Process Synthesis without Integer Variables:
Using Complementarity Constraints for Thermodynamic & Distillation Models

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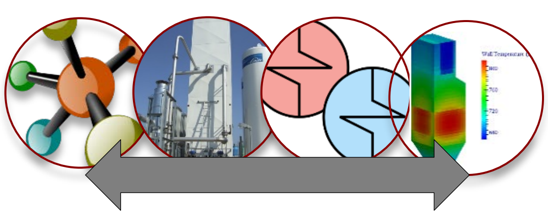
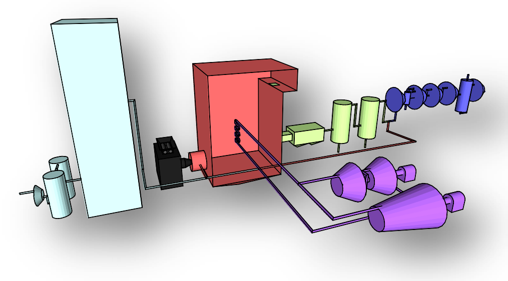
Carnegie Mellon University



AIChE Annual Meeting

November 18th, 2014



Agenda

1. *Motivation*: Oxy-fired Power Plant Optimization

2. Distillation Models
   - Traditional MINLP synthesis approach
   - MESH with tray bypass model
   - Case study: air separation unit design

3. Cubic EOS Thermodynamic Models
   - Equation-based phase selection strategies
   - Reformulation for supercritical region
   - Strategy for avoiding trivial solutions
   - Case study: CO_2 processing unit and compression train

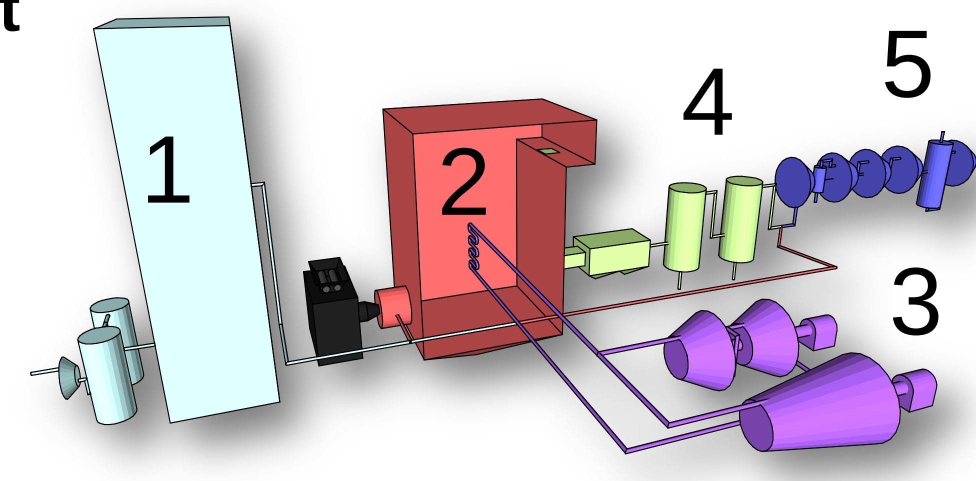
Motivation

Develop framework for full oxycombustion power plant optimization

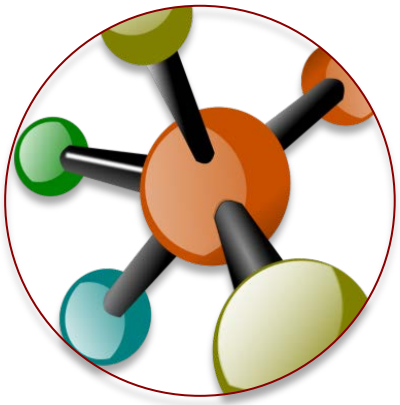
- Estimate *cost of electricity* with carbon capture
- Balance trade-offs between systems

Oxycombustion Power Plant

1. Air Separation Unit
2. Boiler
3. Steam Turbines
4. Pollution Controls
5. CO_2 Compression Train

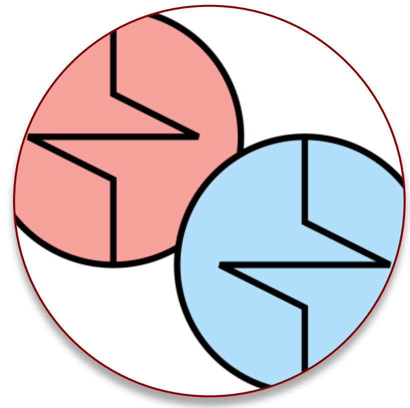


Framework for EO Flowsheet Optimization

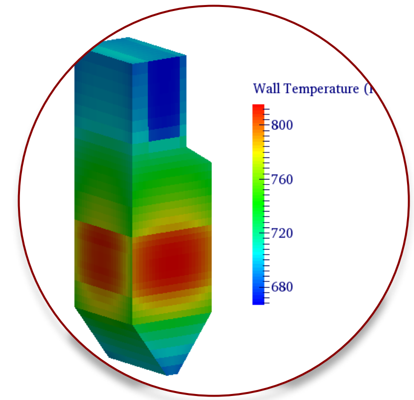


Thermodynamics
&
Flash Calculations

Distillation Cascades



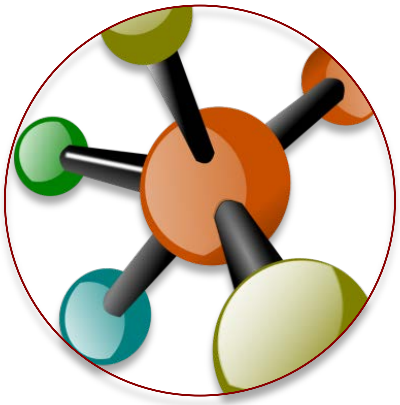
Heat Integration



Complex Reactors

Trust Region Optimization with Filter

Framework for EO Flowsheet Optimization



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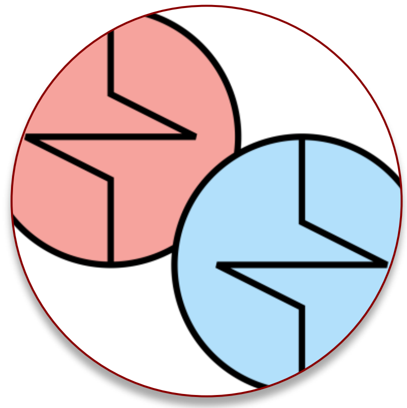

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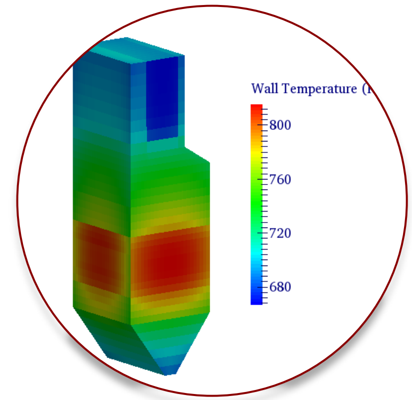


Complex Reactors

Trust Region Optimization with Filter

Classic MINLP

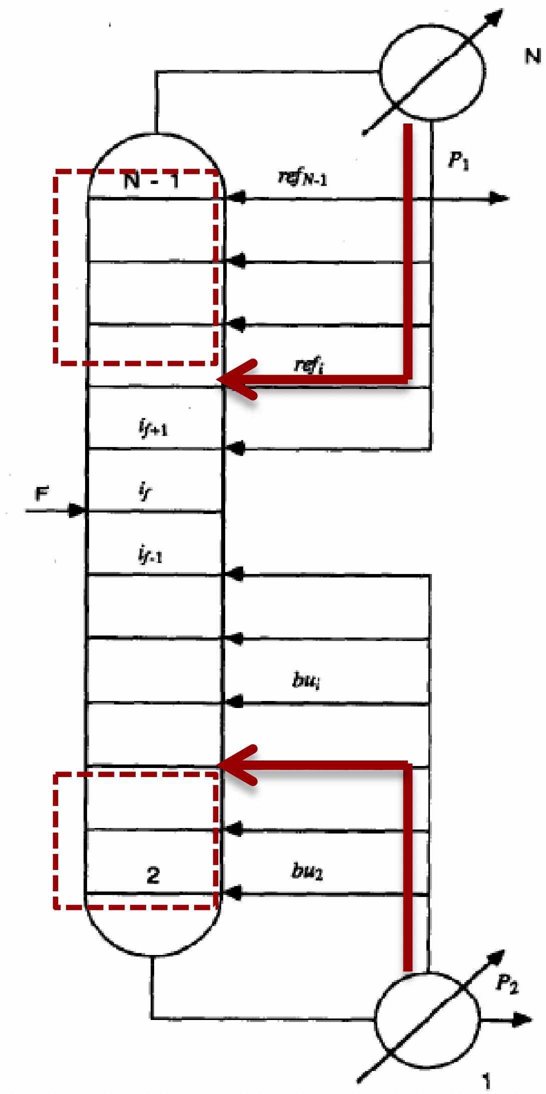


Image from Viswanathan & Grossmann (1990)

- Optimize number of trays and/or feed location
- Disable trays above reflux and below reboil feeds
- Binary variable ensures only one tray selected for reboiler/reflux feed(s)

Pioneered by:

Viswanathan, J., & Grossmann, I. E. (1990). A Combined Penalty Function and Outer-Approximation Method for MINLP Optimization. Computers & Chemical Engineering, 14(7), 769–782.

