97.4	497.8
16	0	0	0	-2.25	95.8	97.7	501
17	0	0	0	-2.33	95.9	97.5	499.3

DoDE Design Table & Responses

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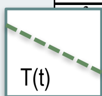
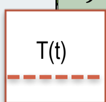
- 3 Static & 2 Dynamic Factors, 21 Runs +3 CPs

Run	x_1 (a_0)	x_2 (a_1)	x_3 (RE)	x_4 (CL)	x_5 (BT)	DE (%)	Y (%)	PI ($/l)
1	-0.88	0.13	-1	1	-2.5	97.3	98.7	142.1
2	0.06	0.06	-1	1	-2.5	96.5	97.4	191.6
[illegible]	-0.88	0.13	1.67	1	-2	97.8	97.2	684.6
[illegible]	0.15	0.15	-1	-1	-2.42	96.1	98	212.8
[illegible]	0.94	-0.06	-1	-1	-2.5	93.6	96.8	288.3
[illegible]	0.5	-0.5	1.67	-1	-1	96.4	19.1	-534.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	-0.5	0.5	1.67	-1	-1	96.7	73.4	436.9
[illegible]	0.5	-0.5	1.67	1	1	94.6	96.2	1294.9
[illegible]	-0.25	-0.25	-1	-1	-2	96.7	98.3	213.7
[illegible]	-0.72	0.28	-1	-1	-0.75	97.6	98.8	155.8
19	-0.5	-0.5	1.67	1	0	97.1	96.7	941.3
20	-1	0	-1	1	-2.33	97.8	98.8	142.2
21	-0.11	-0.11	0	0	-2.17	96.5	98.2	509.1
22	0	0	0	0	-2.33	94.9	97.4	497.8
23	0	0	0	0	-2.25	95.8	97.7	501
24	0	0	0	0	-2.33	95.9	97.5	499.3



BEST DoDE Run

9	0	-1	1.67	-1	1	96.1	83	1076.2



BEST DOE Run

7	-1	--	1.67	-1	0	96.8	95.4	726.1

48%

What Did I Tell You so Far?

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- Design of Dynamic Experiments (DoDE)
  - First Generalization of DoE
    - New Set of Inputs: TIME-VARYING
  - Effective Optimization of Processes
  - SMALL distance from Model-Based Optimum

PART B: Dynamic RSM (DRSM)

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- Use Time-Resolved Output Data
- Classical RSM: $y=\beta_0+\sum_{i=1}^{n}\beta_i x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{ij}x_i x_j+\sum_{i=1}^{n}\beta_{ii}x_i^2$
- Dynamic RSM: $y(\tau)=\beta_0(\tau)+\sum_{i=1}^{n}\beta_i(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{ij}(\tau)x_i x_j+\sum_{i=1}^{n}\beta_{ii}(\tau)x_i^2$

K= # of C Measurements in Time | # of $\beta(\tau)$ functions=1+n+0.5n(n-1)+n

- Parameterization of $\beta_{ij}(\tau)=\gamma_{ij,1}P_0(\tau)+\gamma_{ij,2}P_1(\tau)+\ldots+\gamma_{ij,R}P_{R-1}(\tau)$

R= # of Polynomials

- # of Model parameters < # of Data

R<K

DRSM for Simple Batch Reaction

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$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$r=k_1[A]-k_2[B]$

$k_1=k_{10}\exp\left(-\frac{E_1}{RT}\right)$,

$k_{10}=1.32\times10^8\ \mathrm{h}^{-1}$,

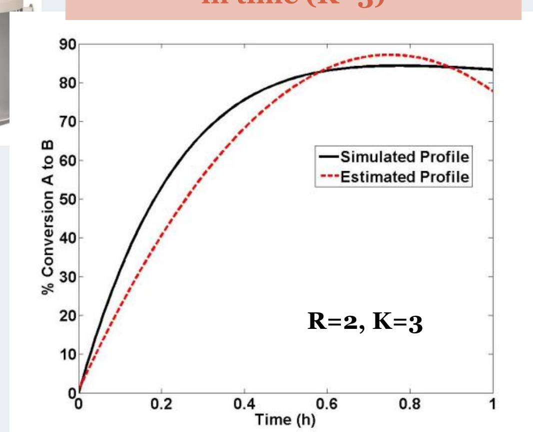
$E_1=10{,}000$ kcal,

$k_2=k_{20}\exp\left(-\frac{E_2}{RT}\right)$,

$k_{20}=5.25\times10^{13}\ \mathrm{h}^{-1}$,

$E_2=20{,}000$ kcal

Not enough measurements in time (K=3)



