New Vistas in Chemical Product & Process Design

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The big picture
Our survival depends on the products we make from the resources we have.
The chemical product tree

Question of what, why & when (how)?

Refined chemicals & Consumer products (~3000)
- Plastics, Pharmaceuticals, Dyes, Solvents, Fertilizers, Fibres, Dispensers, Cosmetics...

Intermediate Products (~300)
- Methanol, Vinyl chloride, Styrene, Urea, Formaldehyde, Ethylene oxide, Acetic acid, Acrylonitrile, Cyclohexane, Acrylic acid, ...

Basic Products (~20)
- Ethylene, Propylene, Butadiene, Benzene, Synthesis-gas, Acetylene, Ammonia, Sulfuric acid, Sodium hydroxide, chlorine, ...

Raw Materials (~10)
- Petroleum, Natural Gas, Biomass, Roack, Salt, Phosphate, Sulfur, Air, Water, ...

Factors:
- High vs. Low
- Product price
- Molecular size
- Number of alternatives
- Production rate
**Chemical product classification**

<table>
<thead>
<tr>
<th>Product Type Issues</th>
<th>Single species</th>
<th>Multiple species</th>
<th>Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Examples</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvents, refrigerants</td>
<td>Small</td>
<td>Formulated</td>
<td>Fuel-cells, microcapsules, hemodialysis device</td>
</tr>
<tr>
<td>APIs, surfactants, membranes</td>
<td>Large</td>
<td>Functional</td>
<td></td>
</tr>
<tr>
<td><strong>Key factors in design</strong></td>
<td>Cost of production</td>
<td>Cost and product functions</td>
<td>Product functions</td>
</tr>
<tr>
<td>Cost of production</td>
<td>N.A.</td>
<td>Time to market (speed)</td>
<td></td>
</tr>
<tr>
<td><strong>Basis of design</strong></td>
<td>Process flowsheet (unit operations)</td>
<td>Synthesis routes (chemistry)</td>
<td>Blend properties and stability</td>
</tr>
<tr>
<td><strong>Measure of performance</strong></td>
<td>Closely related to process</td>
<td>Closely related to application</td>
<td>Closely related to application</td>
</tr>
<tr>
<td><strong>Challenges in design</strong></td>
<td>Translation of needs to molecular structure</td>
<td>Translation of needs to properties</td>
<td>Delivering product functions defined by needs</td>
</tr>
<tr>
<td>Large number of product alternatives</td>
<td>Trial &amp; error approach (non-optimal product)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Risks</strong></td>
<td>Feedstock availability</td>
<td>Absence of engineering science knowledge</td>
<td>Environmental impact and sustainability</td>
</tr>
</tbody>
</table>
The concepts
Design of single species products

Find molecules with desired properties (also valid for mixtures)

"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.

Computer aided molecular design (generate & test)
Generation of Alternatives

Groups as building blocks: \( \text{CH}_3, - \text{CH}_2, - \text{OH}, \text{CH}_3\text{CO}, \ldots \) (a set of about 180 groups available)

Structural constraints (acyclic molecules)

\[
\sum_{j=1}^{m} (2-u_j)n_j = 2q \quad \sum_{i \neq j}^{m} n_i = n_j(u_j - 2) + 2 \quad \forall j
\]

Size constraints

\[
n^l_j \leq n_j \leq n^u_j \quad \forall j \quad 2 \leq \sum_{j=1}^{m} n_j \leq n_{\text{max}} \quad n = \sum_{j=1}^{m} n_j
\]

Example: \( \text{CH}_3 – \text{CH}_2 – \text{OH} : \) Ethanol (3 groups)
Evaluation of Generated Molecules: Models

Group contribution (GC) methods for property prediction

\[ V_C = 17.5 + \sum_j n_j \Delta_j \]

\[ V_c - V_{c0} = \sum_i N_i V_{C1i} + w \sum_j M_j V_{C2j} + z \sum_k O_k V_{C3k} \]

**Examples:**

- UNIFAC (VLE, LLE, SLE)

**Examples:**

\[ \ln \gamma_i = \ln \gamma_i^{\text{COM}} + \ln \gamma_i^{\text{RES}} \]

