Coal Oxycombustion Flowsheet Optimization: An Equation-Oriented Air Separation Unit Model

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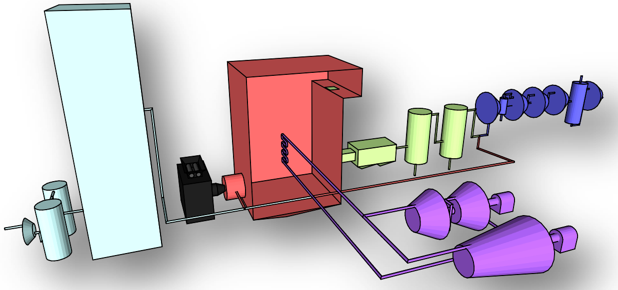
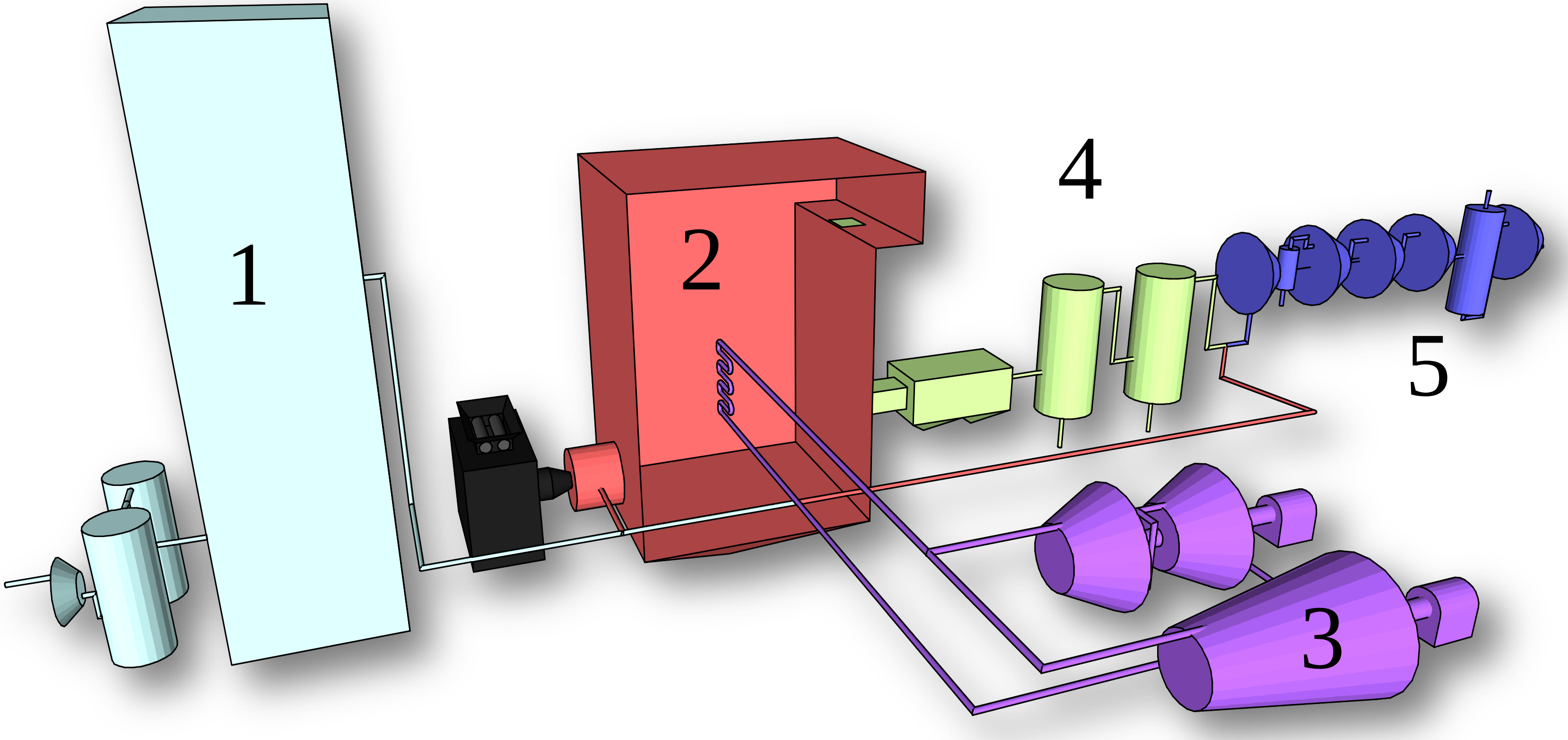
CCSI
Carbon Capture Simulation Initiative

