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STATISTICAL ROBUSTNESS STUDY FOR KINETIC MODELS

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Introduction

- Kinetic (Fundamental) Models
  - *Non-linear systems – depict the dependence between process variables and products*
  - *Process variables are fully controllable*
  - *Full scale production plant – some variables are hard to control*

- Statistical Robustness Studies
  - *Models linear in the parameters (Well documented in literature)*
  - *Models non-linear in the parameters, in particular kinetic models (Not utilized before)*

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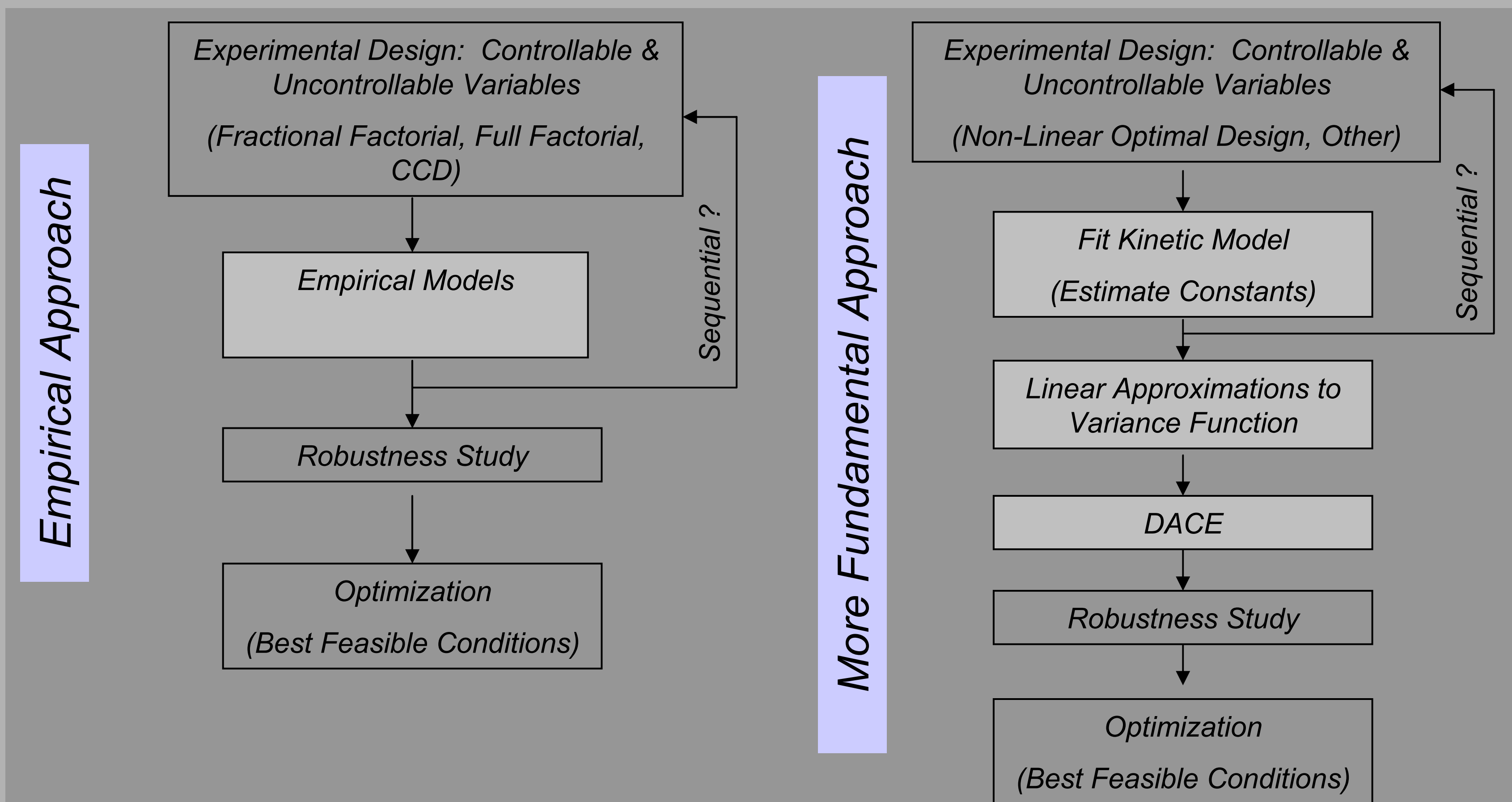
Outline

