Process synthesis: State of the art and future Trends

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OUTLINE

- Motivation
- Problem definition
- Solution approaches
- Issues/needs & tools
  - Future trends
- Conclusions
The objective (challenge) is to identify the important fruits (products), the optimal path to reach them, the feasibility of process, .....
Various stages of the process life cycle

- Conceptual Design

- Business Unit
  - Definition of objective
  - Decision on process
  - Idea for new compound/market strategy

- Chemical Research
  - Preliminary study
  - Information about novel compound

- Process Engineering
  - Preliminary study
  - Proposal for process improvement
  - Conceptual process design
  - Objective
  - Idea of production amount

- Construction Company
  - Site and installation plan
  - Estimated costs
  - Estimated schedule
  - Patents
  - Description of synthesis path
  - First process description
  - Analysis methods for product, product quality, etc.
  - First safety considerations

- Operating Company

- Process Engineering
  - PFD and pre-P&ID
  - Mass and energy balances
  - Datasheets for major units
  - Site and installation plan

- Chemical Research
  - Description of the process

- Business Unit
  - State of the market

- Conceptual Design

What happens after conceptual design?

Various stages of the process life cycle

- **Business Unit (BU)**
  - Decision on project continuation

- **Chemical Research**
  - P&ID
  - Data sheets and equipment drawings
  - Mass and energy balances
  - Information about process at steady state
  - Comments on startup and shutdown

- **Process Engineering (PE)**
  - Detailed process design

- **Construction Company (CC)**
  - Commissioning design and construction
  - Commissioning hand-over

- **Operating Company (OC)**
  - Commissioning, hand-over
  - Operation and maintenance
  - Decommissioning
Typical Design Problem - Requires the solution of a number of inter-related sub-problems

Inputs and outputs may be known but flowsheet, equipment parameters, condition of operation, ... are unknown!

Solution Approaches: knowledge-based, mathematical, ”hybrid”

Properties & Behavior
- Chemicals, Species

Generate Alternatives
- Flowsheet, design

Modeling & Simulation
- Screening, design

Analysis
- Energy, environmental impact

Process synthesis: State of the art and future trends
Problem Definition - I

The forward problem:
Given raw materials & product specifications (identity & quality), determine the process and the conditions of operation.

The reverse problem:
Given the product specifications, product quality & a list of equipments, determine the sequence of operations, the conditions of operation and the product identity.

Diagram:
- Solvent (S)
- Equipment parameters (D₁)
- Condition of operation (D₂)
- Process
- Raw material (F)
- Unwanted material (E)
- Product (P)

Process synthesis: State of the art and future trends
Mathematical Formulation

- Process/Product Synthesis

\[ F_{OBJ} = \min \{C'y + f(x)\} \]
\[ \text{s.t. } x, y \]
\[ h_1 (x, y) = 0 \quad \rightarrow \quad \text{Process model} \]
\[ h_2 (x) = 0 \quad \rightarrow \quad \text{Process constraints} \]
\[ g_1 (x) \leq 0 \quad \rightarrow \quad \text{“Other” constraints} \]
\[ g_2 (x, y) \leq 0 \quad \rightarrow \quad \text{Alternatives (MSA, EA, unit operations, ….)} \]
\[ B'y + C'x \leq d \]

- Existing process (retrofit problem)
  - Variables are fixed
  - Problem more constrained (less degrees of freedom)
  - More difficult to solve?
Solution Approaches - I

Heuristic/knowledge-based: Satisfy only the constraints

\[ F_{OBJ} = \min \{ C^t y + f(x) \} \]

s.t. \quad x, y

\[ h_1 (x, y) = 0 \]
\[ h_2 (x) = 0 \]
\[ g_1 (x) \leq 0 \]
\[ g_2 (x, y) \leq 0 \]
\[ B y + C x \leq d \]

Mathematical Programming: Solve all the optimization problem with process model included or solved separately

Process synthesis: State of the art and future trends
Solution Approaches - II

F_{OBJ} = \min \{C'y + f(x)\}
\begin{align*}
\text{s.t.} & \quad x, y \\
h_1 (x, y) &= 0 \\
h_2 (x) &= 0 \\
g_1 (x) &\leq 0 \\
g_2 (x, y) &\leq 0 \\
By + Cx &\leq d
\end{align*}

Hybrid Approach: Define search space through heuristic/knowledge-based & then apply the mathematical programming approach to solve a well defined optimization problem (x is bounded and dimension of y reduced)
Issues/needs & tools - I

- Optimal matching between hot and cold streams to minimize utility consumption
- Minimum number of heat exchangers needed

How to identify the design targets? What tools?
The CLEANER Production Strategy: A Process Integration Approach to Waste Reduction and Energy Conservation (Dunn et al.)