Statistical Measure of Accuracy

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- **Unmodeled Variance:** $$\hat{SS}_{reg}(R,K)=\frac{\sum_{i=1}^{M}\left[\sum_{k=1}^{K}\left\{y_{RSM,i}(\boldsymbol{t}_k;R,K)-y_{\exp,i}(\boldsymbol{t}_k)\right\}^2\right]}{\sum_{i=1}^{M}\left[\sum_{k=1}^{K}\left\{y_{\exp,i}(\boldsymbol{t}_k)\right\}^2\right]}$$
- **Normal Variability:** $$\hat{SS}_{err}=\frac{\sum_{i=1}^{n_{CP}}\left[\sum_{k=1}^{K}\left\{y_{0,i}(\boldsymbol{\tau}_k)-\bar{y}_{0,i}(\boldsymbol{\tau}_k)\right\}^2\right]}{\sum_{i=1}^{N_{CP}}\left[\sum_{k=1}^{K}\left\{\bar{y}_{0,i}(\boldsymbol{\tau}_k)\right\}^2\right]}$$
- **Hypothesis Testing:** $$\text{Null Hypothesis} ------- H_0: \quad \hat{SS}_{err}=\hat{SS}_{rgr}(R,K)$$ $$\text{Alternative Hypothesis} -- H_1: \quad \hat{SS}_{err}<\hat{SS}_{rgr}(R,K)$$
- ***F*-Statistic:** $$F_0(R,K)=\frac{\hat{SS}_{un}(R,K)/n_1}{\hat{SS}_{err}/n_2}=\frac{\hat{SS}_{un}(R,K)/(MK-Q)}{\hat{SS}_{err}/K(n_{CP}-1)}$$

Reactor Example: K=Measurements, R=Polynomials

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Table 3. p-values of F-test for DRSM of A ⇄ B conversion in batch reactor

R \ K	3	4	5	6	7	8	9	10
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3		1.00	1.00	1.00	1.00	1.00	1.00	1.00
4			0.97	1.00	1.00	1.00	1.00	1.00
5				**0.51**	0.99	**0.90**	**0.95**	**0.70**
6					**0.82**	**0.34**	**0.48**	**0.03**
7						**0.47**	**0.47**	**0.01**
8							**0.58**	**0.01**
9								**0.14**

K = number of time-resolved measurements; R = number of polynomials

$if \quad p(R,K)\le 0.95$ the Null Hypothesis **fails** to be rejected ⇒ **Model GOOD**

$if \quad p(R,K)>0.95$ the Null Hypothesis **is** rejected

D-RSM Model (R=7, K=14)

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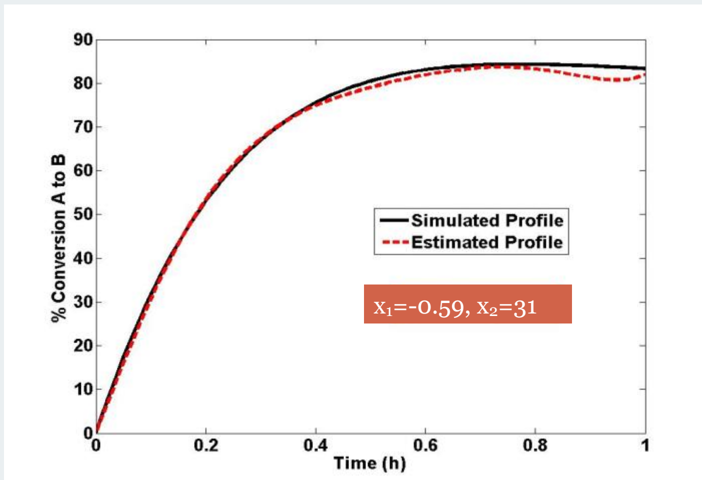

DoDE & DRSM: Generalizations of DoE

More Complex Semi-Batch Case

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- Three inter-related reactions
- **C** is the desired product
  - **Reactant B is fed in semi-batch mode**

$$\text{Rxn1: } A + B \rightarrow C, \quad r_1 = k_1[A][B] \quad \text{with } k_1 = 2 \ \text{l gmol h}^{-1}$$

$$\text{Rxn2: } 2B \rightarrow D, \quad r_2 = k_2[B]^2 \quad \text{with } k_2 = 1 \ \text{l gmol h}^{-1}$$

$$\text{Rxn3: } C \rightarrow E, \quad r_3 = k_3[C] \quad \text{with } k_3 = 1 \ \text{h}^{-1}$$