- Methodology for statistical robustness studies (Linear and Non-Linear)
- Case study: Ethylene Glycol Process
- Evaluate several experimental designs for sampling the computer code for the kinetic models and variance models (DACE)
- Compare response surface and kriging models for approximating the input-output relationship
- Make recommendations for application in industry

Methodology of Process Robustness Studies



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Methodology of Process Robustness Studies (Empirical Approach - Linear)

- With regard to robustness studies, a 2nd order response surface model (linear) in the parameters, is of the form:

$$y(x,z) = f(x) + h(x,z) + \varepsilon$$

where $$f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<} \sum_{j=1}^{k} \beta_{ij} x_i x_j; \qquad h(x,z) = \sum_{j=1}^{r} \gamma_j z_j + \sum_{i=1}^{k} \sum_{j=1}^{r} \delta_{ij} x_i z_j$$

and x_i = controllable variables, z_j = hard to control variables.

- Response surface model for the process mean:

$$E_z(y(x,z)) = f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i\ <} \sum_{j=1}^{k} \beta_{ij} x_i x_j$$

and the response surface model for the process variance:

$$\sigma^2_{y|z} = V_z(y(x,z)) = \sum_{j=1}^{r} \sigma^2_{z_j} \left(\gamma_j + \sum_{i=1}^{k} \delta_{ij} x_i \right)^2 + \sigma^2$$

Methodology of Process Robustness Studies (More Fundamental Approach – Non Linear)

- Assuming the kinetic model describes the true relationship between the response and process variables
- Response model can then be written as:

$$y = f(\underline{x}, \underline{z}, \underline{k}) + \varepsilon$$

where $\underline{x}$ = controllable variables; $\underline{z}$ = hard to control variables; $\underline{k}$ = kinetic constants

- y denotes the output from a kinetic reactor model
- $\hat{y} = f(\underline{x}, \hat{\underline{z}}, \underline{k})$ can be approximated through a 2nd order Taylor series about the true values $\underline{z}$.

Methodology of Process Robustness Studies (More Fundamental Approach)

- The expected value of $\hat{y}$ can be approximated by the equation:

$$E(\hat{y}) \approx y + \frac{1}{2}\sum_i V(\hat{z}_i)\left(\frac{\partial^2 f}{\partial z_i^2}\right) + \sum_{i,j} Cov(\hat{z}_i, \hat{z}_j)\left(\frac{\partial^2 f}{\partial z_i \partial z_j}\right)$$

- And the variance function by:

$$V(\hat{y}) \approx \sum_i V(\hat{z}_i)\left(\frac{\partial f}{\partial z_i}\right)^2 + 2\sum_{i,j} Cov(\hat{z}_i, \hat{z}_j)\left(\frac{\partial f}{\partial z_i}\right)\left(\frac{\partial f}{\partial z_j}\right) + \sigma^2$$

Methodology of Process Robustness Studies

- Propagation of Error

$$POE = \sqrt{V(\hat{y})} \approx \left[V(\hat{z}_i)\left(\frac{\partial f}{\partial z_i}\right)^2 + \sigma^2 \right]^{\frac{1}{2}}; \quad Cov(\hat{z}_i, \hat{z}_j) = 0, i \neq j$$

- Used to minimize the error that is carried over due to the variability of one or more hard to control variables

- Practical value:
  - *Quantifies the convoluted effect of model uncertainty and model input deviation*
  - *Can be used as criteria to over design equipment*

Case study: Ethoxylation and Propoxylation of Ethylene Glycol

- Are extensively used by industry to produce a large number of products such as polypropylene glycols and polyethylene oxide-propylene oxide copolymers