Design Strategy:
CLEANER Design for Waste Reduction and Energy Conservation

Systems Analysis Tools:
- Source-Sink Stream Representation Diagrams
- Mapping Diagrams
- Path Diagrams

Process Integration Design Methodologies:
- End-of-Pipe Methods
- In-Plant Design Methods

Unit Operations Targeted:
- Adsorbers
- Absorption Columns
- Condensers
- Evaporators
- Compressors
- Reverse Osmosis
- Permeation
- Heat Exchangers
- Heat Pumps
- Boilers
- Cooling Towers
- Condensers
- Evaporators
- Compressors
- Reverse Osmosis
- Pervaporation
Azeotropic separation process synthesis, design & analysis

How to identify a feasible configuration & design?
How to identify feasible separation techniques? Optimal design?

Hybrid separation sequence

Distillation column sequence
Issues/needs & tools - IV

- System: H₂O - (l)Asparagine - Alanine - Serine
- Products: (l)Asparagine, Alanine, Serine
- Solubility description:
  - Solubility product:
  - (l)Asparagine, Alanine, Serine
- Number of chemical species: 12
- Phase diagram type: quaternary
- Thermodynamic model:
  - Electrolyte NRTL

Design a process to recover all the three organic salts

How to generate feasible alternatives? How many?
How to identify feasible separation techniques & solvents? Optimal design?

Issues/needs & tools – V : Superstructure

Separation of binary mixture
How to generate alternative operational routes?

Issues/needs & tools - VI

Reaction: $A \rightarrow B$
Maximum conversion of 50% $A$ at $T = 340$ K
Extract $B$ from reactor with a solvent!
Solvent ID and effects need to be modeled

Synthesis of batch operations & design
1. Charge Feed (open F1 & close F2)
2. Close F1
3. Heat until temperature = 340 K
4. Control temperature at 340 K
5. Charge solvent by opening F3
6. Extract B by opening F4
7. …….
Roles of Process (Property) Models - I

Simulation

Process Model

Property Model

Design parameters

Results

Synthesis & Design

Iterative approach

Forward Problem: Service Role for Process (Property) Model

Raw material

T, P, X, compounds

Properties

Product

Process synthesis: State of the art and future trends
Roles of Process (Property) Models - II

Simulation

Process Model

Property Model

Design parameters

Results

Product

Properties

Synthesis & Design

Iterative approach

Design targets & feasibility

Forward Problem: Service & Advice Role for Property Model(s)

Remove redundant alternatives, Define upper & lower bounds
Availability of needed tools

Which types of tools are used?
When are they used?

- **Synthesis tools**
  - Equipment
  - Flowsheet
  - Separation agent

- **Collection tools**
  - Databases
  - Libraries
  - Repositories

- **Simulation tools**
  - Models

- **Analysis tools**
  - Physical behaviour
  - Safety
  - Costing

Process synthesis: State of the art and future trends
Tools Needed

- Process Simulator (steady state, dynamic) & Modelling tool
- Solvers (NLP, MINLP, AE, DAE, etc.)
- Flowsheet generation tool (process synthesis)
- CAMD (solvent selection/design)
- Physical properties database (> 13000 compounds)
- Environmental properties database
- Materials database
- Properties estimation tool (Pure component & mixture properties)
- Impact Assessment tools


**Basis for tools integration**

**Synthesis/Design:** Determine $T$, $P$, $x$ such that the process satisfies the specified objectives

**Control:** Determine the sensitivities of $T$, $P$, $x$ in order to design the control system

**Energy:** Determine $H(T, P, x)$ to compute the energy requirements

**Environmental Impact:** Identify environmental problems through $x$

**Economy:** Cost of operation, equipment are functions of $T$, $P$, $x$

$T$, $P$, $x$

chemicals

Property Model

Properties

Derivatives

Process synthesis: State of the art and future trends
Example 2. Estimation of the normal boiling point of Pyrene

![Pyrene molecule]

(Experimental value: \( T_b = 677.15 \))

<table>
<thead>
<tr>
<th>First-order Groups</th>
<th>Occurrences</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>aC (fused with arom. ring)</td>
<td>6</td>
<td>1.7324x6</td>
</tr>
<tr>
<td>aCH</td>
<td>10</td>
<td>0.8365x10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \sum N_i T_b i ) = 18.7593</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_b = 222.543 \ln(18.7593) = 652.43 \text{ K} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(first-order approx., error: 24.72 K)</td>
</tr>
</tbody>
</table>