Joback & Reid 1987
## Amino acids property modelling

### Compound:
- L-Phenylalanine methyl ester hydrochloride

### Molecular structure

![Molecular structure of L-Phenylalanine methyl ester hydrochloride](image)

### C6H5CH2CH(NH2)COOCH3 · HCl

<table>
<thead>
<tr>
<th>First-order groups</th>
<th>Occurrences</th>
<th>Group-contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>1</td>
<td>0.7473</td>
</tr>
<tr>
<td>aCH</td>
<td>5</td>
<td>0.4297</td>
</tr>
<tr>
<td>aC-CH₂</td>
<td>1</td>
<td>-0.2869</td>
</tr>
<tr>
<td>COO (except as above)</td>
<td>1</td>
<td>1.966</td>
</tr>
<tr>
<td>-HCl</td>
<td>1</td>
<td>0.4662</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Second-order groups</th>
<th>Occurrences</th>
<th>Group-contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Third-order groups</th>
<th>Occurrences</th>
<th>Group-contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(NH₃+Cl)-(CH₂)n-COO-</td>
<td>1</td>
<td>-0.9282</td>
</tr>
</tbody>
</table>

\[
\exp \left( \frac{T_m}{T_m^0 + a \cdot MW} \right) = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k E_k O_k \quad \Rightarrow \quad T_m^{\text{pred}} = 430.9 \quad \text{(Note: } T_m^0 = 237.0611 \text{ K; } a = -0.0914 \text{ K mol g}^{-1})
\]

The experimental value of \(T_m\) is 433.2 K. Hence, absolute deviation = 2.2 K
Polymer Design: MINLP Applied to CAMD

Fobj = $\sum \left[ \frac{(P_i - P_i^*)}{P_i^*} \right]^2$

s.t.

353 K < $T_g = \frac{\sum (Y_k n_k)}{\sum (M_k n_k)}$ < 393 K

1.4 < $\rho = \frac{\sum (M_k n_k)}{\sum (V_k n_k)}$ < 1.5 g/cm$^3$

0.0045 < $W = \frac{\sum (H_k n_k)}{\sum (M_k n_k)}$ < 0.0055 g H$_2$O/g polymer)

$2 \leq \sum y_j \leq 3$ ; $y_j : 0$ or $1$ for $j=1,7$

$2 \leq \sum y_k n_k \leq 9$

-CH2- ; -CO- ; -COO- ; -O- ; -CONH- ; -CHOH- ; -CHCL-

Note: objective function and constraints are non linear; $n_k$, the optimization variables are integer (0-9)

Polymer repeat units designed for bottle-stops; synthetic fibers; coatings, etc (CACE 2009)
CAMD versus CAFD

Computer aided molecular design: CAMD

Computer aided flowsheet design: CAFD
Sustainable Product-Process Development

Applicaitons: Biorefinery; CCU; CAMD; Waste-water treatment; ….
The problem definitions
Problems may have multiscale & multidiscipline features
Mathematical generic problem formulation

\[ \text{Fobj} = \min \left\{ C^T y + f(x, y, u, d, \theta) + S_e + S_i + S_s + H_c + H_p \right\} \] (1)

0 = h_1(x, y) \quad \text{process constraints (Eq. 2)}

0 = P(f, x, y, d, u, \theta) \quad \text{process model (Eq. 3)}

\theta = \theta(f, x, y) \quad \text{product-property model (Eq. 4)}

l_1 \leq g_1(x, u, d) \leq u_1 \quad \text{process variable constraints (Eq. 5)}

l_2 \leq g_2(x, y) \leq u_2 \quad \text{molecular structure constraints (Eq. 6)}

B x + C^T y \geq D \quad \text{process networks (Eq. 7)}

\[ x: \text{real-process variables; } y: \text{integer-decision variables; } \]
\[ u: \text{process design variables; } d: \text{process input variables; } \]
\[ \theta: \text{property; } B, C, D \text{ coefficient matrices} \]
Different problem formulations

- Eq. 1: Objective function
- Eq. 2: Process constraints
- Eq. 3: Process models
- Eq. 4: Property models
- Eq. 5: Process variable constraints
- Eq. 6: Molecular structural constraint
- Eq. 7: Processing networks

Product – Process Design (Eq. 1)