MESH with Tray Bypass

Mass Balance: $x_{i+1}^{c} L_{i+1} + y_{i-1}^{c} V_{i-1} = x_i^c L_i + y_i^c V_i\,, \quad \forall\, i \in \{Trays\}, \forall c \in \{Comps.\}$

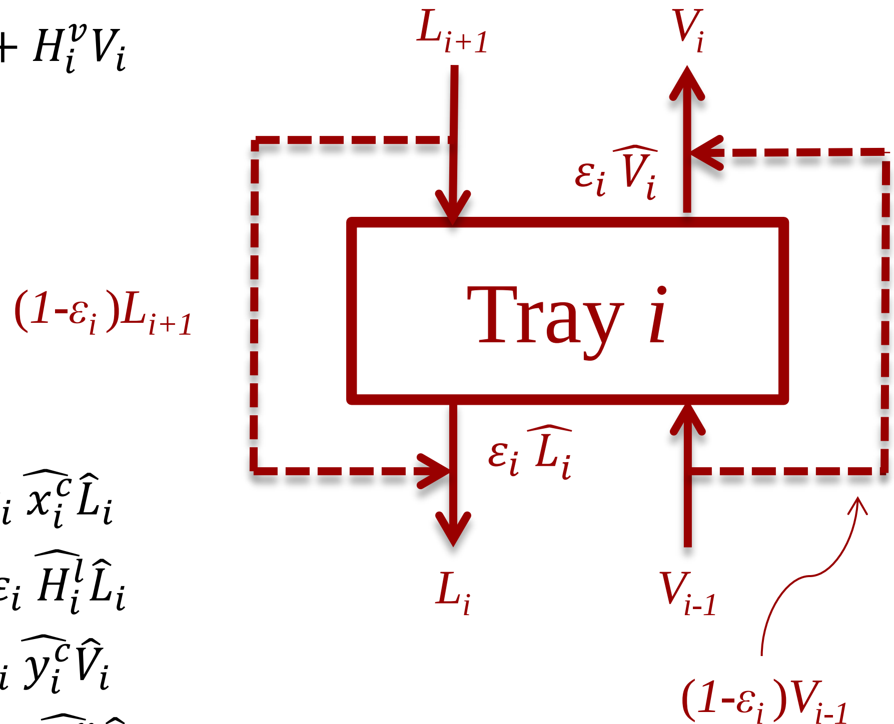
Equilibrium: $y_i^c = K_i^c x_i^c, \ \forall\, i, c$

Summation: $\sum_c y_i^c - x_i^c = 0\,, \quad \forall\, i$

Heat Balance: $H_{i+1}^{l} L_{i+1} + H_{i-1}^{v} V_{i-1} = H_i^l L_i + H_i^v V_i$

$$Number\ of\ Trays \approx \sum_i \varepsilon_i$$

$$\varepsilon_i = 1 - \frac{Bypassed\ Flowrate}{Total\ Flowrate}$$



Liquid Mixer: $x_i^c L_i = (1 - \varepsilon_i)\, x_{i+1}^{c} L_{i+1} + \varepsilon_i\, \widehat{x_i^c} \hat{L}_i$

Liquid Mixer: $H_i^l L_i = (1 - \varepsilon_i)\, H_{i+1}^{l} L_{i+1} + \varepsilon_i\, \widehat{H_i^l} \hat{L}_i$

Vapor Mixer: $y_i^c V_i = (1 - \varepsilon_i)\, y_{i-1}^{c} V_{i-1} + \varepsilon_i\, \widehat{y_i^c} \hat{V}_i$

Vapor Mixer: $H_i^v V_i = (1 - \varepsilon_i)\, H_{i-1}^{v} V_{i-1} + \varepsilon_i\, \widehat{H_i^v} \hat{V}_i$

Case Study: Simple Cascade

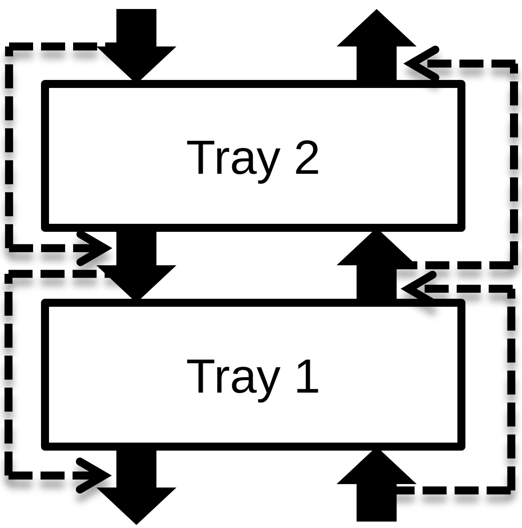
Vapor-liquid equilibrium: $y_c = K_c x_c$

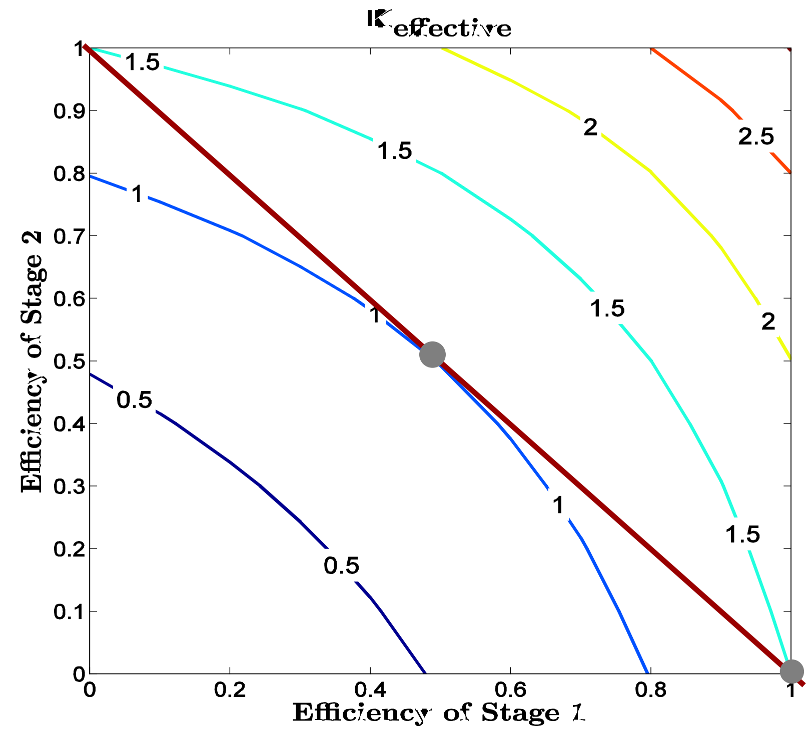
Binary separation

Two stages

$\uparrow$ Constant

$$K_c^{effective} = \frac{y_c^{out}}{x_c^{out}}$$





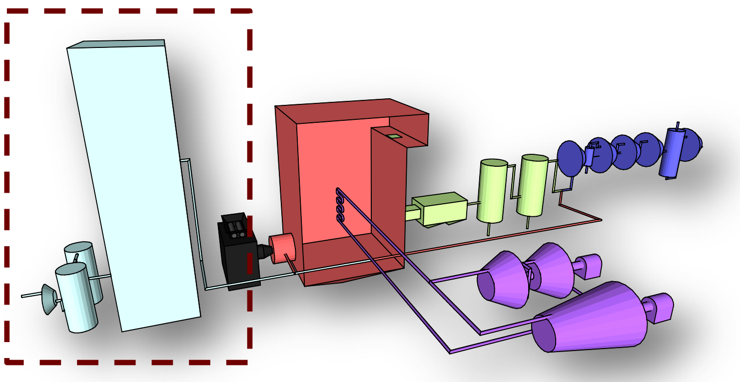
$\varepsilon_1 + \varepsilon_2 = 1$

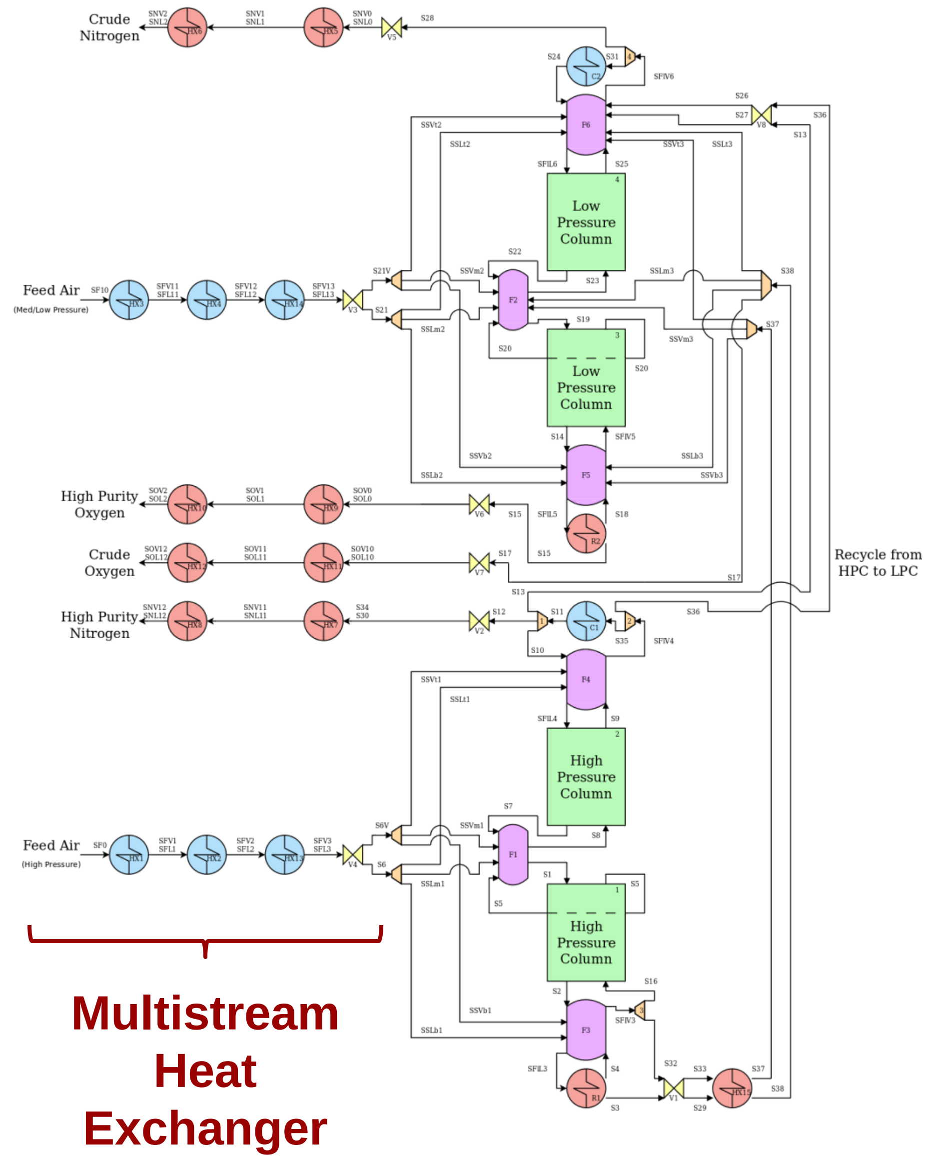
Conclusion: Mixing is inefficient.

Conjecture: Integer solutions are preferred.

Dowling, A. W., & Biegler, L. T. (2014). 24th European Symposium on Computer Aided Process Engineering. Computer Aided Chemical Engineering (Vol. 33, pp. 55–60).