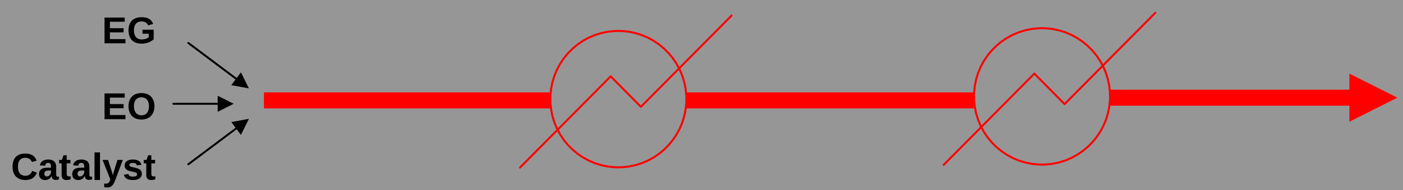
- These products are that are largely used as chemical intermediates, lubricants, industrial surfactants and components for cosmetic formulations

- Ethylene glycol oligomers are formed by reacting EG with EO

- Di Serrio# published a kinetic model for predicting the reactions and selectivities for an ethylene glycol process

M. Di Serrio et al. Kinetics of Ethoxylation and Propoxylation of Ethylene glycol Catalysed by KOH, nd. Eng. Chem. Res. 2002, *41, pp 5196 – 5206.*

Case study: Ethoxylation of EG# in an Intercooled Pipe Reactor



- Exothermic reaction – use intercoolers to limit maximum temperature.
- Reactions: EG + EO → DEG
  DEG + EO → TEG
  TEG + EO → Tetra

- Reactor design criteria:
  - *Selectivities of products*
  - *Volume of reactor*
  - *Number of intercoolers*

- Reactor design variables:
  - *EG : EO ratio*
  - *Inlet temperature*
  - *Temperature increase*
  - *Catalyst concentration*

M. Di Serrio et al. Kinetics of Ethoxylation and Propoxylation of Ethylene glycol Catalysed by KOH, Ind. Eng. Chem. Res. 2002, *41, pp 5196 – 5206.*

Robustness Study: Data Description and Ranges of Variables

- Selectivity product considered: DEG:TEG Ratio
- Variable ranges for the calculation of POE's and selectivities:

Inlet Temperature:	*[393 Kelvin; 423 Kelvin]*
ΔTemperature:	*[5; 60]*
EG:EO Ratio:	*[5; 7]*
Catalyst Concentration:	*[0.01; 0.1]*

- Standard deviation (Assumed):

Inlet Temperature:	*5 Kelvin (σ^2=25)*
ΔTemperature:	*5 Kelvin (σ^2=25)*
EG:EO ratio:	*0.1 (σ^2=0.01)*
Catalyst Concentration:	*(Negligibly small)*

Reactor Modelling

- Kinetic model is non-linear for which no analytical solution can be obtained.
- Model contains all the characteristics of reactor modelling and analysis – could therefore be used to illustrate the application and advantages of statistical robustness studies for kinetic models.
- Reactor is modelled as an ideal plug flow reactor.
- Kinetic equations are integrated numerically using a 5^{th} order adaptive step Runge-Kutta method with Cash-Carp coefficients.

Kinetics of Ethoxylation Reactions

- Kinetic Rate Equations:

$$\frac{d[EG]}{dt} = -r_0 \qquad r_0 = k_0[EG.K][EO]$$

$$\frac{d[DEG]}{dt} = r_0 - r_1 \qquad r_1 = k_p[DEG.K][EO]$$

$$\frac{d[TEG]}{dt} = r_1 - r_2 \qquad r_2 = k_p[TEG.K][EO]$$

$$\frac{d[Tetra]}{dt} = r_2$$

where *[i]* = concentration of species *i.*

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Kinetics of Ethoxylation Reactions

- $[EG.K]=\frac{C\,M_0}{M_0+K_e\,M}$ $\quad [DEG.K]=\frac{K_e\,C[DEG]}{M_0+K_e\,M}$ $\quad [TEG.K]=\frac{K_e\,C[TEG]}{M_0+K_e\,M}$