• Process simulation
• Process optimization
• Product evaluation
• Optimal product
• Product + implicit application
• Product-process-application
• ………

Product Design (Eqs. 4, 6)

Process Design (Eqs. 3, 5, 7)

Simultaneous Product – Process Design ( multiscale & multidiscipline)
SPEED

Concept of model based framework

Methods and Tools

- Databases
- Knowledge base
- Model libraries
- Model generation
- Grand Product Design model

Work Flow

START

Step 1: Problem Definition
(1) Define the problem
(2) Translate needs into target properties
(3) Set the target property values

Step 2: CAMD constraint selection
(1) Structure model, groups & backbone
(2) Property Thermodynamic model
(3) Process model selection
(5) Objective function selection

Step 3: CAMD formulation

Step 4: Solution strategy
(1) Selection of solution algorithm
(2) Selection of MI(N)LP solver
(3) Solution of MI(N)LP

Solution found?

N

END

Information Flow

- Product needs
- Target property values
- Economic/Sustainability/Environment models
- Set of candidate groups
- Objective function
- Upper and lower bound of target properties
- Process/Product model equations
- MI(N)LP model
- List of candidates
- Report generation

Zhang et al. CACE, 2015
Mathematical Problem Solution

Our target optimal solution

Where is Wally?

Donde está Waldo?

Hvor er Holger?

........

........
Examples: Molecular design (single species products)
- Solvents
- Process fluids
- Surfactants
- Active ingredients
- Polymer repeat units
- …

Eqs. 4, 6 with or without Eq. 1
(product design and implicit performance verification)
**Examples:** Molecular design (single molecular products) - Surfactants

Eqs. 4, 6 with or without Eq. 1 (product design and implicit performance verification)

Homogeneous reactions
• **Step 1:** Design of a UV sunscreen, in the emulsified form, with a high sun protection factor. The phenol ring is fixed as backbone structure in this case study.

• **Step 2:** Convert needs-functions to properties
  
  - **Objective:** Toxicity should be minimized, but higher than a lower bound
  
  - **Group selection:** CH$_3$, CH$_2$, CH, C, aCH, aC-OH, CH$_2$COO, CH$_3$O, CH$_2$O, aC-O, OCH$_2$CH$_2$OH from 220 groups (Marrero and Gani, 2001).

  - **Backbone selection:** -C$_6$H$_4$OH

  - **Structural and property constraints:**

<table>
<thead>
<tr>
<th>Need</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_G$</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>$N_F$</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>$lc50$</td>
<td>3.16log(mol/L)</td>
<td>-</td>
</tr>
<tr>
<td>$Sp$</td>
<td>-</td>
<td>25MPa$^{0.5}$</td>
</tr>
<tr>
<td>$clp$</td>
<td>343.15K</td>
<td>-</td>
</tr>
<tr>
<td>$Fp$</td>
<td>343.15K</td>
<td>-</td>
</tr>
<tr>
<td>$Vm$</td>
<td>0.1cc/mol</td>
<td>0.3cc/mol</td>
</tr>
</tbody>
</table>

$LC_{50}$: Fathead Minnow 96-hr exposure; $Sp$: Hildebrand solubility parameter; $clp$: cloud point; $Fp$: Flash point; $Vm$: Liquid molar volume at 298K.
Surfactant Design (2/3)

• Step 3: Formulate the mathematical problem

\[
\text{max } l_{c50} = lco + \sum_{i_1} n^{(1)}_{i_1} l_{c50}^{(1)} + \sum_{i_2} n^{(2)}_{i_2} l_{c50}^{(2)}
\]

2. Pure component property constraints:

1. Structural constraints:

1.1 Octet rule and group number constraints:

\[
\sum_i (2 - \nu_{i_1}) n^{(1)}_{i_1} = 0
\]

\[
\sum_{i_1,i_1 \neq i_1'} n^{(1)}_{i_1} \geq n^{(1)}_{i_1'} \left( \nu_{i_1'} - 2 \right) + 2 \quad \forall i_1'
\]

\[
1 \leq n^{(1)}_{i_1} \leq 5 \quad \forall i
\]

\[
10 \leq \sum_{i_1} n^{(1)}_{i_1} \leq 15
\]