- DRSMs for A(t), B(t), C(t), D(t), and E(t)

DoDE & DRSM: Generalizations of DoE

Statistical Test of Goodness-of –Fit (GoF)

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Table 6. Corresponding F-test p values for DRSM of product [C] in semi-batch 3-reaction network

R	*K* = 3	4	5	6	7	8	9	10
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3		1.00	1.00	1.00	1.00	1.00	1.00	1.00
4			1.00	1.00	1.00	1.00	1.00	1.00
5				2.33E-06	8.06E-06	2.89E-05	1.45E-02	2.22E-05
6					3.18E-26	1.22E-29	5.18E-27	6.14E-37
7						6.89E-36	9.60E-38	1.07E-50
8							9.60E-38	1.07E-50
9								1.07E-50

K = number of time-resolved measurements; R = number of polynomials

Excellent Model

Some C(t) Profiles

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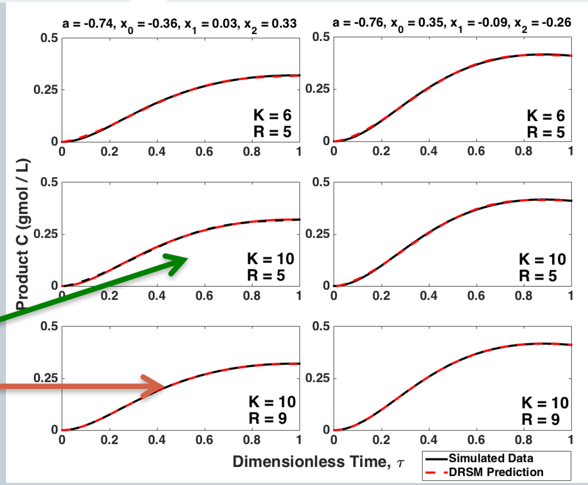
- Excellent fits:



No Significant Difference

Using Stepwise Regression

Part C: DRSM Usage → Door to Knowledge

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- Revisit Semi-Batch Reactor Example
  - Five DRSMs at Hand

$$\Rightarrow \begin{cases} R_1: \ A+B \to C \\ R_2: \ 2B \to D \\ R_3: \ C \to E \end{cases}$$

$$c_A(\tau)=\beta_{A0}(\tau)+\sum_{i=1}^{n}\beta_{Ai}(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{Aij}(\tau)x_ix_j+\sum_{i=1}^{n}\beta_{Aii}(\tau)x_i^2$$

$$c_B(\tau)=\beta_{B0}(\tau)+\sum_{i=1}^{n}\beta_{Bi}(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{Bij}(\tau)x_ix_j+\sum_{i=1}^{n}\beta_{Bii}(\tau)x_i^2$$

$$c_C(\tau)=\beta_{C0}(\tau)+\sum_{i=1}^{n}\beta_{Ci}(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{Cij}(\tau)x_ix_j+\sum_{i=1}^{n}\beta_{Cii}(\tau)x_i^2$$

$$c_D(\tau)=\beta_{D0}(\tau)+\sum_{i=1}^{n}\beta_{Di}(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{Dij}(\tau)x_ix_j+\sum_{i=1}^{n}\beta_{Dii}(\tau)x_i^2$$

$$c_E(\tau)=\beta_{E0}(\tau)+\sum_{i=1}^{n}\beta_{Ei}(\tau)x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\beta_{Eij}(\tau)x_ix_j+\sum_{i=1}^{n}\beta_{Eii}(\tau)x_i^2$$

- Can Calculate Derivatives wrt Time

$$\frac{dc_A(\tau)}{d\tau}=\frac{d\beta_{A0}(\tau)}{d\tau}+\sum_{i=1}^{n}\frac{d\beta_{Ai}(\tau)}{d\tau}x_i+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{d\beta_{Aij}(\tau)}{d\tau}x_ix_j+\sum_{i=1}^{n}\frac{d\beta_{Aii}(\tau)}{d\tau}x_i^2$$

... for ALL experiments

Calculate Rate of Appearance (Disappearance)