NETL
NATIONAL ENERGY TECHNOLOGY LABORATORY



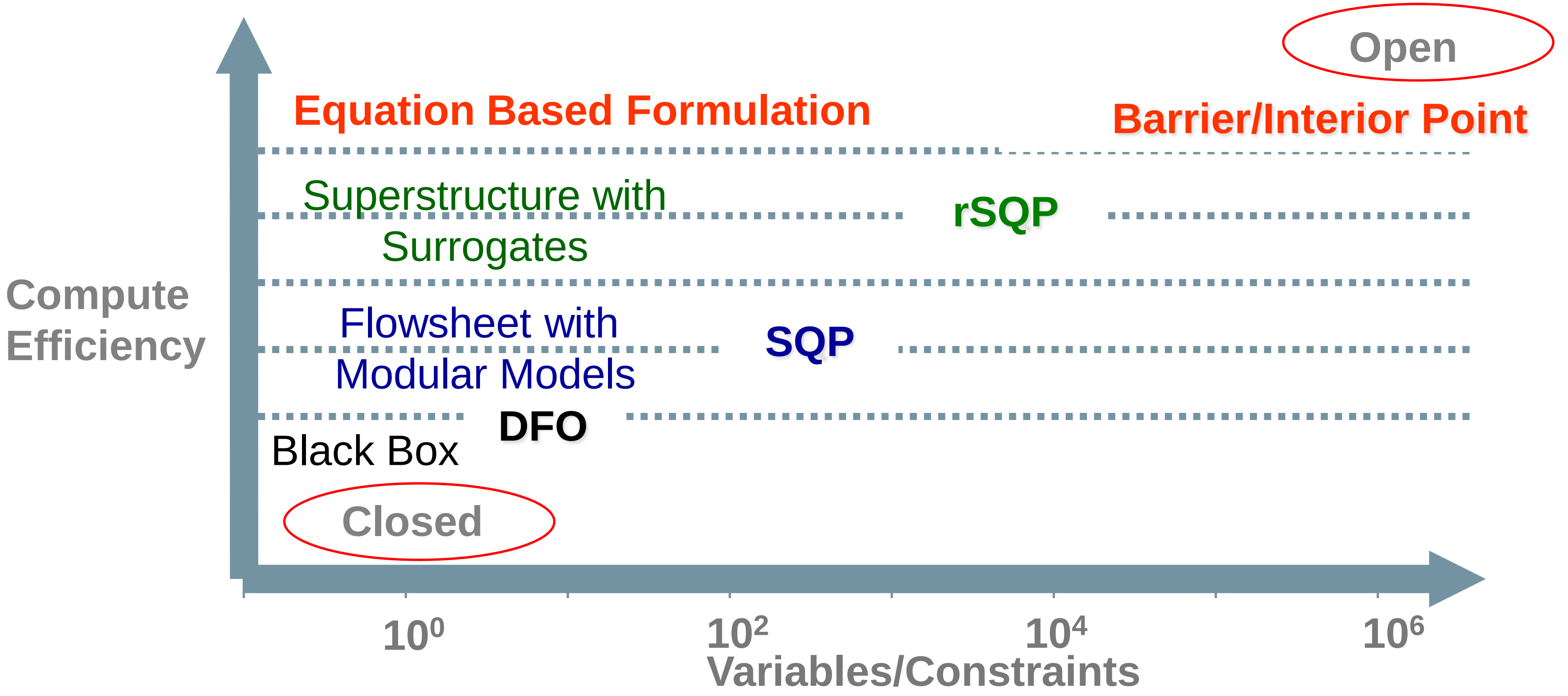
Oxycombustion Flowsheet



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

Project Objective

Develop an **equation oriented** framework to optimize an entire coal oxycombustion flowsheet.



Open

Equation Based Formulation

Barrier/Interior Point

Superstructure with Surrogates

rSQP

Flowsheet with Modular Models

SQP

DFO

Black Box

Closed

Compute Efficiency

10^0 10^2 10^4 10^6

Variables/Constraints

Project Summary

Objective: Develop an **equation oriented** framework to optimize an entire coal oxycombustion flowsheet.

- Characterize potential of coal oxycombustion technology for **carbon capture**
- Explore **complex design trade-offs** in highly coupled flowsheet
- Demonstrate equation oriented methods on an **industrial size flowsheet**

Outline

1. Cryogenic Air Separation Model
2. Thermodynamic Model and Phase Detection
3. Heat Integration
4. Optimization Results
5. Future Work and Conclusions