1.2 Adjacency matrix constraints.

1.3 Second-order group constraints.

\[
\sum_{i_1} n^{(1)}_{i_1} c_{p_{i_1}} \geq 343.15^2
\]

\[
F_{po} + \sum_{i_1} n_{i_1}^{(1)} F_{p_{i_1}} + \sum_{i_2} n_{i_2}^{(2)} F_{p_{i_2}} \geq 343.15
\]

\[
0.1 \leq V_{mo} + \sum_{i_1} n_{i_1}^{(1)} V_{m_{i_1}} + \sum_{i_2} n_{i_2}^{(2)} V_{m_{i_2}} \leq 0.3
\]

#Equations: 1,324,764; #Variables: 1,286,278 (1,286,266 Integer variables).

• Step 4: This design problem can also be solved directly using the GAMS CPLEX solver.
Table: Optimization results of surfactant design problem

<table>
<thead>
<tr>
<th>$n_1$</th>
<th>1 CH$_3$, 5 CH$_2$, 1 CH, 4 aCH, 1 aC–OH, 1 CH$_2$COO, 1 aC–O, 1 OCH$_2$CH$_2$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_2$</td>
<td>1 AROMRINGs1s4</td>
</tr>
<tr>
<td>$lc_{50}$</td>
<td>4.124 log(mol/L)</td>
</tr>
<tr>
<td>$Sp$</td>
<td>24.732 MPa$^{0.5}$</td>
</tr>
<tr>
<td>$clp$</td>
<td>300.016 K</td>
</tr>
<tr>
<td>$Fp$</td>
<td>552.383 K</td>
</tr>
<tr>
<td>$Vm$</td>
<td>0.281 cc/mol</td>
</tr>
</tbody>
</table>

Backbone
Examples: Molecular and/or mixture design with process application

- Solvents for separations and/or product recovery
- Process fluids for specific operations
- Reactive agents
- .....
Objective of the study: Identify possible process hotspots to improve the process in terms of:

- Conversion to continuous manufacturing
- Solvent selection to improve productivity
  - Reaction improvement
  - Separation improvement
Solvent based reaction-separation processes

Generation of alternatives for the production of L-2-aminobutyric acid

Reaction type Database

A. Single phase system
B. Biphasic system

Experimental data available
Kinetic model is not available

Solvent selection:
Organic solvent that is,
- Immiscible with the aqueous phase
- Higher by-product selectivity

Inhibits the enzyme
Generation of alternatives for the production of L-2-aminobutyric acid

Model development method: Multiphase reaction modeling (Anantpinijwatna et al. 2016)

Physical Equilibrium

Mass Balance

Reaction type Database:

Experimental data
### Extractive solvent selection:

<table>
<thead>
<tr>
<th></th>
<th>Benzyllamine</th>
<th>2OA</th>
<th>AABA</th>
<th>Benzaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.986</td>
<td>8.33E-06</td>
<td>4.50E-06</td>
<td>8.06E+03</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.178</td>
<td>5.41E-06</td>
<td>3.56E-06</td>
<td>8.33E+03</td>
</tr>
<tr>
<td>Isooctane</td>
<td>3.096</td>
<td>8.33E-06</td>
<td>6.85E-06</td>
<td>1.59E+04</td>
</tr>
<tr>
<td>Octane</td>
<td>2.959</td>
<td>3.73E-04</td>
<td>1.19E-04</td>
<td>1.30E+04</td>
</tr>
</tbody>
</table>

**Batch to continuous database**

**Enzyme membrane reactor**
Facilitates enzyme stability and avoid the enzyme contact with the organic solvent in a continuous operation
SPEED Solvent based reaction-separation processes

Generation of alternatives for the production of L-2-aminobutyric acid

Objectives:

- Recover the main product
- Recover and recycle the extraction solvent (Hexane) and the reaction solvent (water)
- Recycle unreacted Benzamine

