Group Contribution and Property Clustering for Simultaneous Process and Molecular Design

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Property Based Design

Why Design Based on Properties?

- Many processes are driven by properties NOT components
- Performance objectives often described by properties
- Often objectives can not be described by composition alone
- Product/molecular design is based on properties
- Properties bridge gap between process & molecular design
- Insights hidden by not integrating properties directly

Property Clusters & Group Contribution

- Extension to existing composition based methods
- Reduces problem dimensionality and enables visualization
- Property estimation in molecular design via group contribution
- Novel and systematic method of representing processes and molecular fragments from a properties perspective

Property Clustering

Property clusters are conserved surrogate properties described by ***property operators***, which have linear mixing rules, even if the operators themselves are nonlinear.

Process Property Operators

$$\psi_j^P = \sum_{s=1}^{N_s} x_s \cdot P_{js}$$

Linear Expression for Mixing 2 Ternary Clusters

$$C_{jMIX} = \sum_{s=1}^{N_s} \beta_s \cdot C_{js}$$

$$\Omega_j = \frac{\psi_j}{\psi_j^{ref}}$$

$$AUP = \sum_{j=1}^{N_j} \Omega_j$$

$$C_j = \frac{\Omega_j}{AUP}$$

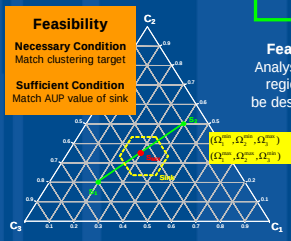
Molecular Property Operators

$$\psi_j^M = \sum_{g=1}^{N_g} n_g \cdot P_{jg}$$

G_1 and G_2, are added linearly on the ternary diagram. The location of β_1, corresponds to the location of G_1-G_2 molecule

$$\beta_1 = \frac{n_1 \cdot AUP_1}{n_1 \cdot AUP_1 + n_2 \cdot AUP_2}$$

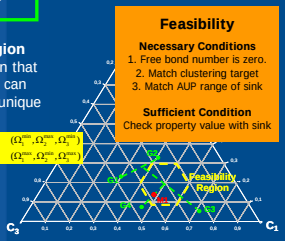
Feasibility
Necessary Condition
Match clustering target
Sufficient Condition
Match AUP value of sink



Feasibility Region
Analysis has shown that region boundary can be described by 6 unique points

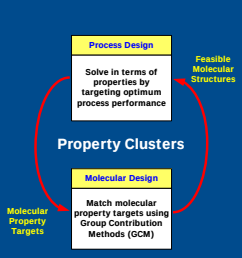
Feasibility
Necessary Conditions
1. Free bond number is zero.
2. Match clustering target
3. Match AUP range of sink

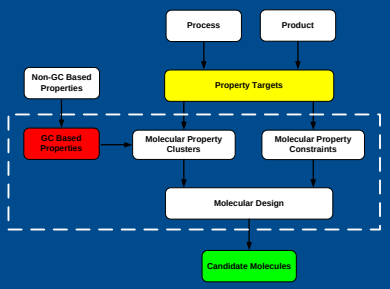
Sufficient Condition
Check property value with sink



Simultaneous Approach

Traditionally process design and molecular design have been treated as two separate problems. A simultaneous approach is introduced to overcome the limitations encompassed by decoupling the process and molecular design problems



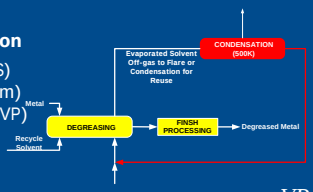


Case Study – VOC Recovery

Process Design

The objective is to maximize use of off-gas condensate & to minimize fresh solvent use to the degreaser.

Stream Characterization
1. Sulfur Content (S)
2. Molar Volume (Vm)
3. Vapor Pressure (VP)



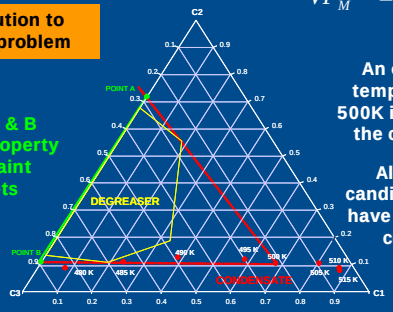
Property Operators

$$S_M = \sum_{s=1}^{Ns} x_s \cdot S_s$$

$$V_{m_M} = \sum_{s=1}^{Ns} x_s \cdot V_{m_S}$$

$$VP_M^{1.44} = \sum_{s=1}^{Ns} x_s \cdot VP_s^{1.44}$$

Visual solution to degreaser problem



Point A & B dictate property constraint targets

An operating temperature of 500K is chosen for the condenser.

All solvent candidates must have zero sulfur content.

Case Study – VOC Recovery

Molecular Design

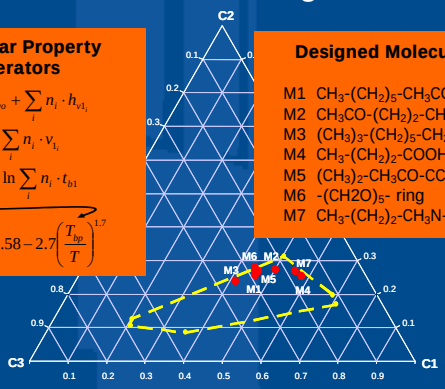
Molecular Property Operators

$$\Delta H_v = h_{vo} + \sum_i n_i \cdot h_{v1_i}$$

$$V_m = d + \sum_i n_i \cdot v_{1_i}$$

$$T_{bp} = t_{bo} \cdot \ln \sum_i n_i \cdot t_{b1}$$

$$\log_{10} VP = 5.58 - 2.7\left(\frac{T_{bp}}{T}\right)^{1.7}$$



Designed Molecules

M1 CH_3-$(CH_2)_5$-CH_3CO
M2 CH_3CO-$(CH_2)_2$-CH_3CO
M3 $(CH_3)_3$-$(CH_2)_5$-CH_2N
M4 CH_3-$(CH_2)_2$-COOH
M5 $(CH_3)_2$-CH_3CO-CCL
M6 -$(CH2O)_5$- ring
M7 CH_3-$(CH_2)_2$-CH_3N-COOH

Applying Feasibility Conditions

- All formulations satisfy first two necessary conditions
- Candidates M5 & M6 fail to satisfy sink AUP range
- M3 and M7 did not satisfy primary and secondary property targets
- M1, M2 and M4 are valid molecular formulations

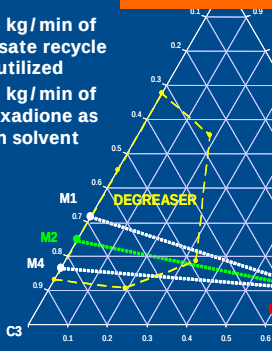
Results and Conclusions

Results from Process Design

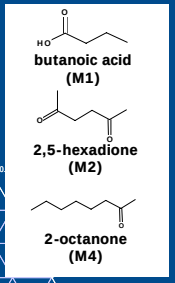
17.44 kg/min of condensate recycle is utilized

19.36 kg/min of 2,5-hexadione as fresh solvent

Combined Solution



Results from Molecular Design



- Property clustering provides a framework for solving property driven processes without commitment to specific components
- Molecular property clusters, systematically design candidates to satisfy process/product property targets
- Unifying methodology for simultaneous solution of process & molecular design problems