The Paradigm After Next: 50 Years On

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(Special thanks to Jeffrey Frumkin & Lorenz Fleitmann)

2040 Visions of Process Systems Engineering
Circa 1976 Minnesota CEMS
1. Develop a solution procedure for a set of non-linear algebraic equations with the following incidence matrix.

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<th>x_2</th>
<th>x_3</th>
<th>x_4</th>
<th>x_5</th>
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2. Using the "Maximum Product" criterion, find the O/P assignment that will enhance the convergence properties of the successive substitution during the solution of the following system:

\[ f_1 = 3x_2 + x_5 = 2 \]
\[ f_2 = x_2 + \exp(x_1) + \sin(x_9) + x_8 = -1 \]
\[ f_3 = x_4^2 + 9x_6 + x_3 = 0 \]
\[ f_4 = 2x_1 - x_3 + x_4 + x_7 = 5 \]
\[ f_5 = -x_1 + 3x_5 - x_6 = 0 \]
\[ f_6 = x_5 + x_7 = 8 \]
\[ f_7 = -x_1^2 + x_7 = -5 \]
In the context of the chemical process design, the following general items will be treated.

Synthesis:
1. General problem of synthesis
2. Generation of initial process flowsheets
   - AIDES system
   - predicate calculus
   - structural parameters approach
   - evolutionary synthesis
3. Synthesis of specialized systems
   - heat-exchange networks
   - multicomponent separation sequence
   - reactor networks

Analysis:
1. Modular approach
   - PACKR system
   - block building
   - physical properties package
2. Analysis and Design through the solution of large sets of algebraic equations
   - overall strategy
   - grouping, precedence ordering
   - output set assignment
   - selection of decision variables
My Theme: Conceptual Design

You can’t understand the process if you don’t understand the chemistry
Synthesis of Reaction Mechanisms Consisting of Reversible and Irreversible Steps. 1. A Synthesis Approach in the Context of Simple Examples

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The analysis of pseudo-steady states of a chemical system can be aided by the identification of mechanisms responsible for overall reactions, from a known set of elementary steps that involve overall reactants and products as well as reaction intermediates. In the context of examples of catalytic synthesis of ammonia and methanol, an alternative approach for the construction of mechanisms from steps is presented. The approach is based on successive processing and elimination of reaction intermediates which should not appear in the net stoichiometry of the overall reactions accomplished.

Introduction
Consider a given set of elementary reaction steps which are feasible in a system, and the species involved in these steps. Following Happel and Sellers (1982, 1983, 1989), Happel (1986), Sellers (1984, 1989), and Happel et al. (1990)—this set of references is hereafter referred to as H&S—species can be classified as either intermediates, which occur in very small amounts, or terminal species which can occur in significant amounts and constitute the raw materials and products of the process. An overall mechanism, depending on the choice of species, can either consist of the accumulation term in the mass balance for an intermediate to zero. Overall reactions can thus be defined as the set of net transformations permissible under the pseudo-steady-state assumption, while overall mechanisms are the combinations of steps that accomplish this. This article focuses on the synthesis of reaction mechanisms, the systematic identification of sets of mechanism steps that accomplish net reactions involving only terminal species.

One is particularly interested in direct mechanisms (Müller, 1984), which are the smallest possible physically
2040 and Beyond

The future of chemical engineering is in prediction not correlation
Why Modeling?

“If you can’t model your process, you don’t understand it. If you don’t understand it, you can’t improve it. And, if you can’t improve it, you won’t be competitive in the 21st century.”

Jim Trainham, DuPont
Perspectives

- Engineers believe that their models approximate nature

- Scientists believe that nature approximates their models

- Mathematicians don’t give a damn either way
Process design for a complex reaction network

Production of Acrolein\textsuperscript{[1]}

What is the process design with the highest selectivity?

Selectivity = \frac{\text{Product produced}}{\text{Limiting reactant consumed}}

\textsuperscript{[1]} Bui, Chakrabati & Bhan, \textit{ACS Catalysis}, 6(10), 6567-6580, 2016
Feinberg Decomposition

The Overall PFD Structure

**Diagram:**

- **Top Diagram:**
  - Flow: $F_F$ to $F$ to $P$ to Separator System to $P_{exit}$.
  - RMS System.

- **Bottom Diagram:**
  - Flow: $F_F$ to $F$ to $F_1$, $F_2$, $F_{R+1}$.
  - Perfect Separator with CFSTRs 1, 2, $R+1$.
  - $P_1$, $P_2$, $P_{R+1}$.
  - Separator System.
  - FD of RMS System.

**Symbols:**
- $F_F$: Feedforward Flow
- $F$: Flow
- $P$: Pressure
- $P_{exit}$: Exit Pressure
- CFSTR: Continuous Stirred Tank Reactor
- $R$: Number of stages
- $F_1$, $F_2$, $F_{R+1}$: Inlet Flows
- $P_1$, $P_2$, $P_{R+1}$: Pressures
Production of acrolein by partial oxidation of propylene at 350°C

All reaction irreversible with following kinetics, e.g.:

\[ \hat{r}_1 = k_1 p_{C_3H_6} \]  
\[ \hat{r}_8 = k_8 p_{C_3H_6} p_{H_2O} \]  
\[ \hat{r}_{15} = k_{15} \frac{p_{CH_3COOH}}{p_{H_2O}} \]

All rates independent of oxygen partial pressure!

LR = propylene

\[ F = \begin{bmatrix} 5\% \ \\ 20\% \ \\ 75\% \end{bmatrix} \begin{bmatrix} C_3H_6 \ \\ O_2 \ \\ N_2 \end{bmatrix} \]
Results: Maximum selectivity to acrolein

For given feed:

More complex processes than PFR and CFSTR only required

Feinberg Decomposition:

No inerts and only as little oxygen as necessary (separate air)

→ high molar ratio

→ increase rate for production of acrolein \( \hat{r}_1 = k_1 p_{C_3H_6} \)

Higher selectivity for excess of propylene, not oxygen

Improve existing design!
Improving the process design

**New feed:** $F_{\text{total}} = 200.5 \text{ mol/min}$

\[
F = \begin{bmatrix}
91.5 \\
22.9 \\
86.1
\end{bmatrix} \quad \text{mol/min C}_3\text{H}_6 \\
\text{mol/min O}_2 \\
\text{mol/min N}_2
\]

\[
\frac{F_{\text{C}_3\text{H}_8}}{F_{\text{O}_2}} = 4
\]

**Old feed:** $F_{\text{total}} = 200.5 \text{ mol/min}$

\[
F = \begin{bmatrix}
10 \\
40 \\
150.5
\end{bmatrix} \quad \text{mol/min C}_3\text{H}_6 \\
\text{mol/min O}_2 \\
\text{mol/min N}_2
\]

\[
\frac{F_{\text{C}_3\text{H}_8}}{F_{\text{O}_2}} = 0.25
\]

Significant improvement using the Feinberg results!
Let’s not forget what the alchemists knew!
Which Leads to Such Questions as:

- Does a decomposition exist for reactor systems when thermodynamic constraints are placed on the perfect separation system?

- Does a similar decomposition exist for separation systems (independent from the reactor system)?

- Can an entire process flowsheet be decomposed in a Feinbergian way?

- Does there exist an abstract kinetic/thermodynamic theory of process flowsheets?
40 years on
Shade is Good
50 years on: The Real Paradigm After Next

Stairs & Door in Lindos
Bravo George
“These smug pilots have lost touch with regular passengers like us. Who thinks I should fly the plane?”