<table>
<thead>
<tr>
<th>Rank</th>
<th>Process alternatives [SFIES]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(rABCDEF)(spABCD/EF)(ImE/F)<a href="crD/ABC">[(oE)]1(pF)</a>[<a href="dsAB/C">(oD)</a>[<a href="oC">(oAB)</a>]</td>
</tr>
<tr>
<td>2</td>
<td>(rABCDEF)(spABCD/EF)(ImE/F)<a href="crD/ABW%5BoAB%5D%5BscsC/D">[(oE)]1(pF)</a>[<a href="scS/C">(oD)</a><a href="oABC">2(oS)</a>]</td>
</tr>
<tr>
<td>3</td>
<td>(rABCDEF)(spABCD/EF)(ImE/F)<a href="crD/ABW%5BoAB%5D%5BscsC/D">[(oE)]1(pF)</a>[<a href="scS/C">(oD)</a><a href="oABC">2(oS)</a>]</td>
</tr>
<tr>
<td>4</td>
<td>(rABCDEF)(spABCD/EF)(ImE/F)<a href="crD/ABW%5BoAB%5D%5BscsC/D">[(oE)]1(pF)</a>[<a href="scS/C">(oD)</a><a href="oABC">2(oS)</a>]</td>
</tr>
</tbody>
</table>

A: water
B: BA
C: 2OA
D: AABA
E: BD
F: Hexane
Other biphasic reaction-separation systems
Examples: Molecular design (single molecular products) with process constraints

- Solvents for separations and/or product recovery
- Process fluids for specific operations
- Reactive agents
- .....

**Eqs. 1-7: simultaneous product design & process application**
SPEE

Simultaneous product and application process design

- Refrigeration cycle and fluid affect each other. Therefore, product and process application considered.

- Objective is to determine novel working fluids and mixtures that comply with current and upcoming regulations.

- Requirements for substitution of existing fluids:
  - New fluid should have same or improved cycle efficiency.
  - New fluid should have similar operational behavior.
  - New fluid should improve sustainability.

➢ Relate process with product properties.
➢ Find optimal product-cycle design.
SPEE

Simultaneous product and application process design

Refrigerant-cycle design: Step 1

• R134a is a commonly used refrigerant that is being phased out.
• Product properties that affect the process cycle:
  – Critical properties;
  – Heat capacity;
  – Compressibility;
  – Centric factor;
  – Vapor pressure;
  – Heat of vaporization...
• These product properties influence the process cycle and its efficiency.
• Also, other properties (enthalpy, entropy, fugacity) are needed for process cycle design.
• Equation of state and for estimation of PVT relationship.
SPEED Simultaneous product and application process design

- Look for novel fluids that can contain C, H, F and Cl (up to 10 groups).
- 30 molecular groups are selected from M-G method.
- Target properties are chosen for product and process:

<table>
<thead>
<tr>
<th>Target Property</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass</td>
<td>110 g/mol</td>
<td></td>
</tr>
<tr>
<td>Normal boiling point</td>
<td>250 K</td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td>350 K</td>
<td>400 K</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>30 bar</td>
<td>50 bar</td>
</tr>
<tr>
<td>Thermal conductivity (liquid, Tb)</td>
<td>0.08 W/m.K</td>
<td></td>
</tr>
<tr>
<td>Enthalpy of Vaporization at Tb</td>
<td>200 kJ/kg</td>
<td></td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>GWP</td>
<td>1400</td>
<td></td>
</tr>
<tr>
<td>Atmospheric Lifetime *</td>
<td>14 years</td>
<td></td>
</tr>
<tr>
<td>Number of groups</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Number of functional groups</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Evaporation temperature</td>
<td>313.15 K</td>
<td>333.15</td>
</tr>
<tr>
<td>Condensation temperature</td>
<td>265.65 K</td>
<td>280.15</td>
</tr>
</tbody>
</table>
Refrigerant-cycle design: Step-3 (complete model-1)

- Molecular constraints
  \[ \sum_i n_i (2 - \nu_i) = 2 \]
  \[ 1 \leq \sum_i n_i \leq 10 \]
  \[ 0 \leq \sum_i n_i \leq 3 \]