No second-order groups are involved

<table>
<thead>
<tr>
<th>Third-order Groups</th>
<th>Occurrences</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>AROM.FUSED[3]</td>
<td>2</td>
<td>0.0402x2</td>
</tr>
<tr>
<td>AROM.FUSED[4p]</td>
<td>2</td>
<td>0.9126x2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \sum O_i T_b 3k = 1.9056 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_b = 222.543 \ln(18.7593+1.9056) = 673.96 \text{ K} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(third-order approx., error: 3.19 K)</td>
</tr>
</tbody>
</table>

Estimation through Joback and Reid [1]: 651.56 K
error: -24.41 K
Computational issues: Derivatives

- In process design, simulation and optimisation property models are required to have continuous first, second and even third order derivatives.
- Property models must be continuous and well behaved within the region bounded by \((P, T, z)\).

Example: Energy optimisation of a flash drum

\[
\begin{align*}
\min_{P, T} & \quad Q \\
\text{s.t.} & \quad \beta = \text{constant value} \\
& \quad T \in [T_{\text{lower}}, T_{\text{upper}}] \\
& \quad P \in [P_{\text{lower}}, P_{\text{upper}}] \\
& \quad F \cdot z_i = V \cdot y_i + L \cdot x_i ; i = 1, \text{NC} \\
& \quad y_i = K_i (P, T, x, y) \cdot x_i ; i = 1, \text{NC} \\
& \quad F \cdot H_F + Q = V \cdot H_v + L \cdot H_L
\end{align*}
\]
The Lagrange function

\[
L(X, \lambda, \mu) = Q(X) + \sum h_i(X) \cdot \lambda_i + \sum g_i(X) \cdot \mu_i
\]

At the optimal condition the necessary and sufficient Kuhn-Tucker conditions must be satisfied

\[
\nabla L_x (X^*, \lambda^*, \mu^*) = \nabla Q(X^*) + \nabla h(X^*) \cdot \lambda^* + \nabla g(X^*) \cdot \mu^* = 0
\]

\[
\mu^T \cdot g(X^*) = 0, \quad \mu \geq 0
\]

\[
g(X^*) \leq 0, \quad h(X^*) = 0
\]

\[
\nabla^2_{xx} L(X^*) \text{ is positive definite Hessian}
\]

Energy balance:

\[
H = H^{ig} + H^R \\
H^R = -RT^2 \left( \frac{\partial \ln \varphi}{\partial T} \right)_{P,x}
\]
Roles of Property Models in Design

Simulation

Process Model

Property Model

Synthesis & Design

Raw material

\( N \times M \) variables of \( Y \)

Design parameters

Results

Product

Properties & \( M \) variables from \( Y \)

Vector \( Y(N) \):

T, P, X, compounds

Design targets & feasibility

Reverse Problem: Service, Advice & Solve

Roles for Property (process) Models

Problem size reduced & does not need property model for solution!

Future trends: Problem reformulation but not model simplification
**Definition of driving force parameter**

\[
f_{ij} = y_i - x_i = x_i \beta_{ij} / (1 + x_i (\beta_{ij} - 1)) - x_i
\]

\[
\beta_{ij} = f(T, P, x, y, \theta)
\]

*Therefore, for fixed P & \( \theta \), driving forces and operating lines can be visualized in the same 2-dimensional plot.*

Process models consist of balance, constraint and constitutive equations. The driving force model equations represent the constraint and constitutive equations while the balance equations represents the process operating lines.
Future trends: Use of a driving force based approach

**Secondary Separation Efficiency, Methanol MTBE**

Separation by single distillation operation not feasible; hybrid separation schemes (solvent based extraction or distillation plus pervaporation or pressure swing distillation) feasible

Future trends: Use of a driving force based approach
Hybrid Separation: Optimal design

Superstructure representing various alternatives

One hybrid separation scheme

Distillation plus pervaporation requires 34.5% less energy if the product from the first distillation = 62% MTBE. Distillation columns in both schemes optimized in terms of intersection of operating lines

Future trends: use of driving force based approach
Another Example: Distillation Train

Energy saving: 16.9% (also gives higher purity products)

Future trends: Use of a driving force based approach
Identification of feasible separation techniques

For each binary pair,
1. Compute for property \( k \), \( B_{ij} = \frac{p_{ik}}{p_{jk}} \)
2. If \( B_{ij} > \theta \), separation technique \( k \) is feasible
Visualization of Synthesis & Design

- System: H₂O - (l)Asparagine - Alanine - Serine
- Products: (l)Asparagine, Alanine, Serine
- Solubility description:
  Solubility product:
  (l)Asparagine, Alanine, Serine
- Number of chemical species: 12
- Phase diagram type: quaternary
- Thermodynamic model:
  Electrolyte NRTL