ASU Superstructure





- *Many* different column configurations realizable
- NLP optimizer selects the best configuration

Optimization Formulation

$$
\begin{array}{ll}
\min & \text{ASU Compression Energy} \\
 & \text{(kWh / kg } O_2 \text{ product)} \\
\text{s.t.} & \text{Flowsheet Superstructure} \\
 & \text{Peng-Robinson Thermodynamics} \\
 & \text{Unit Operation Models} \\
 & \textbf{Distillation Model} \\
 & \text{Heat Integration} \\
 & O_2 \text{ product purity} \geq 95 \text{ mol\%} \\
 & \textit{Complementarity Constraints} \text{ (thermo, etc.)}
\end{array}
$$

Note: **Upper and lower bounds not shown above** are considered for many variables including stream/equipment temperatures and pressures.

Implementation Details

- Non-convex problem
  - 16,000 variables & constraints
- Penalty formulation for *complementarity constraints*
- Automated initialization
  - Simple → complex models
  - Custom multistart procedure
- Solved using **CONOPT3** in GAMS
  - **16 CPU minutes** average for sequence on NLPs

Ideal Thermo & Shortcut Cascade

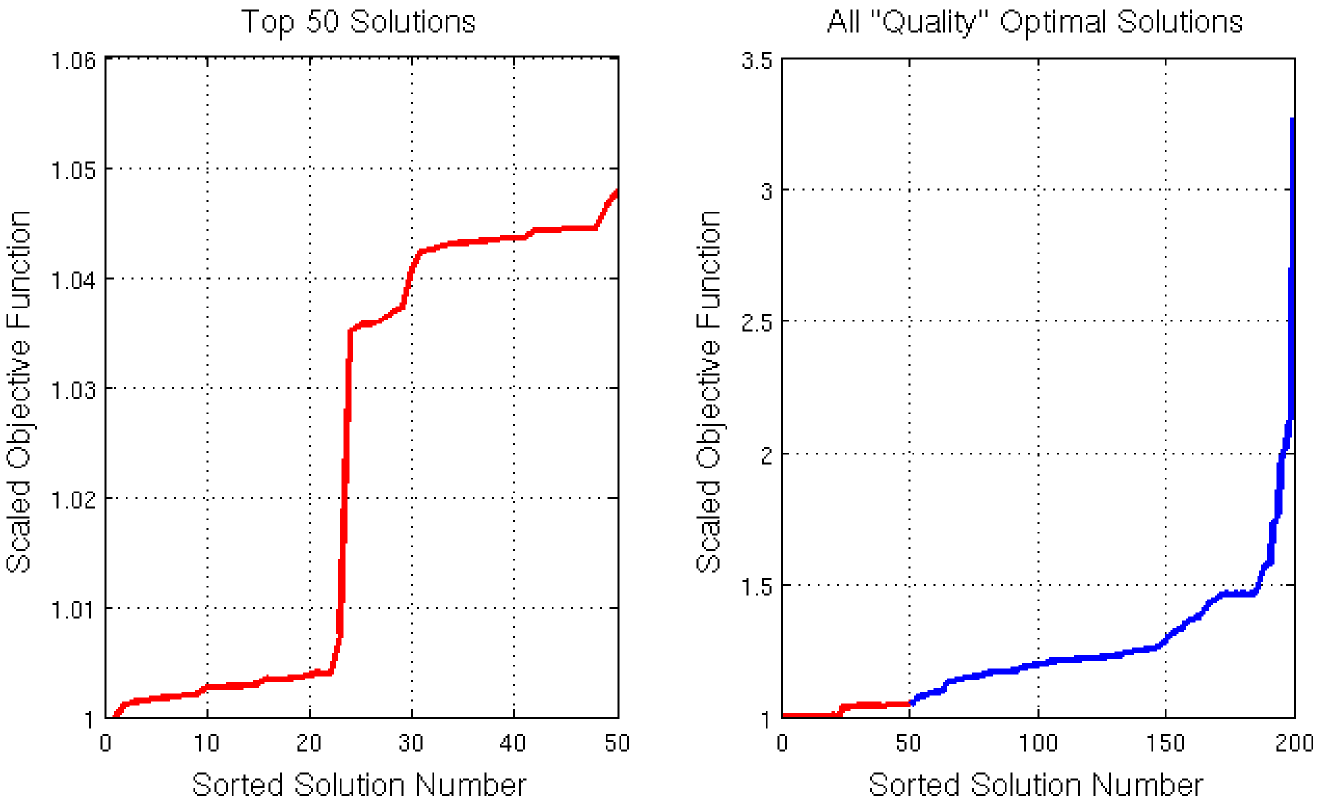
CEOS Thermo & Shortcut Cascade

CEOS Thermo & MESH Cascade

Decompose Heat Exchange Units & Reoptimize

Multi-start Initialization

Concern: Mixers (bypass) and complementarities (thermodynamics) add non-convexities



<u>"Quality" Solution</u>

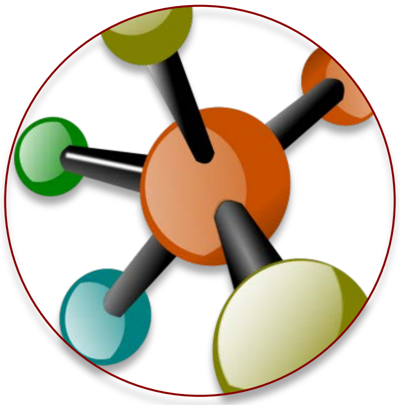
- Self heat integrated
- No ⊥ violation
- Locally optimal

288 initial points (<u>factorial design</u>) considered in 7 hours

Careful initialization allows for many "quality" solutions

Out of the best 150 solutions, only 11 (7.3%) have partially bypassed trays.

Framework for EO Flowsheet Optimization



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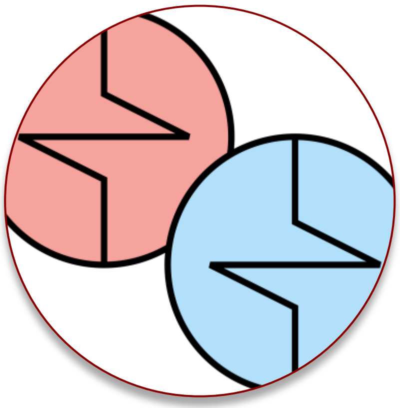
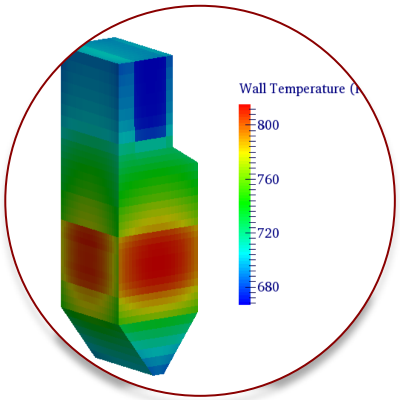


Heat Integration



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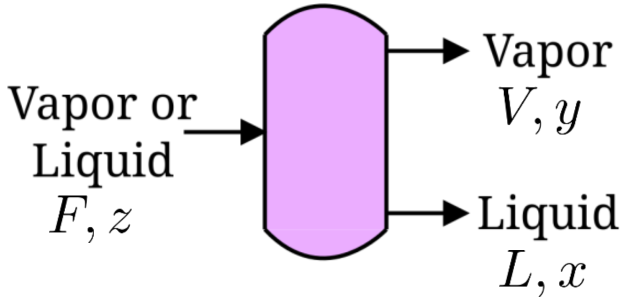


$$
\left.
\begin{aligned}
F &= L + V \\
F z_c &= L x_c + V y_c, \quad \forall c \in \{Comps\}
\end{aligned}
\right\}
$$

Mole balances

$$
F H^F + Q = L H^L + V H^V \quad \}
$$

Enthalpy balance

$$
y_c = \quad K_c(T, P, x, y) x_c \quad \}
$$

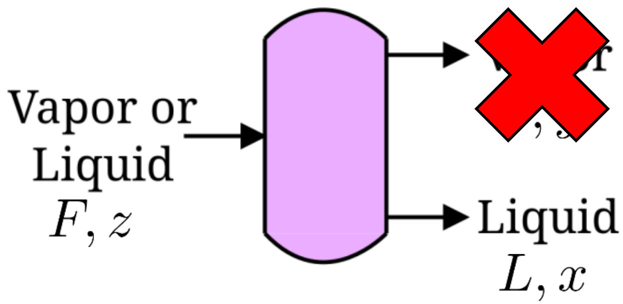
Equilibrium

$$
\begin{gathered}
0 \leq x_c, y_c \leq 1 \\
0 \leq L, V \leq F
\end{gathered}
$$

Raghunathan, A. U., & Biegler, L. T. (2003). Comp. & Chem. Eng. 27, 1381–1392.

Biegler, L.T. (2010). *Nonlinear Programming.* Ch. 11.

Flash Calculations



$$F = L + V$$

$$Fz_c = Lx_c + Vy_c, \quad \forall c \in \{Comps\}$$

$$FH^F + Q = LH^L + VH^V$$

$$y_c = \beta \; K_c(T, P, x, y) x_c$$

$$0 \leq x_c, y_c \leq 1$$

$$0 \leq L, V \leq F$$

Raghunathan, A. U., & Biegler, L. T. (2003). Comp. & Chem. Eng. 27, 1381–1392.

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Complementarity Constraints

$$0 \leq x_1 \perp x_2 \geq 0$$

$$x_1 = 0 \text{ “inclusive OR” } x_2 = 0$$

$$0 \leq \boxed{s_V} \perp V \geq 0$$

$$0 \leq \boxed{s_L} \perp L \geq 0$$

Slack variables for outlet streams

$$-s_L \leq \beta - 1 \leq s_V$$

2-phase outlet: $\beta = 1$

Vapor only outlet: $\beta \geq 1$

Liquid only outlet: $\beta \leq 1$

Cubic Equations of State

Analytic formulas for physical properties

$$H = f_h(x,y,T,P) \qquad S = f_s(x,y,T,P) \qquad \phi_c = f_{\phi,c}(x,y,T,P)$$

Popular for general process modeling

Ex: Peng–Robinson, Soave–Redlich–Kwong

Three roots for Z

$$\underbrace{\boxed{Z^3} - (1+B-uB)\boxed{Z^2} + (A+wB^2-uB-uB^2)\boxed{Z} - AB - wB^2 - wB^3 = 0}_{\boldsymbol{f_z(Z)=0}}$$

$$Z = \frac{PV}{RT} \quad A = \frac{\hat{a}\alpha(\omega,T)P\bar{T}^2}{T^2\bar{P}} \quad B = \frac{\hat{b}P\bar{T}}{T\bar{P}}$$