- Property constraints
  \[ \sum_i n_i M_{wi} \geq 110 \text{g/mol} \]
  \[ T_{b0} \ln \left( \sum_i n_i T_{bi} \right) \geq 250 \text{K} \]
  \[ 350 \text{K} \leq T_{e0} \ln \left( \sum_i n_i T_{ei} \right) \leq 400 \text{K} \]
  \[ 30 \text{bar} \leq \frac{1}{\left( \sum_i n_i P_{ci} + P_{c02} \right)^2} + P_{e01} \leq 50 \text{bar} \]
  \[ \frac{1.11}{\left( \sum_i n_i M_{wi} \right)^{\frac{1}{2}}} \times \left( 3 + 20 \left( 1 - \frac{T}{T_c} \right)^{\frac{2}{3}} \right) \geq 0.1 \text{W/m.K} \]

\[ \Delta H_v \left( T_0 \right) \left( \frac{1 - \frac{T_1}{T_c}}{\frac{T_0}{T_c} - 1} \right)^{0.38} \geq 200 \text{kJ/kg} \]

- Process constraints
  \[ f \left( Z_{V1} \right) = 0 = Z_{V1}^3 - Z_{V1}^2 + Z_{V1} (-B^2 + A - B) - AB \]
  \[ f \left( Z_{V2} \right) = 0 = Z_{V2}^3 - Z_{V2}^2 + Z_{V2} (-B^2 + A - B) - \]
  \[ AB \]
  \[ f \left( Z_{L3} \right) = 0 = Z_{L3}^3 - Z_{L3}^2 + Z_{L3} (-B^2 + A - B) - AB \]

Needed for efficient solution of cubic EoS [4]:

\[ f' \left( Z_{V1} \right) \geq 0 \quad f'' \left( Z_{V2} \right) \geq 0 \]
\[ f \left( Z_{V1} \right) = 0 \quad f' \left( Z_{V2} \right) \geq 0 \]
\[ f' \left( Z_{L3} \right) = 0 \quad f'' \left( Z_{L3} \right) \geq 0 \]
\[ f \left( Z_{V1} \right) = 0 \quad f' \left( Z_{L3} \right) \geq 0 \]
\[ f' \left( Z_{V2} \right) = 0 \quad f'' \left( Z_{L3} \right) \leq 0 \]

Simultaneous product and application process design

**Refrigerant-cycle design: Step-3 (complete model-2)**

- **Process constraints**

  \[
  \ln \varphi_{V1} = \ln \varphi_{L1} \\
  \ln \varphi_{V2} = \ln \varphi_{L2} \\
  H_{L3}(T_3, P_3) - H_{L4}(T_4, P_4) = 0 \\
  S_{V2}(T_2, P_2) - S_{V1}(T_1, P_1) = 0 \\
  P_1 = P_4 \\
  P_2 = P_3 \\
  T_1 = T_4 \\
  P_1 \geq P_0 \\
  P_2 \leq 0.8P_c \\
  T_2 \leq 0.8T_c \\
  265.65K \leq T_1 \leq 280.15K \\
  313.15K \leq T_3 \leq 333.15K
  \]

- **Objective function**

  \[
  \max COP = \frac{H_{L3}(Z_{V1}, T, P) - H_{L4}(Z_{V1}, T, P)}{H_2(Z_{V2}, T_2, P_2) - H_1(Z_{V1}, T_1, P_1)}
  \]
Case study: Product-process design

Cycle design for each molecules is given by Problem (II)

<table>
<thead>
<tr>
<th></th>
<th>r134a</th>
<th>r152a</th>
<th>3,3,3-triFluoro propyne</th>
<th>3,3-diFluoro butene</th>
<th>2,2-diFluoro butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mw</td>
<td>102 g/mol</td>
<td>66 g/mol</td>
<td>94 g/mol</td>
<td>92 g/mol</td>
<td>94.1 g/mol</td>
</tr>
<tr>
<td>Tb</td>
<td>236 K</td>
<td>230 K</td>
<td>242 K</td>
<td>246 K</td>
<td>252 K</td>
</tr>
<tr>
<td>Tc</td>
<td>374 K</td>
<td>366 K</td>
<td>369 K</td>
<td>392 K</td>
<td>389 K</td>
</tr>
<tr>
<td>Pc</td>
<td>37.32 bar</td>
<td>46.75 bar</td>
<td>38.13 bar</td>
<td>39.27 bar</td>
<td>37.8 bar</td>
</tr>
<tr>
<td>ω</td>
<td>0.33</td>
<td>0.27</td>
<td>0.28</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>k</td>
<td>0.082 W/m.k</td>
<td>0.097 W/m.k</td>
<td>0.086 W/m.K</td>
<td>0.093 W/m.K</td>
<td>0.092 W/m.K</td>
</tr>
<tr>
<td>ΔH &lt;sub&gt;v&lt;/sub&gt; at T&lt;sub&gt;b&lt;/sub&gt;</td>
<td>26523 J/mol</td>
<td>28562 J/mol</td>
<td>18635 J/mol</td>
<td>21312 J/mol</td>
<td>26991 J/mol</td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GWP</td>
<td>1370 (ASHRAE, 2005)</td>
<td>133 (ASHRAE, 2005)</td>
<td>134.6</td>
<td>2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Atmospheric lifetime</td>
<td>13.4 years (ASHRAE, 2005)</td>
<td>1.5 years (ASHRAE, 2005)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>COP</td>
<td>10.1</td>
<td>12.8</td>
<td>9.5</td>
<td>11.0</td>
<td>11.1</td>
</tr>
</tbody>
</table>
Examples: Formulated and/or blend design