Simultaneous problem solution and visualization for batch & continuous operations/processes

CAMD Framework

"I want acyclic alcohols, ketones, aldehydes and ethers with solvent properties similar to Benzene"

A set of building blocks: CH3, CH2, CH, C, OH, CH3CO, CH2CO, CHO, CH3O, CH2O, CH-O

A set of numerical constraints

A collection of group vectors like:
3 CH3, 1 CH2, 1 CH, 1 CH2O
All group vectors satisfy constraints

Pre-design

Design (Start)

Design (Higher levels)

Start of Post-design

2. order group

Group from other GCA method

Refined property estimation. Ability to estimate additional properties or use alternative methods.
Rescreening against constraints.
Molecule Generation

Level 3

Level 4
CAMD Solution step
Reverse Problem: Retrofit Design

\[ N_p = f(K, RR, x_D, x_B) \]

\[ N_p = f(F_{dMax}(K(\alpha), R_{min}), C) \]

1. Given \( N_p & C \), determine \( F_{dMax} \) and then upper & lower limits of \( \alpha \)

2. Given limits of \( \alpha \), find the set of binary pairs and pressure that match the desired range

\[ F_{dMax} = \frac{d\left( x \frac{\alpha}{1 + x (\alpha - 1)}\right)}{dx} - 1 \]

Composition free retrofit design of distillation column
# Problem solution

<table>
<thead>
<tr>
<th>Given:</th>
<th>Find (Step 1):</th>
<th>Solution:</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP = 60</td>
<td>$\text{FDi}_{\text{Max}} \sim 0.07$</td>
<td>Butane – iButane</td>
</tr>
<tr>
<td>$N_F = 33-38$</td>
<td>$\text{RRmin} \sim 6.4$</td>
<td>$P = 5 \text{ atm}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Desired:</th>
<th>Find (Step 2):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{B,HK} = 0.995$</td>
<td>Binary mixtures with $\alpha \sim 1.3 - 1.4$</td>
<td>$\text{FDi}_{\text{Max}} 0.074$</td>
</tr>
<tr>
<td>$X_{D,LK} = 0.995$</td>
<td>Operating Conditions</td>
<td>$\alpha = 1.33 - 1.34$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_F = 33$</td>
</tr>
</tbody>
</table>
Consider the reverse problem of simulation – given the design variables, solve the process model equations to determine the corresponding property values.

- **Heat Exchanger**: For assumed $U$ and given $A$, $Q$ & $F$, determine $\Delta T$ and then the property (design) target value for $\Delta H$.

- For given $\Delta T$ and $\Delta H$, generate a list of process fluids that satisfy the desired targets.

Note that in the 1st step, calculations are composition independent & 2nd step is reverse of property prediction!
Other examples of reverse problem

Consider the reverse problem of simulation – given the design variables, solve the process model equations to determine the corresponding property values.

Mass Exchanger

Product + waste

Solvent

Product

Solvent + waste

Process synthesis: State of the art and future trends
Future Trends: Simultaneous solution approach

Given: Models

Operation
- Heat Exchange
- Mass Exchange
- Mixing
- Reaction

Stream
- Bubble-point
- Dew-point

Performance Criteria, product specification, ...

Determine: The sequence of operations & streams at optimal performance criteria

Simultaneous solution approach where the process model & property model equations are decomposed

Solution provides model, flowsheet & design simultaneously!
**Composition Free Design**

**Design Algorithm:**

I. Generate phase diagrams ($b^L$ vs. $b^V$, $b^L$, $b^V$ vs. $T$ & $a^L$, $a^V$ vs. $T$)

II. Draw operating lines and determine the number of trays

III. For each tray determine $T$, $b^L$, $b^V$ and the corresponding $a^L$, $a^V$ (figure not shown)

IV. Generate compositions and equilibrium constants for each tray and compound

* Mix 5 streams each with 50 compounds
* Separate the mixed stream into five products in a distillation column
* Find the optimal design
  - Determine the $a$ and $b$ parameters for the total mixture & design targets
  - Determine the $K$-values for each compound and the column temperatures
  - Solve the process model for the compositions
  - Use these results in a rigorous model (saving = 50% to 90%)
Conclusions

* Properties can be made to play various roles in process/product/operation design/synthesis.
* Process synthesis problems require the solution of a number of inter-related problems and integration saves time of the engineer.
  • Reverse problem & simultaneous solution approach may be able to expand the application range of current tools and solve future synthesis problems.
  • In order to obtain the desired fruits from the product tree, modeling & simulation roles need to be played more efficiently.