EOS Specific Constants: $u,\ w,\ \hat{a},\ \hat{b}$

Critical Point Data: $\bar{T},\ \bar{P}$

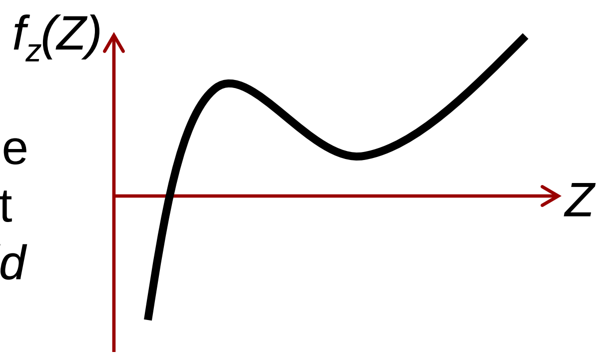
Other Component Data: ω

Not shown: mixing rules

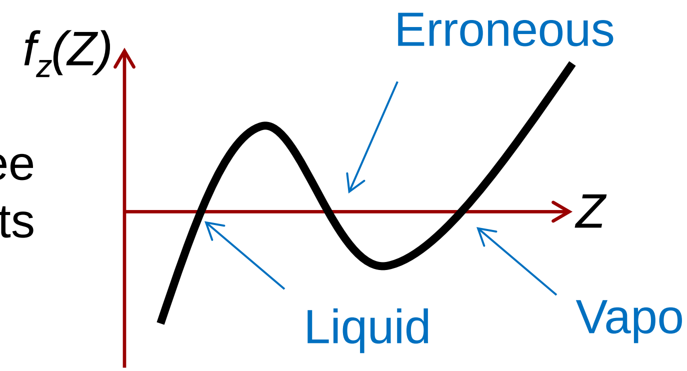
Roots for Z

1 or 3 distinct real solutions for $f_z(Z) = 0$ depending on (T, P, x, y)

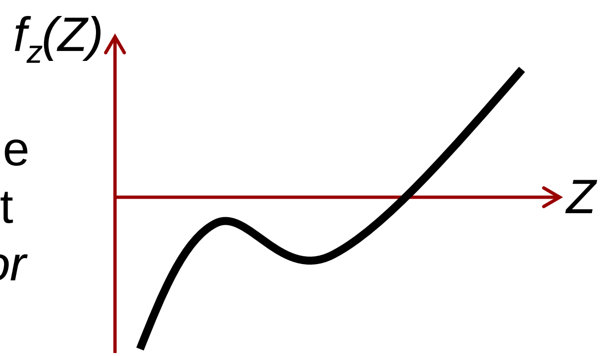
Single
Root
Liquid

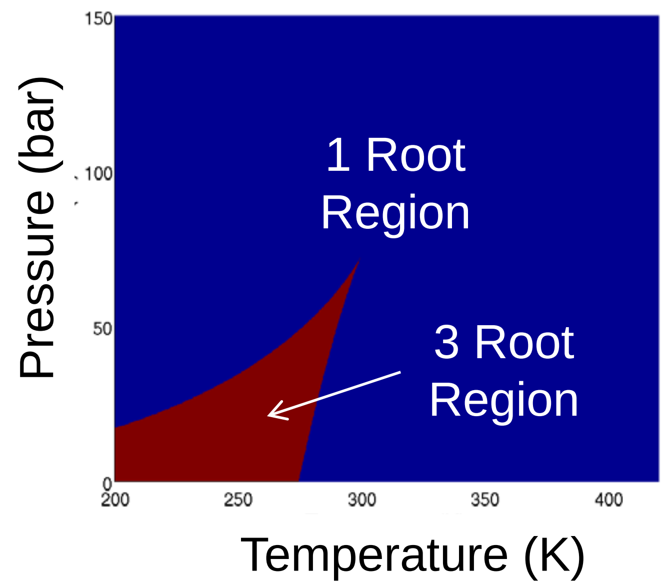


Three
Roots



Single
Root
Vapor





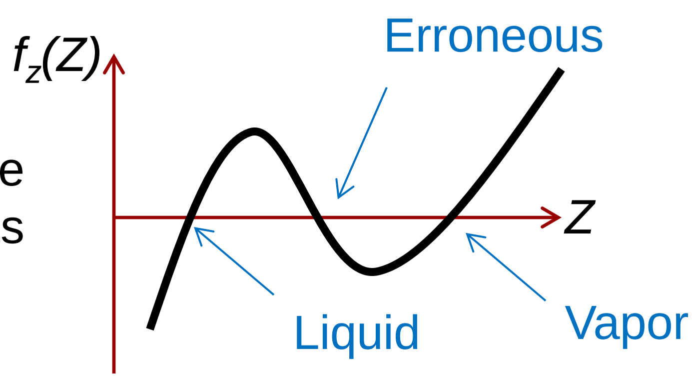
Challenge: Root Selection

Process simulators use heuristics, loops and conditional statements to select roots

– Not differentiable

Kamath *et al* proposed an equation-based approach

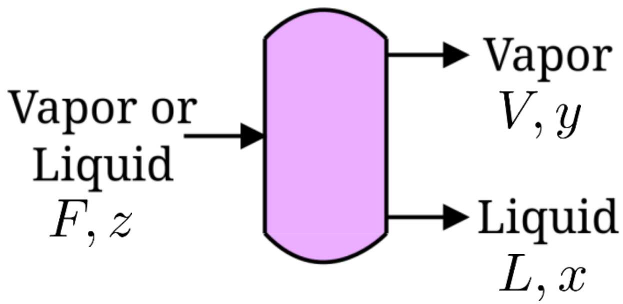
Three Roots



<u>Liquid</u>	<u>Vapor</u>
$f_z(Z_L) = 0$	$f_z(Z_V) = 0$
$f'_z(Z_L) \geq 0$	$f'_z(Z_V) \geq 0$
$f''_z(Z_L) \leq 0$	$f''_z(Z_V) \geq 0$

Kamath, R. S., Biegler, L. T., & Grossmann, I. E. (2010). Comp. & Chem. Eng., 34(12), 2085–2096.

Challenge: Root Selection



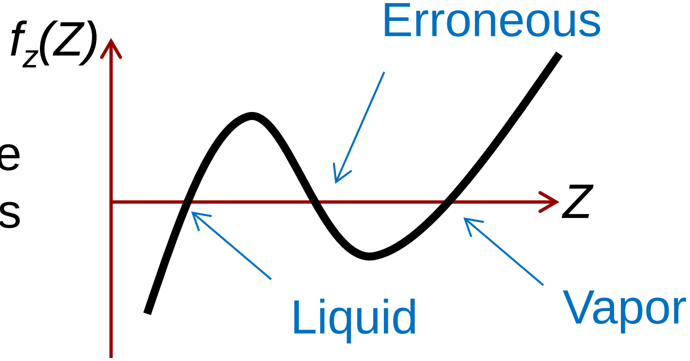
$$0 \leq s_V \perp V \geq 0$$

$$0 \leq s_L \perp L \geq 0$$

$$-s_L \leq \beta - 1 \leq s_V$$

Kamath *et al* proposed an equation-based approach

Three Roots

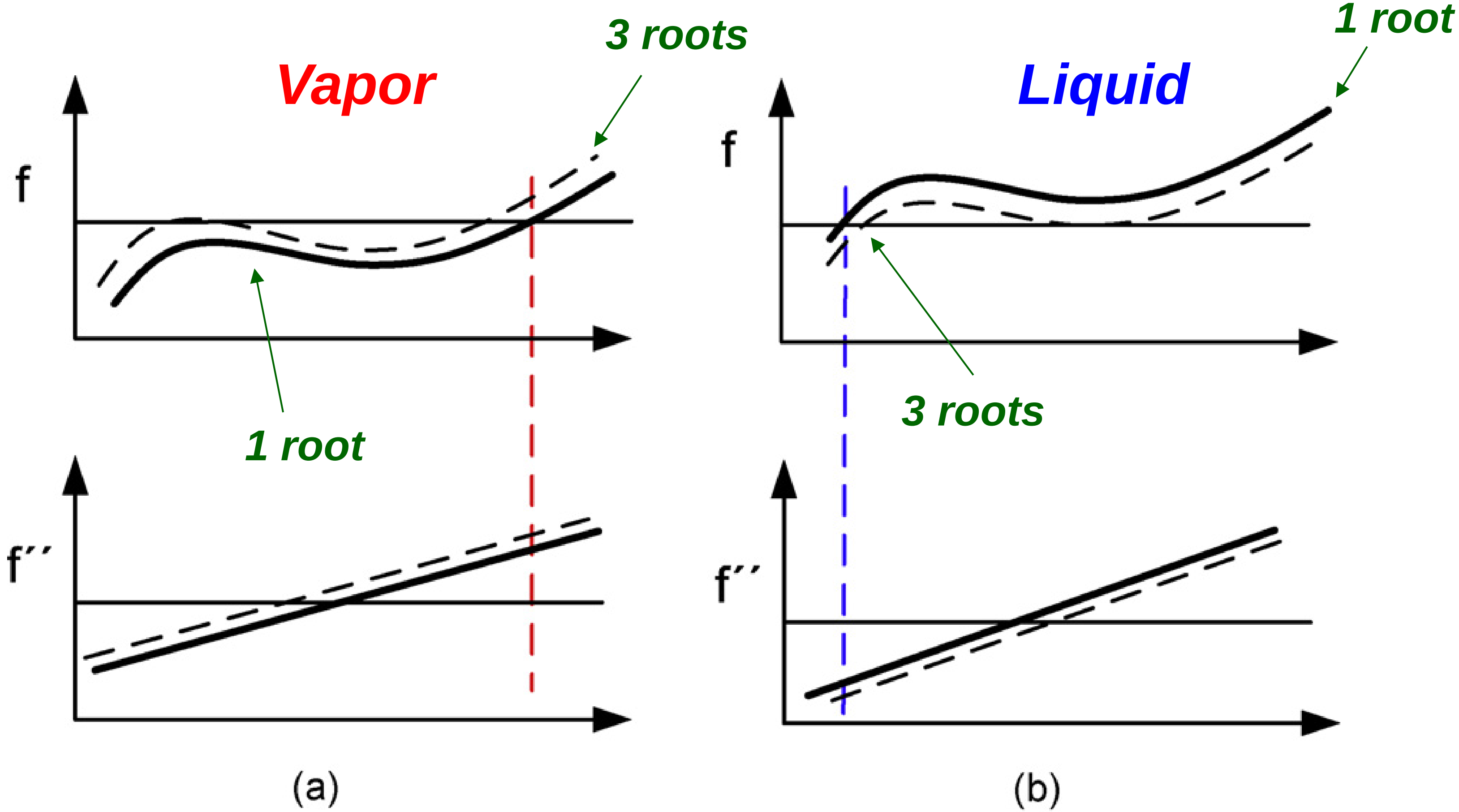


<u>Liquid</u>	<u>Vapor</u>
$f_z(Z_L) = 0$	$f_z(Z_V) = 0$
$f_z'(Z_L) \geq 0$	$f_z'(Z_V) \geq 0$
$f_z''(Z_L) \leq M s_L$	$f_z''(Z_V) \geq -M s_V$

Kamath, R. S., Biegler, L. T., & Grossmann, I. E. (2010). Comp. & Chem. Eng., 34(12), 2085–2096.