- Liquid formulated products
- Tailor-made blends
- Emulsified products
- ........

Eqs. 1, 4 & 6: mixture-blend design
The main challenge involves how to identify the blends that satisfy the blend target properties with various types of additives.

Problems solved: Tailor made design of gasoline blends, diesel blends, jet-fuel blends and lubricant blends.

Example: Blending gasoline with different additives:
✓ impact of fuel consumption on the environment.
✓ performances can be retained and improved.

Blend templates help to efficiently narrow down the search space of feasible chemicals to be added and obtain improved tailor-made blends in a faster, reliable and robust manner.

* Collaboration with Texas A&M in Qatar.

* To be presented at Session I-2, paper OL5, 16:40 by Sawitree Kalakul
**Task 1 Problem Definition**

1.1 Identify product needs

1.2 Translate needs into physico-chemical properties

1.3 Set target values

<table>
<thead>
<tr>
<th>Need</th>
<th>Target property</th>
<th>Target value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ability to be burned</td>
<td>$RVP$</td>
<td>$45 \leq RVP \leq 60$</td>
</tr>
<tr>
<td>Engine efficiency</td>
<td>$RON$</td>
<td>$RON \geq 92$</td>
</tr>
<tr>
<td></td>
<td>$HHV$</td>
<td>$HHV \geq 40$</td>
</tr>
<tr>
<td>Consistency of fuel flow</td>
<td>$\eta$</td>
<td>$0.30 \leq \eta \leq 0.60$</td>
</tr>
<tr>
<td></td>
<td>$\rho$</td>
<td>$0.720 \leq \rho \leq 0.775$</td>
</tr>
<tr>
<td>Flammability</td>
<td>$T_f$</td>
<td>$T_f \leq 300$</td>
</tr>
<tr>
<td>Toxicty</td>
<td>$LC_{50}$</td>
<td>$-log LC_{50} &lt; 3.08$</td>
</tr>
<tr>
<td>Stability</td>
<td>$\Delta G^{mix}$</td>
<td>$\Delta G^{mix} &lt; 0$</td>
</tr>
<tr>
<td>Environmental aspect</td>
<td>$W_{tO_2}$</td>
<td>$2 \leq W_{tO_2} \leq 20$</td>
</tr>
<tr>
<td>Low oxidation</td>
<td>Choice of chemicals</td>
<td></td>
</tr>
</tbody>
</table>
Tailor-made fuels

Task 2 Mixture/blend design

2.1 Pure component constraints (HHV, ρ, η, LC50, WtO2)
2.2 Miscibility constraint ($\Delta G^{\text{mix}}$)
2.3 Linear constraints (HHV, ρ, η, LC50, WtO2)
2.4 Non-linear constraints (RVP, Tf)

Miscibility test:
$\Delta G^{\text{Mix}} < 0$

$$\min \text{ or } \max f_{\text{obj}}(x)$$

s. t.
$$\zeta^k_{\text{LB}} \leq \sum_{i} x_i \zeta^k_i \leq \zeta^k_{\text{UB}}$$