  $[Tetra.K]=\frac{K_e\,C[Tetra]}{M_0+K_e\,M}$

  $$where\ C=[KOH]_0,\ \ M_0=[EG]\ and\ \ M=[DEG]+[TEG]+[Tetra].$$

- Rate constants were assumed to follow an Arrhenius temperature dependency, i.e.

  $$k_i = A_i \exp\left(\frac{-E_i}{RT}\right)$$

- Values from published paper[#] were used – focus on robustness

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Application of DACE to Reactor Model

- Applied DACE to the kinetic model and its variance function in order to sample the analysis code.
- Selected five different experimental designs as alternatives for collecting the sample data points
- Constructed two types of approximation models for the Ethylene Glycol process namely, RS and Kriging

Error Analysis of Approximation Models

- Selectivities of the products as well as the derivatives for calculating the variance model were obtained numerically.
- Additional validation points (3^4) were collected in the design variables' ranges to assess the accuracy of each approximation model over the region of interest.
- Error defined as difference between actual response from computer analysis and the predicted value from RS or Kriging model. Define the root mean square error as:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} \left(y_i - \hat{y}_i\right)^2}{n}}$$

Error Analysis of Approximations (RMSE)

DEG:TEO Ratio

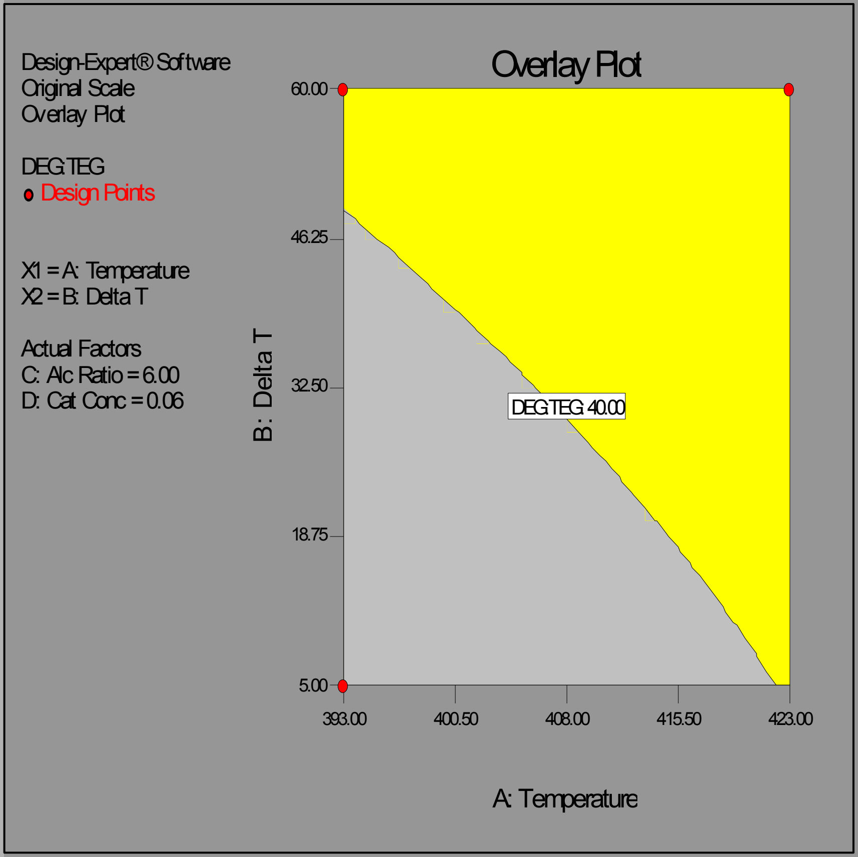
Design	Kriging	RS
CCD FC	0.43	0.46
D-Opt	0.67	0.67
$U_{32}(4^4)$	0.92	0.86
$U_{24}(4^4)$	1.20	1.20
$U_{30}(3^4)$	0.31	0.45

POE (DEG:TEG Ratio)