Single Root Region

Conjecture: $f_z''(Z_L) \leq 0$ and $f_z''(Z_V) \geq 0$ also apply in the *single root region*



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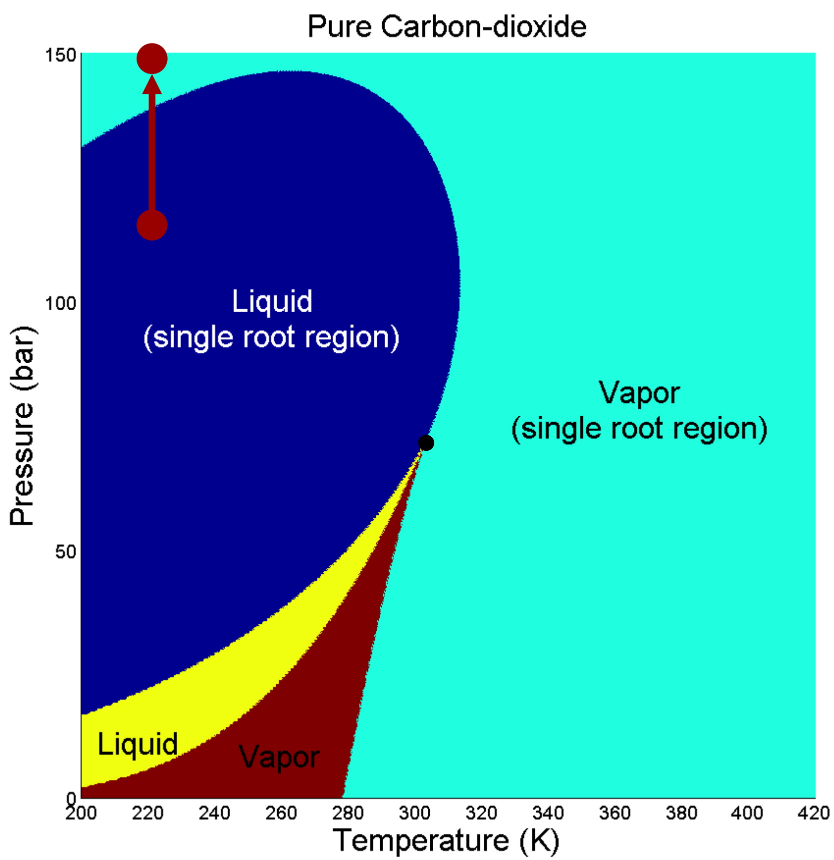
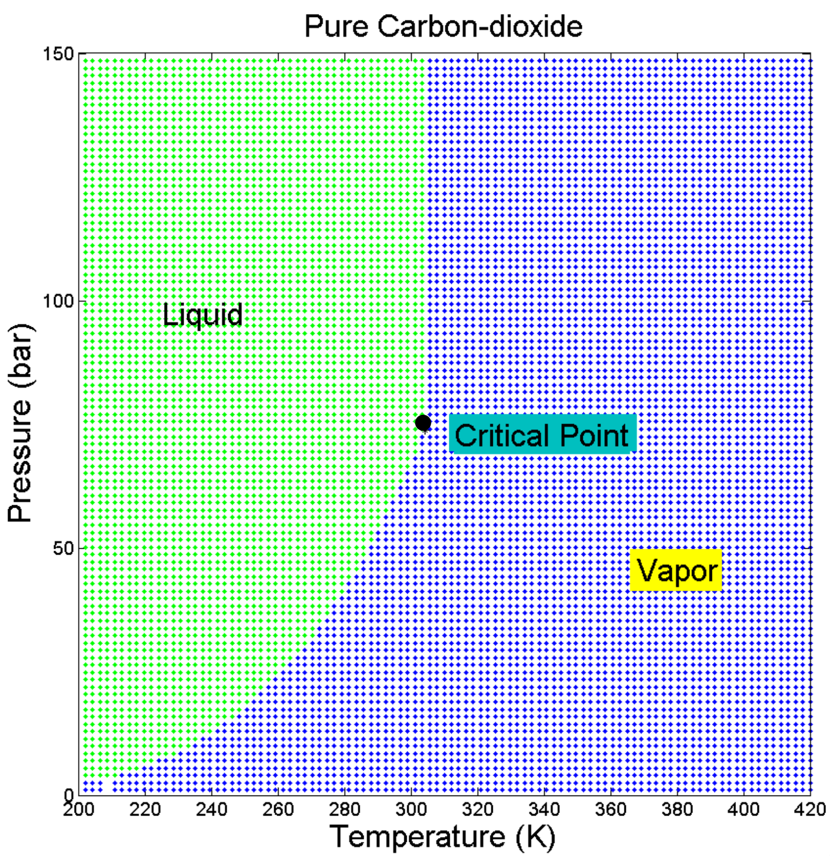
Supercritical Region

Issue 1: *Conjecture fails in the supercritical region*

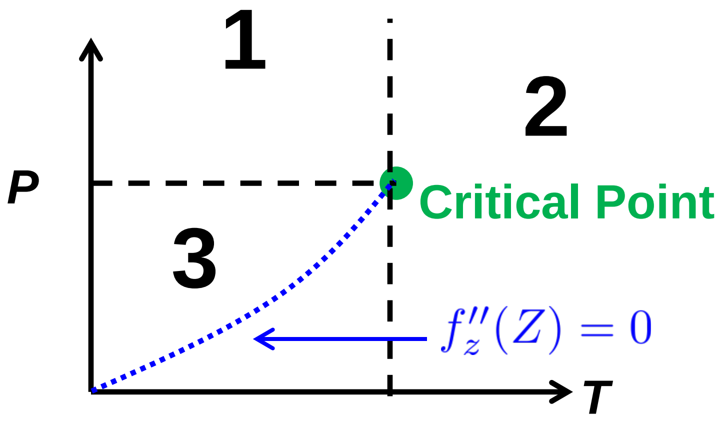
Kamath *et al* formulation



Aspen Plus®



Proposed Reformulation



Region 1: Relax $f_z''(Z)$ → Always **liquid**

Region 2: Relax $f_z''(Z)$ → Always **vapor**

Region 3: $f_z''(Z)$ conditions holds → possible **2-phase**

Region 2: $T \geq \bar{T}$

$$T - \bar{T} = s_2^a - s_2^b$$

$$0 \leq s_2^a \perp s_2^b \geq 0$$

When $s_2^a > 0$, relax $f_z''(Z)$

$$0 \leq s_2^a \perp L \geq 0$$

$$f_z''(Z_L) \leq M(s_L + s_2^a + s_1^b)$$

Region 1: $T \leq \bar{T}$ and $P \geq \bar{P}$

$$0 \leq \tau - (\bar{P} - P) \perp \tau - (T - \bar{T}) \geq 0$$

$$\tau = s_1^a - s_1^b$$

$$0 \leq s_1^a \perp s_1^b \geq 0$$

When $s_1^b > 0$, relax $f_z''(Z)$

$$0 \leq s_1^b \perp V \geq 0$$

$$f_z''(Z_V) \geq -M(s_V + s_2^a + s_1^b)$$

Critical Point Calculations

Need formula for $\bar{T}$ and $\bar{P}$ consistent with mixing rules

$$a^m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - \bar{k}_{i,j})$$

$\bar{p_i}$ and $\bar{t_i}$ are component critial properties

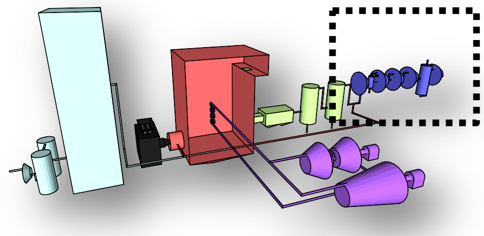
$$b^m = \sum_i x_i b_i$$

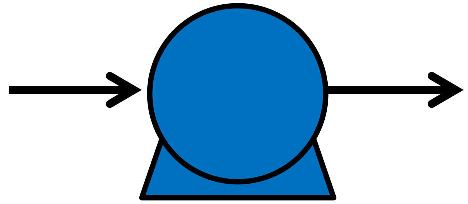
Solve for T and P

$$\bar{A} = \frac{a^m P}{T^2 R^2} \qquad \bar{B} = \frac{b^m P}{T R} \qquad a_i = \frac{\hat{a} R^2 \bar{t}_i^2}{\bar{p_i}} \alpha(\omega_i, \bar{t}_i, T) \qquad b_i = \frac{\hat{b} R \bar{t}_i}{\bar{p_i}}$$

	$\bar{Z}$	$\bar{A}$	$\bar{B}$
Peng-Robinson	0.30740...	0.45724...	0.077796...
SRK	$\frac{1}{3}$	0.42748...	0.086640...

Demonstration Example

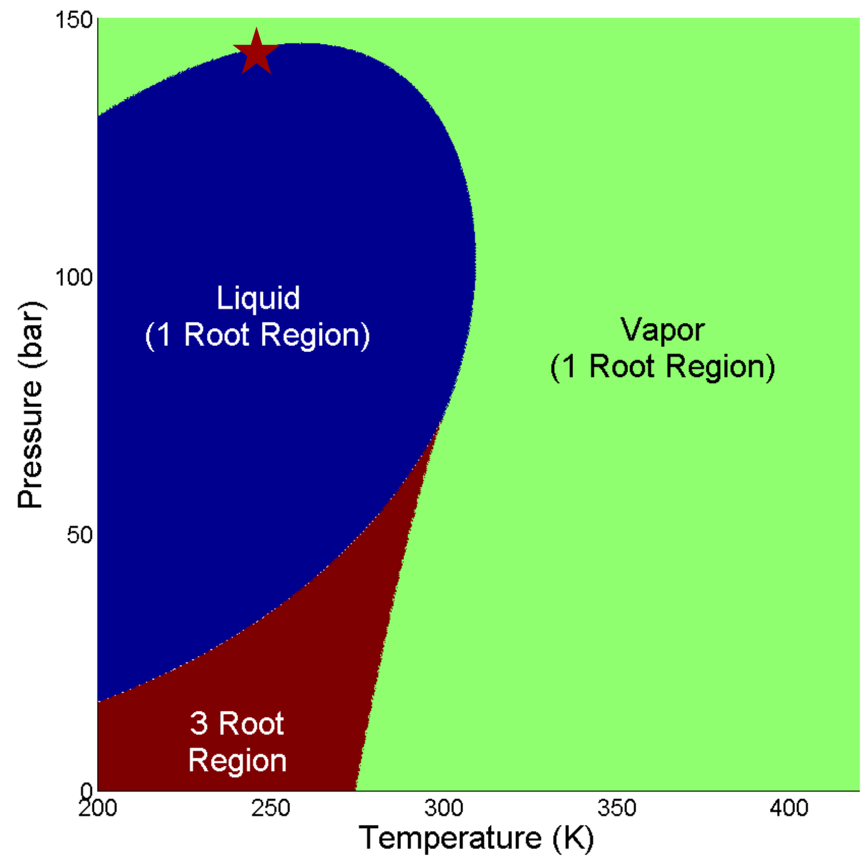




Super/near-critical CO_2

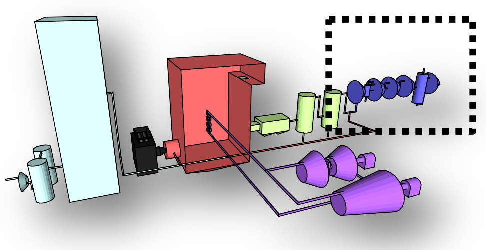
$$
\begin{aligned}
\text{maximize} \quad & P \\
\text{s.t.} \quad & f_z(Z) = 0 \\
& f_z'(Z) \geq 0 \\
& f_z''(Z) \leq 0 \\
& T = 250 \text{ K} \\
& x_{CO_2} = 0.97 \\
& x_{N_2} = x_{O_2} = x_{Ar} = 0.01 \\
& P \leq 150 \text{ bar}
\end{aligned}
$$