(5 Eqs. One for each prop-erty)

$$\sum_{i=1}^{NC} x_i - 1 = 0$$

$$0 < x_i < 1$$

$$\sum_{i=1}^{NC} x_i = N_C$$

$$\sum_{i=1}^{NC} \gamma_i P_{i}^{\text{sat}} (310.95 \text{ K}) = 1$$

Nonlinear Program

$$\sum_{i=1}^{NC} x_i Y_i T_{f,i} = T_{f,mix}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0$$

$$x_{\text{LB}} < x_i < x_{\text{UB}}$$

Linear Program
**Task 3 Rank blend candidates according to a selection criterion**

<table>
<thead>
<tr>
<th>Blend</th>
<th>Composition (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend 1</td>
<td>MI (69), Tetrahydrofuran (11), 2-Methyl Tetrahydrofuran (20)</td>
</tr>
<tr>
<td>Blend 2</td>
<td>MI (67), Acetone (13), 2-Methyl Tetrahydrofuran (20)</td>
</tr>
<tr>
<td>Blend 3</td>
<td>MI (72), Acetone (10), 2-Butanone (18)</td>
</tr>
<tr>
<td>Blend 4</td>
<td>MI (75), 2-Butanone (13), 2-Methyl Tetrahydrofuran (12)</td>
</tr>
<tr>
<td>Blend 5</td>
<td>MI (77), Ethanol (12), 2-Methyl Tetrahydrofuran (11)</td>
</tr>
</tbody>
</table>

**Task 4 Experimental verification**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density at 15°C (g/〖cm〗^3)</th>
<th>Dynamic Viscosity (mPa.s)</th>
<th>Vapor Pressure at 37.8°C (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target Values</td>
<td>0.720 – 0.775</td>
<td>0.3 – 0.6</td>
<td>45 - 60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main Ingredient</td>
<td>0.71</td>
<td>0.50</td>
<td>51.0</td>
</tr>
<tr>
<td>Blend 1</td>
<td>0.76</td>
<td>0.54</td>
<td>46.2</td>
</tr>
<tr>
<td>Blend 2</td>
<td>0.75</td>
<td>0.46</td>
<td>60.4</td>
</tr>
<tr>
<td>Blend 3</td>
<td>0.73</td>
<td>0.45</td>
<td>58.9</td>
</tr>
<tr>
<td>Blend 4</td>
<td>0.74</td>
<td>0.46</td>
<td>50.1</td>
</tr>
<tr>
<td>Blend 5</td>
<td>0.74</td>
<td>0.61</td>
<td>55.1</td>
</tr>
</tbody>
</table>
Some interesting developments:

- The chemical product simulator
- Product-process development
  - ....
There is a need for a product simulator with similar and more useful features than a typical process simulator. Based on available data, models, methods and analysis tools, the first chemical product simulator has been developed: ProCAPD

Examples: Molecular design (single molecular products) with process constraints

- Solvents for separations and/or product recovery
- Hybrid process design with membranes
- Process fluids for specific operations
- Reactive agents

Eqs. 1-7: simultaneous product design & process application – decomposition-based solution approach
Design of hybrid modules

Which is the product design problem?

Permeate (X)

Feed (I)

Retentate

Multiscale modelling

Close to 50% or more energy reduction compared to original process achievable
Collaborative effort needed!

- Solution approaches
  - Integrated multiscale modeling, experiments and synthesis
  - Ability to find predictive-innovative solutions
Design Problem from 60 Years Ago

• Non-scumming “soap bar” (world’s best-selling soap bar) – Launched by Lever Bros (US division of Unilever) in 1955
• Attributes comparable to ordinary soap bars
  – Firmness
  – Lather
  – Rate of wear
  – Slipperiness
  – Mildness
  – No unpleasant odors
  – No “cracking” from wet/dry cycles

• Processable on ordinary soap bar line: model-based system yet to be developed

M Hill & Associates
Mahwah, NJ

Published by Wiley

Suitable for BSc, MSc level teaching of
- Product design
- Process design
- Integrated product-process design
The academic tree of Prof Rafiqul Gani

PROFESSOR RAFIQUL GANI ACADEMIC TREE
1985-2017

Product Synthesis-Design

Rafiqul Gani, 1985

Process Synthesis-Design

Modelling

Computer-aided Systems