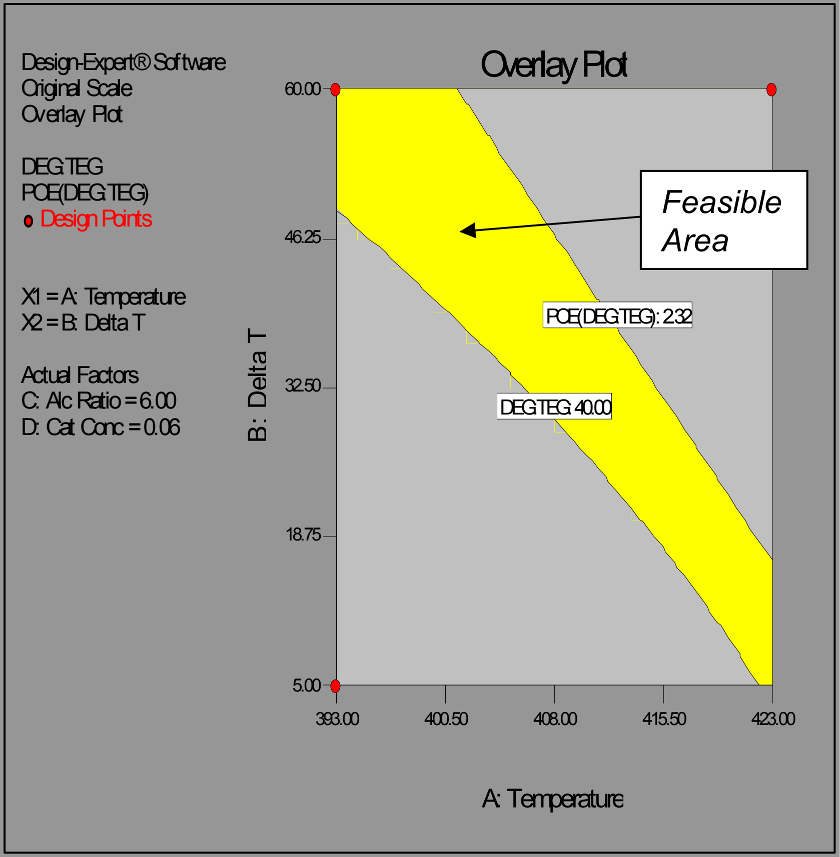
Design	Kriging	RS
CCD FC	2.63	2.62
D-Opt	1.66	1.66
$U_{32}(4^4)$	0.33	0.53
$U_{24}(4^4)$	0.32	0.32
$U_{30}(3^4)$	0.25	0.27

$U_n(q^s)$; where n denotes the number of runs, q the number of levels and s the number of factors.

Results



Design-Expert® Software
Original Scale
Overlay Plot
DEG:TEG
Design Points
X1 = A: Temperature
X2 = B: Delta T
Actual Factors
C: Alc Ratio = 6.00
D: Cat Conc = 0.06
Overlay Plot
DEG:TEG: 40.00
B: Delta T
A: Temperature
60.00
46.25
32.50
18.75
5.00
393.00
400.50
408.00
415.50
423.00



Design-Expert® Software
Original Scale
Overlay Plot
DEG:TEG
POE(DEG:TEG)
Design Points
X1 = A: Temperature
X2 = B: Delta T
Actual Factors
C: Alc Ratio = 6.00
D: Cat Conc = 0.06
Overlay Plot
Feasible Area
POE(DEG:TEG): 2.32
DEG:TEG: 40.00
B: Delta T
A: Temperature
60.00
46.25
32.50
18.75
5.00
393.00
400.50
408.00
415.50
423.00

Concluding Remarks

- Ethoxylation of Ethylene Glycol was used to demonstrate the use of Kriging models as an alternative approximation method to second order response surface models
- RS and Kriging approximations yield comparable results with minimal difference in predictive capability
- Based on this case study, the $U_{30}(3^4)$ uniform design seems to be superior in terms of its better predictive capability for both the DEG:TEG selectivity and POE

Concluding Remarks

- Shown that statistical robustness studies can be used for processes not only described by models that are linear in the parameters, but also by models that are non-linear in the parameters, such as kinetic models.