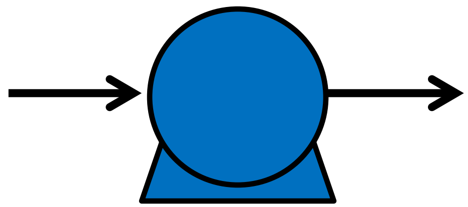
Liquid Phase



Solution: $P = 144.6$ bar

Demonstration Example

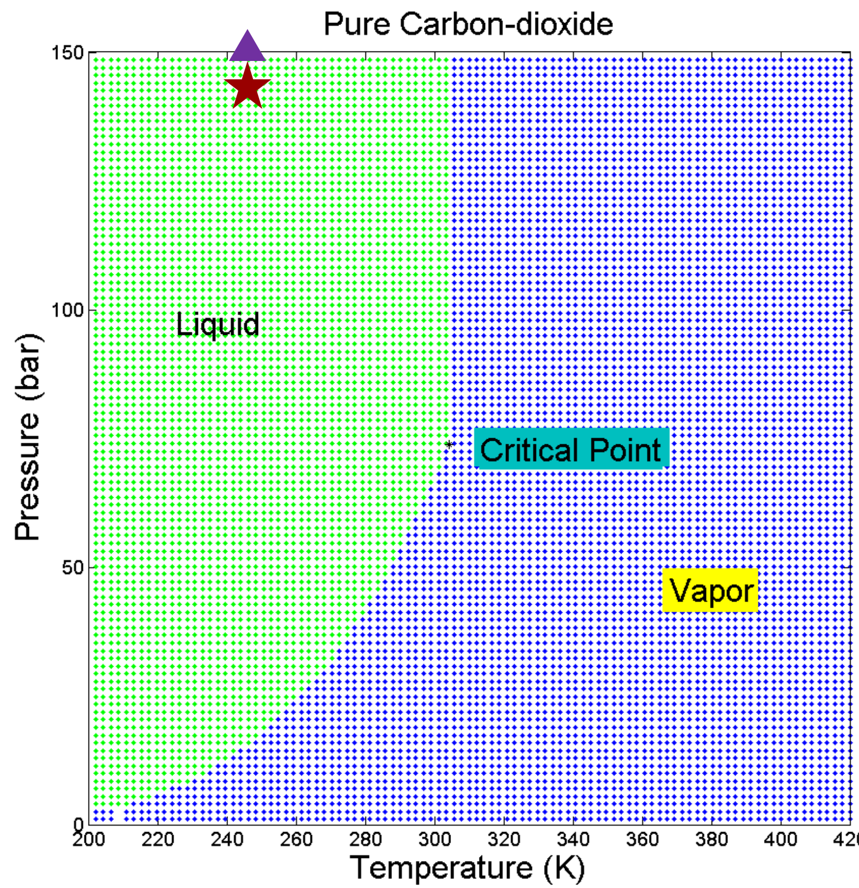




Super/near-critical CO_2

$$\begin{aligned}
\text{maximize} \quad & P \\
\text{s.t.} \quad & f_z(Z) = 0 \\
& f'_z(Z) \geq 0 \\
& {\color{red} f''_z(Z) \leq M(s_2^a + s_1^b)} \\
& {\color{red} \textit{Add'n Proposed Eqns.}} \\
& T = 250 \text{ K} \\
& x_{CO_2} = 0.97 \\
& x_{N_2} = x_{O_2} = x_{Ar} = 0.01 \\
& {\color{blue} P \leq 150 \text{ bar}}
\end{aligned}$$

Solution: $P = 150.0 \text{ bar}$



Spurious Phase Equilibrium Solutions

Issue 2: *Complementarities allow for K = 1, β = 1 solutions*

Example: Consider a liquid stream

$$f_z''(Z_L) \leq 0, \quad s_L = 0$$

$$\left.\begin{aligned} y &\leftarrow x \\ T^V &\leftarrow T^L \\ P^V &\leftarrow P^L \end{aligned}\right\} \text{Copy to vapor stream}$$

Therefore

$$Z_L = Z_V$$

$$\phi_c^L = \phi_c^V$$

$$K_c = \frac{\phi_c^L}{\phi_c^V} = 1$$

Check VLE equations

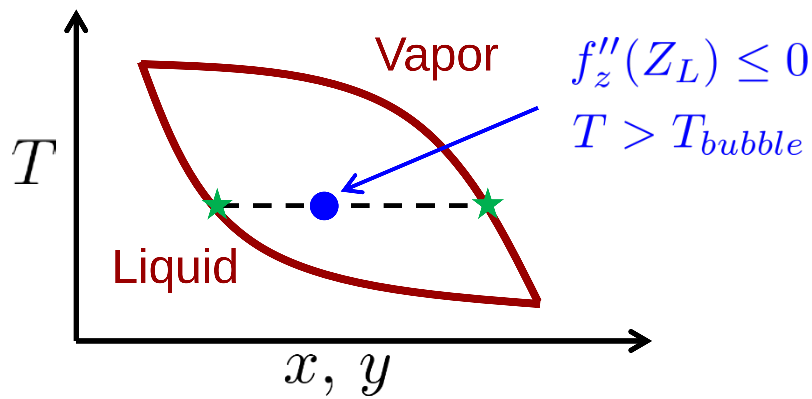
$$s_V > 0, \; V = 0$$

$$f_z''(Z_V) \geq -M s_V$$

$$0 \leq s_V \perp V \geq 0$$

$$y_c = \beta K_c x_c, \quad \beta = 1$$

$$-s_L \leq \beta - 1 \leq s_V$$



Bubble & Dew Point Calculations

***Strategy*: Introduce shadow stream pairs for BP/DP calculations**

Consider a liquid stream with properties T, P, x

Create liquid and vapor shadow streams with properties T^{bub}, p, $\bar{x}$, $\bar{y}$

$$x = \bar{x}$$

$$p = P$$

$$y_c \; \phi_c^V(T^{bub}, \bar{y}) = x_c \; \phi_c^L(T^{bub}, \bar{x})$$

Bubble point calculations without complementarities

→ Previous pathway to $K = 1$ solutions not possible

Liquid Streams

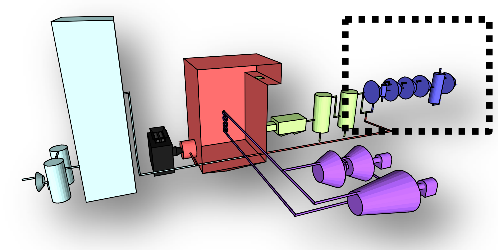
$$T \leq T^{bub}(P, x) + M s_L$$

Vapor Streams

$$T \geq T^{dew}(P, y) + M s_V$$

Implementation note:
Typically only necessary for a few trouble streams

Case Study: CO_2 Processing Unit

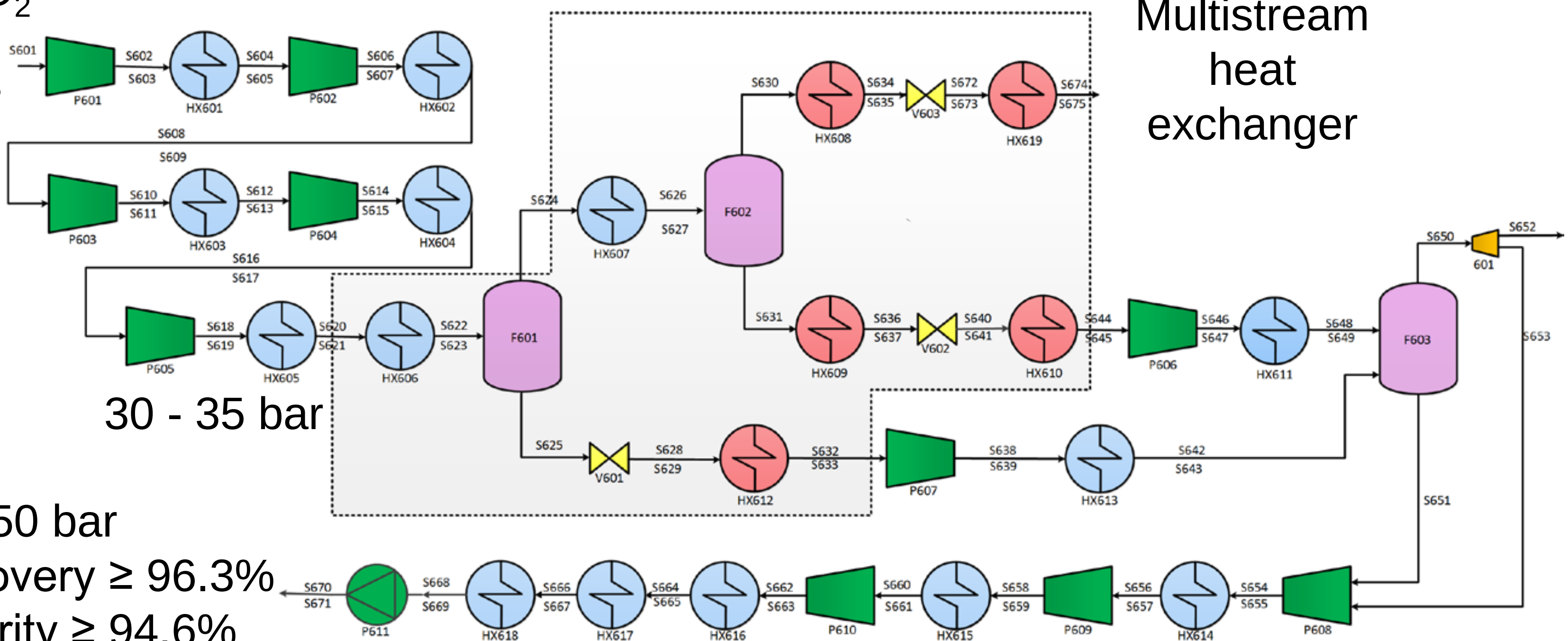


Minimize Shaft Work + 0.01 $Q_{\text{cooling water}}$

using Peng-Robison thermodynamics

83.5% CO_2
330 K
1.03 bar

Multistream
heat
exchanger



30 - 35 bar

150 bar
CO_2 Recovery ≥ 96.3%
CO_2 Purity ≥ 94.6%

Based on two-flash system from Fu, C. & Gundersen, T. (2012). *Int. J. of Green. Gas Control*, 9, 419-727.