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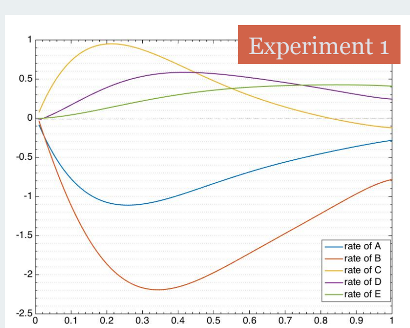
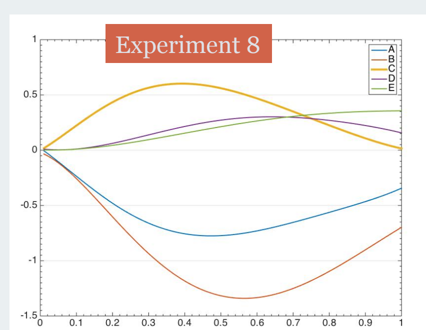
- Calculate at 100 time points in each Run:
  - τ=0.01, 0.02, ..., 0.99, 1.00
- Can plot the Rates vs. Time
  - Can Understand what is Happening

$$r_A(\tau)=\frac{dc_A(\tau)}{d\tau},\ r_C(\tau)=\frac{dc_C(\tau)}{d\tau},$$

$$r_D(\tau)=\frac{dc_D(\tau)}{d\tau},\ r_E(\tau)=\frac{dc_E(\tau)}{d\tau}$$

$$but\ \ r_B(\tau)=\frac{dc_B(\tau)}{d\tau}-\frac{q_B(\tau)}{V}$$





Discover the Stoichiometry

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- Define Big Rate Data Matrix: DataM

$$\mathbf{DataM} = \begin{pmatrix} \mathbf{D}_1 \\ \mathbf{D}_2 \\ \vdots \\ \mathbf{D}_Q \end{pmatrix}, \mathbf{D}_k = \text{Data from } k\text{-th Experiment}$$

$$Q = 1 + n + 0.5n(n-1) + n + 6(3)$$

for $n = 2 \Rightarrow Q = 12(9)$

$$\mathbf{D}_k = \begin{pmatrix} r_{kA}(0.01) & r_{kB}(0.01) & r_{kC}(0.01) & r_{kD}(0.01) & r_{kE}(0.01) \\ r_{kA}(0.02) & r_{kB}(0.02) & r_{kC}(0.02) & r_{kD}(0.02) & r_{kE}(0.02) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ r_{kA}(1.00) & r_{kB}(1.00) & r_{kC}(1.00) & r_{kD}(1.00) & r_{kE}(1.00) \end{pmatrix}$$

- DataM is a 909 x 5 matrix !!!
- SVD of DataM
  - **S has three Dominant Singular Values** → three Reactions !!
  - **Matrix V is KEY to Stoichiometry**

$$SVD(\mathbf{DataM}) = \mathbf{USV}^T$$

DoDE & DRSM: Generalizations of DoE

Testing Stoichiometries (measure A, B. C. D, and E)

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- SVD Results

$$\mathbf{V}^T = \begin{pmatrix} 0.4072 & 0.8365 & -0.2557 & -0.2145 & -0.1516 \\ -0.2596 & 0.2086 & 0.7629 & -0.2333 & -0.5027 \\ 0.5955 & -0.2826 & 0.0140 & 0.4417 & -0.6084 \end{pmatrix}$$

R_1: $A + B \rightarrow C$

R_2: $2B \rightarrow D$

R_3: $C \rightarrow E$

- TEST: $\mathbf{N}_r = \mathbf{NVV}^T$; is $\mathbf{N}_r = \mathbf{N}$???
- Test TRUE Stoichiometry
  - Score: 99.74%

$$\mathbf{N} = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ 0 & -2 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 1 \end{pmatrix}$$

- Test *Incorrect* Stoichiometry
  - Score: 64.97%

$$\mathbf{N} = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 1 \end{pmatrix}$$

- Can Test **One** Reaction at a Time

DoDE & DRSM: Generalizations of DoE

Testing Stoichiometries (measure A, B. C. and D - **NO** E)

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- SVD Results

$$\mathbf{V}^T = \begin{pmatrix} 0.4125 & 0.8456 & -0.2608 & -0.2164 \\ -0.2841 & 0.3233 & 0.8503 & -0.3029 \\ 0.7620 & -0.1172 & 0.4571 & 0.4435 \end{pmatrix}$$

R_1: $A + B \rightarrow C$
R_2: $2B \rightarrow D$
R_3: $C \rightarrow E$

- Test TRUE Stoichiometry
  - Score: 99.67%

$$\mathbf{N} = \begin{pmatrix} -1 & -1 & 1 & 0 \\ 0 & -2 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

- Test *Incorrect* Stoichiometry
  - Score: 64.87%

$$\mathbf{N} = \begin{pmatrix} -1 & -1 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