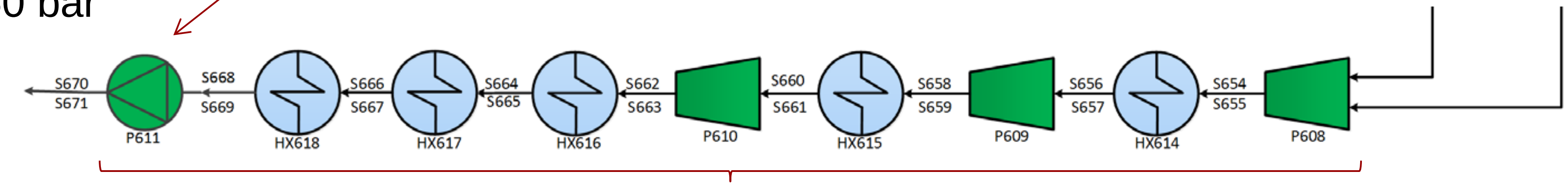
Computational Results

Remainder of CPU included in optimization problems, but not shown

150 bar

Pump

High Purity CO_2



CO_2 compression train

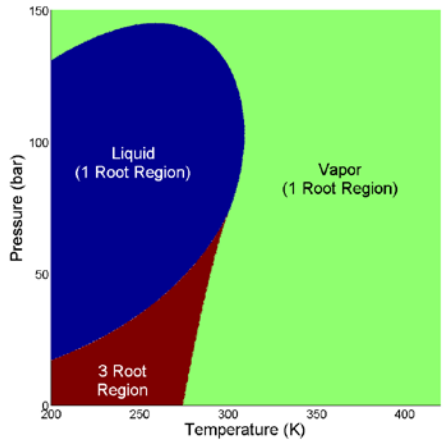
Phase Stability	Supercritical Region Correction		
	No Streams	Pump Inlet and Outlet Only	CO_2 Compress. Train
No Streams	**11.7%** **73.7 sec**	65.6% 72.8 sec	**65.6%** **70.2 sec**
4 Streams	10.2% 79.3 sec	50.0% 90.3 sec	54.7% 96.8 sec
8 Streams	12.5% 198.9 sec	39.5% 123.8 sec	**49.6%** 90.74 sec

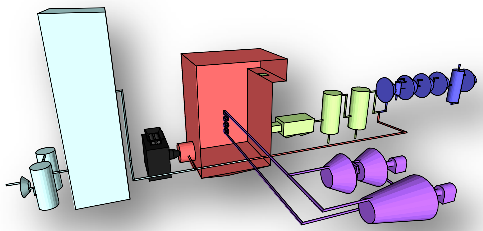
Top: Fraction of problems terminating at "good" solutions using multi-start init.
Bottom: Average CPU time for "good" solutions

"Good" solution criteria: No ⊥ violations, $Q_w^{MHEX} < 0.1$, $Q_s < 0.1$

Conclusions & Future Work

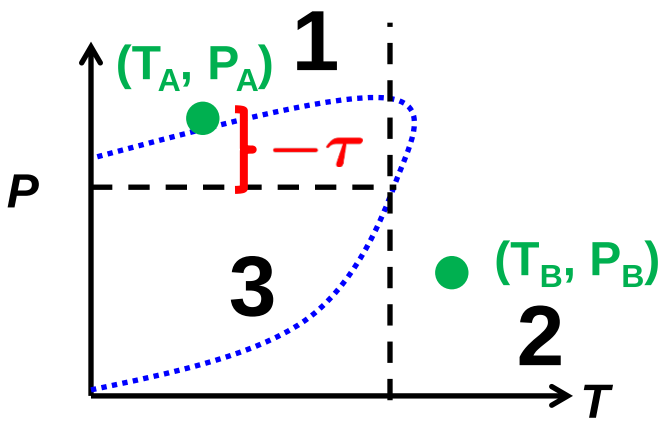
- New NLP distillation model using tray bypasses
  - Tends to prefer integer solutions
- Reformulation with *complementarity constraints* for correct phase prediction in supercritical region
- Embedded bubble/dew point calculations to avoid spurious ($K = 1$) phase equilibrium solutions
- **Ongoing work**: link cryogenic system models with boiler and steam cycle models





Funding:

Example: Region 1



Region 1: $T \leq \bar{T}$ and $P \geq \bar{P}$

$$0 \leq \tau - (\bar{P} - P) \perp \tau - (T - \bar{T}) \geq 0$$

$$\tau = s_1^a - s_1^b, \quad 0 \leq s_1^a \perp s_1^b \geq 0$$

When $s_1^b > 0$, relax $f_z''(Z)$

Point A

$$T < \bar{T},\ P > \bar{P}$$

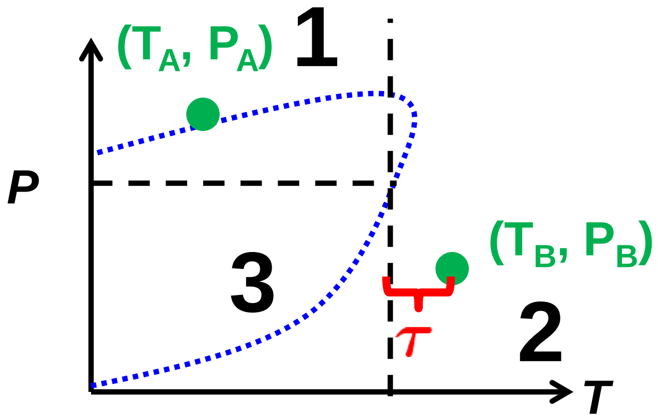
$$\tau - \bar{P} - P = 0$$

$$\tau - (T - \bar{T}) \geq 0$$

$$\tau < 0 \rightarrow s_1^a = 0,\ \ s_1^b > 0$$

Forced Relaxation

Example: Region 1 Relaxation



Region 1: $T \leq \bar{T}$ and $P \geq \bar{P}$

$$0 \leq \tau - (\bar{P} - P) \perp \tau - (T - \bar{T}) \geq 0$$

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<u>Point A</u>

$$T < \bar{T},\ P > \bar{P}$$

$$\tau - \bar{P} - P = 0$$

$$\tau - (T - \bar{T}) \geq 0$$

$$\tau < 0 \rightarrow s_1^a = 0,\ \ s_1^b > 0$$

Forced Relaxation

<u>Point B</u>

$$T > \bar{T},\ P < \bar{P}$$

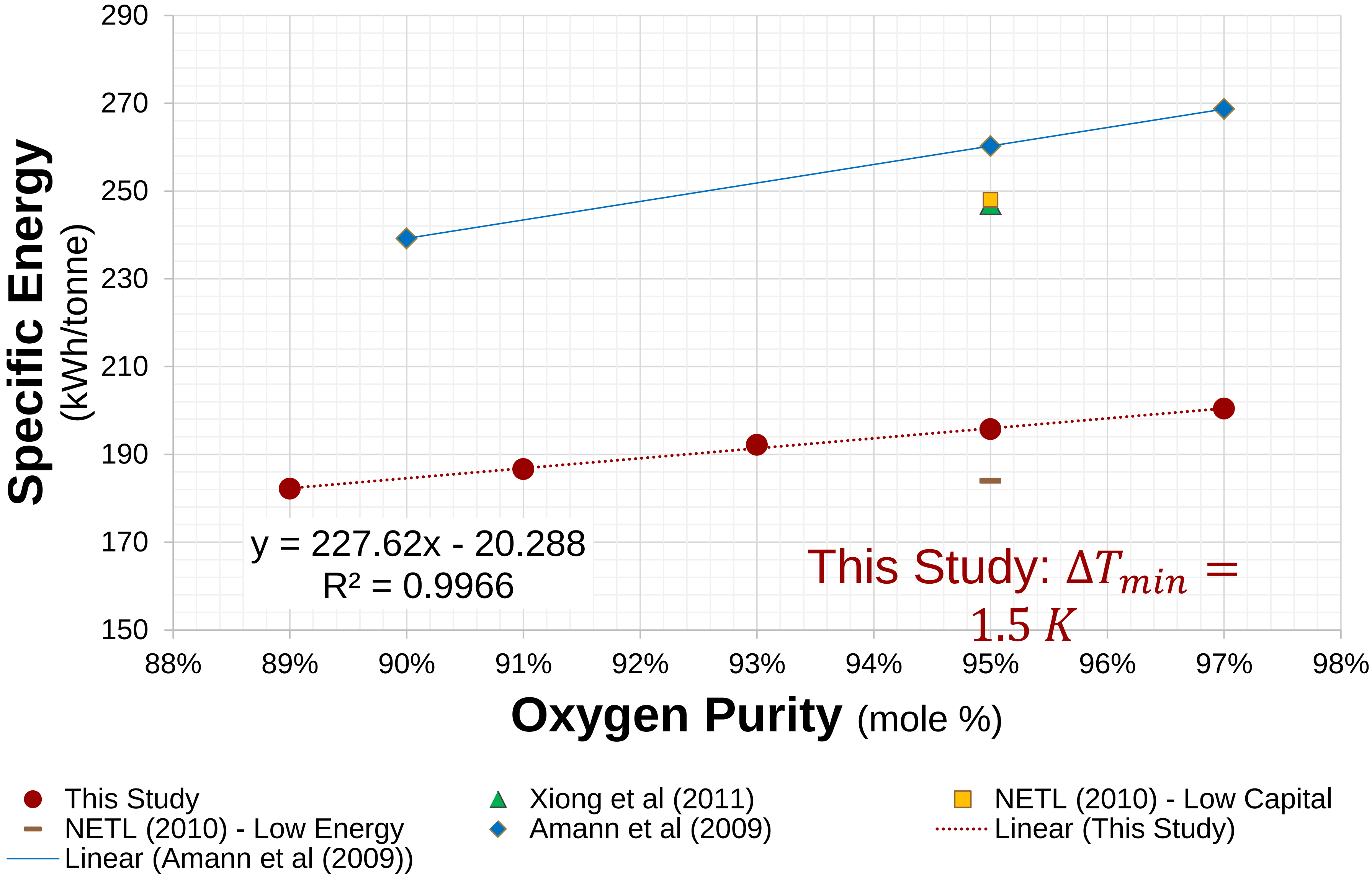
$$\tau - \bar{P} - P \geq 0$$

$$\tau - (T - \bar{T}) = 0$$

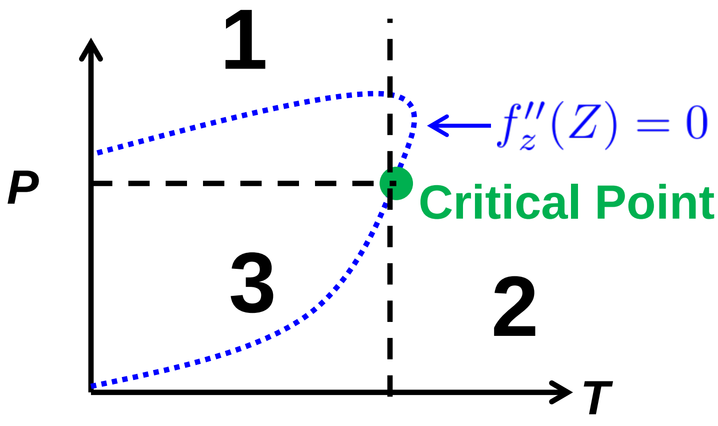
$$\tau > 0 \rightarrow s_1^a > 0,\ \ s_1^b = 0$$

No Relaxation

O_2 Purity Sensitivity



Proposed Reformulation



Region 1: Relax *f_z''(Z)* → Always **liquid**

Region 2: Relax *f_z''(Z)* → Always **vapor**

Region 3: *f_z''(Z)* conditions holds → possible **2-phase**

Region 2: $T \geq \bar{T}$

$$T - \bar{T} = s_2^a - s_2^b$$

$$0 \leq s_2^a \perp s_2^b \geq 0$$

When $s_2^a > 0$, relax $f_z''(Z)$

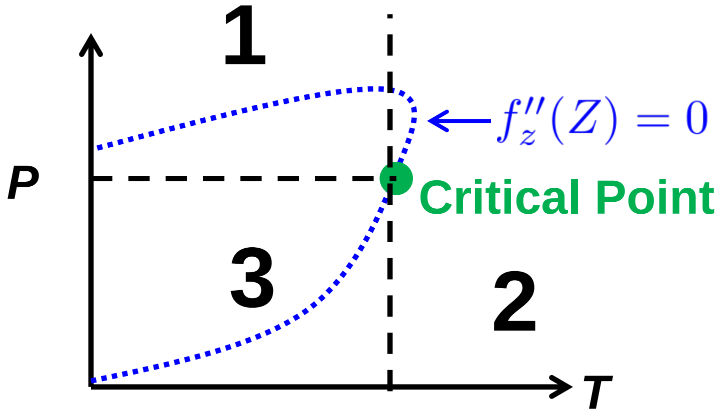
$$0 \leq s_2^a \perp L \geq 0$$

Complementarity Constraints

$$0 \leq x_1 \perp x_2 \geq 0$$

$$x_1 = 0 \text{ ``inclusive OR'' } x_2 = 0$$

Proposed Reformulation



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$$f_z''(Z_L) \leq M(s_L + s_2^a + s_1^b)$$

Region 1: $T \leq \bar{T}$ and $P \geq \bar{P}$

$$\tau = \min(\bar{P} - P,\ T - \bar{T})$$

$$\tau = s_1^a - s_1^b$$

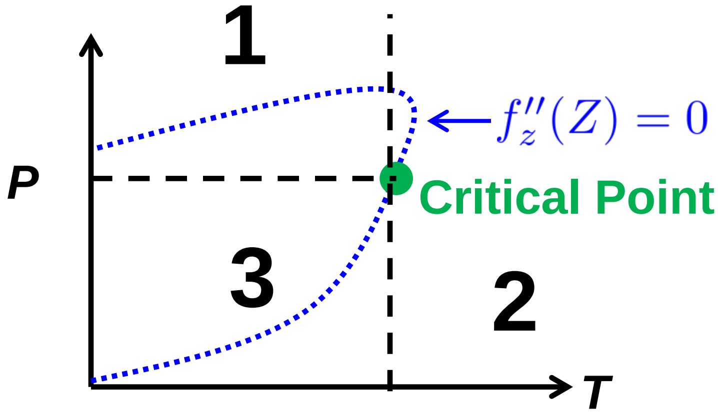
$$0 \leq s_1^a \perp s_1^b \geq 0$$

When $s_1^b > 0$, relax $f_z''(Z)$

$$0 \leq s_1^b \perp V \geq 0$$

$$f_z''(Z_V) \geq -M(s_V + s_2^a + s_1^b)$$

Proposed Reformulation



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Critical Point Calculations

Need formula for $\bar{T}$ and $\bar{P}$ consistent with mixing rules

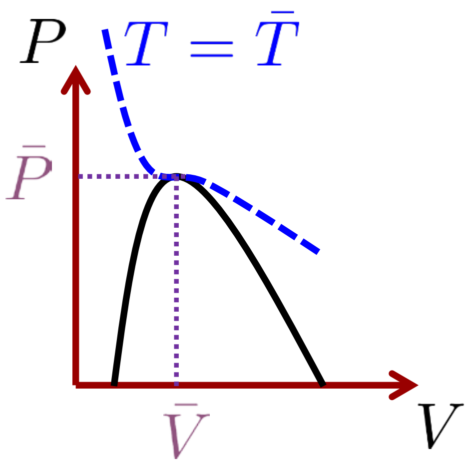
$$a^m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - \bar{k}_{i,j}) \qquad i, j \in \{Components\}$$

$\bar{k}_{i,j}$ are binary inter. param.

$$b^m = \sum_i x_i b_i$$

a_i and b_i are for pure comps.

Critical Point Definition:



$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad \xrightarrow{\text{Chain Rule}} \qquad \left(\frac{\partial f_z}{\partial Z}\right)_{A,B} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad \qquad \left(\frac{\partial^2 f_z}{\partial Z^2}\right)_{A,B} = 0$$

Critical Point Calculations

Need formula for $\bar{T}$ and $\bar{P}$ consistent with mixing rules

$$a^m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - \bar{k}_{i,j})$$

$$b^m = \sum_i x_i b_i$$

$i, j \in \{Components\}$

$\bar{k}_{i,j}$ are binary inter. param.

a_i and b_i are for pure comps.

$$f(Z) = 0$$

$$f'(Z) = 3Z^2 - 2(1 + B - uB)Z + A + wB^2 - uB - uB^2 = 0$$

$$f''(Z) = 6Z - 2(1 + B - uB) = 0$$

	$\bar{Z}$	$\bar{A}$	$\bar{B}$
Peng-Robinson	0.30740...	0.45724...	0.077796...
SRK	$\frac{1}{3}$	0.42748...	0.086640...

Critical Point Calculations

Need formula for $\bar{T}$ and $\bar{P}$ consistent with mixing rules

$$a^m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - \bar{k}_{i,j})$$

$\bar{p}_i$ and $\bar{t}_i$ are component critial properties

$$b^m = \sum_i x_i b_i$$

Solve for T and P

$$\bar{A} = \frac{a^m P}{T^2 R^2} \qquad \bar{B} = \frac{b^m P}{T R} \qquad a_i = \frac{\hat{a} R^2 \bar{t}_i^2}{\bar{p}_i}\alpha(\omega_i, \bar{t}_i, T) \qquad b_i = \frac{\hat{b} R \bar{t}_i}{\bar{p}_i}$$

	$\bar{Z}$	$\bar{A}$	$\bar{B}$
Peng-Robinson	0.30740...	0.45724...	0.077796...
SRK	$\frac{1}{3}$	0.42748...	0.086640...

Proof: $f''(Z)$ Condition

Assumption: Three distinct real roots exist

$$f_z(Z) = Z^3 + a_1 Z^2 + a_2 Z + a_3$$

$$f_z(Z) = (Z - r_L)(Z - r_M)(Z - r_V)$$

$$a_1 = -(r_L + r_M + r_V)$$

$$a_2 = r_L r_M + r_M r_V + r_V r_L$$

$$a_3 = -r_L r_M r_V$$

From differentiation:

$$f_z''(Z) = 6Z + 2a_1$$

By definition:

$$r_L \leq r_M \leq r_V$$

<u>Liquid Case</u>

$$f_z''(r_L) = 6r_L + 2a_1$$

$$f_z''(r_L) = 6r_L - 2(r_L + r_M + r_V)$$

$$f_z''(r_L) = 4r_L - 2r_M - 2r_V$$

$$f_z''(r_L) \leq 0$$

<u>Vapor Case</u>

$$f_z''(r_V) = 6r_V + 2a_1$$

$$f_z''(r_V) = 6r_V - 2(r_L + r_M + r_V)$$

$$f_z''(r_V) = 4r_V - 2r_M - 2r_L$$

$$f_z''(r_V) \geq 0$$

Kamath, R. S., Biegler, L. T., & Grossmann, I. E. (2010). Comp. & Chem. Eng., 34(12), 2085–2096.

Proof: f'(Z) Condition

Assumption: Three distinct real roots exist

From differentiation: $f_z'(Z) = 3Z^2 + 2a_1 Z + a_2$

Liquid Case

$$f_z'(r_L) = r_L^2 - r_V r_L - r_L r_M + r_V r_M$$

$$f_z'(r_L) = \underbrace{(r_L - r_M)}_{\leq 0}\underbrace{(r_L - r_V)}_{\leq 0}$$

$$\therefore \quad f_z'(r_L) \geq 0$$

By definition:

$r_L \leq r_M \leq r_V$

Vapor Case

$$f_z'(r_V) = r_V^2 - r_V r_L - r_V r_M + r_L r_M$$

$$f_z'(r_V) = (r_V - r_M)(r_V - r_L)$$

$$\therefore \quad f_z'(r_V) \geq 0$$

Kamath, R. S., Biegler, L. T., & Grossmann, I. E. (2010). Comp. & Chem. Eng., 34(12), 2085–2096.