- Can Test **One** Reaction at a Time

Calculate Reaction Rates

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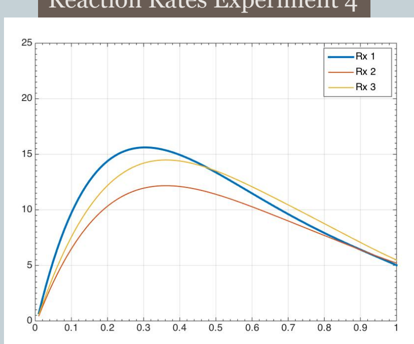
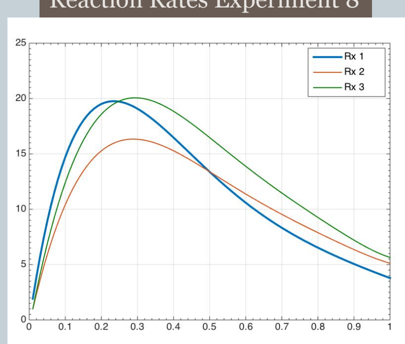
- From: $r_A(\tau), r_B(\tau), r_C(\tau), r_D(\tau), r_E(\tau)$
  - **TO:** $r_1(\tau), r_2(\tau), r_3(\tau)$

Reaction Rates Experiment 4



Reaction Rates Experiment 8



Derive Kinetic Laws

33

- From: $r_1(\tau)$, $C_A(\tau)$, $C_B(\tau)$
  - TO: Kinetic Rates $r_1(\tau)=f(C_A(\tau), C_B(\tau))$
- Work in Progress
  - Stay … Tuned

What did I just Tell you?

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- DRSM is a Generalization of RSM
  - Using Time-Resolved Measurements
    - Excellent Approximation of Composition Profiles
  - Stepping Stone to Stoichiometry and a Kinetic Model

Industrial Applications

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- Dow Batch Polymerization Reactor
  - Use DoDE to Increase Productivity by 20%
    - Presented at the Houston AIChE Meeting
    - ***Can Give you the Highlights***
- Pfizer Pharmaceutical Reaction System
  - Develop DRSMs & Discover Complex Stoichiometry
    - 10 Species involved in 8 reactions
- ExxonMobil Continuous Polymerization Process
  - Develop Meta-Models of KDM
    - Make Them More Accurate with Plant Data
    - USE for Optimization and Control Between SS Transition

DRSM Model for the Optimization and Control of Batch Processes

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DYCOPS 2016

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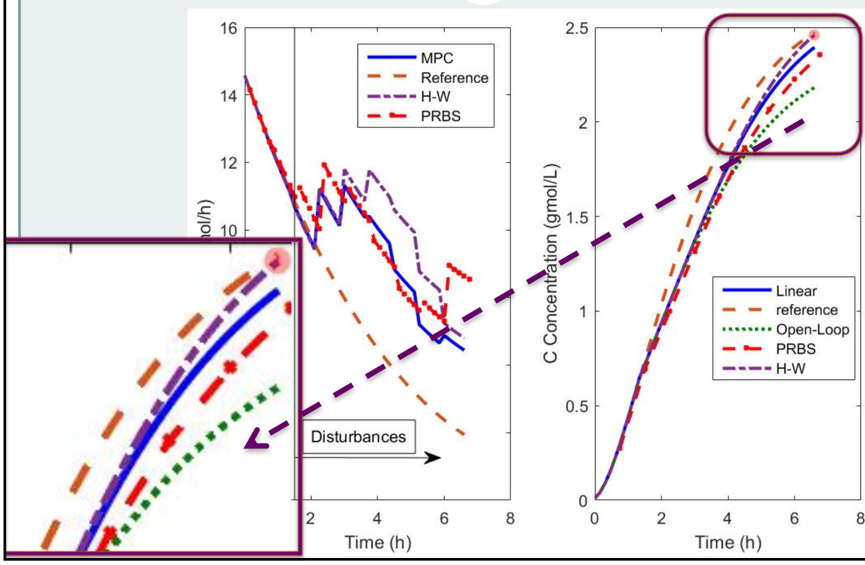
Control for Maximum Yield



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What You Should Remember Tomorrow

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- DoDE: First Generalization of DoE
  - Time-varying Inputs
- DRSM: Second Generalization of DoE
  - Using Time-Resolved Outputs
    - Excellent Approximation of Composition Profiles
  - Stepping Stone to a Kinetic Model
- Towards Non-Linear Models for Control
- Potential Benefits: ***Substantial***

THANK YOU

MAY I ANSWER YOUR QUESTIONS?

DoDE & DRSM: Generalizations of DoE