Cryogenic Air Separation

Boiling Points @ 1 atm

Oxygen:	-183 °C
Argon:	-185.7 °C
Nitrogen:	-195.8 °C

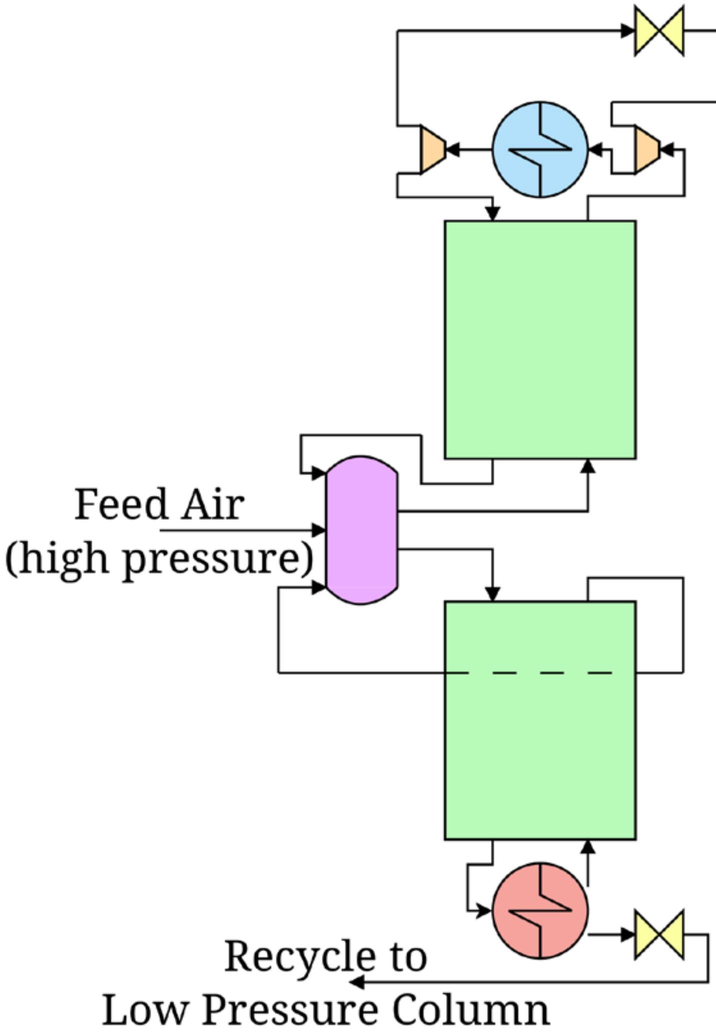
Multicomponent distillation with tight heat integration

Low pressure section

Photo from wikipedia.org

High pressure section

High Pressure Column

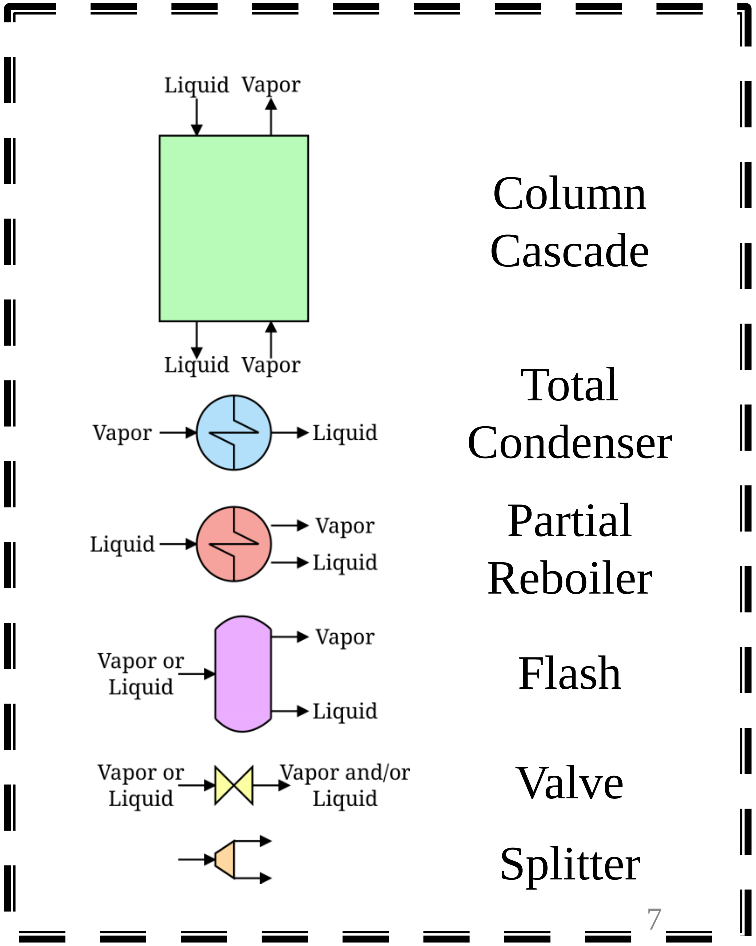


Nitrogen rich product (liquid and/or vapor)

Nitrogen rich product (vapor)

Feed Air
(high pressure)

Recycle to
Low Pressure Column



Column Cascade

Total Condenser

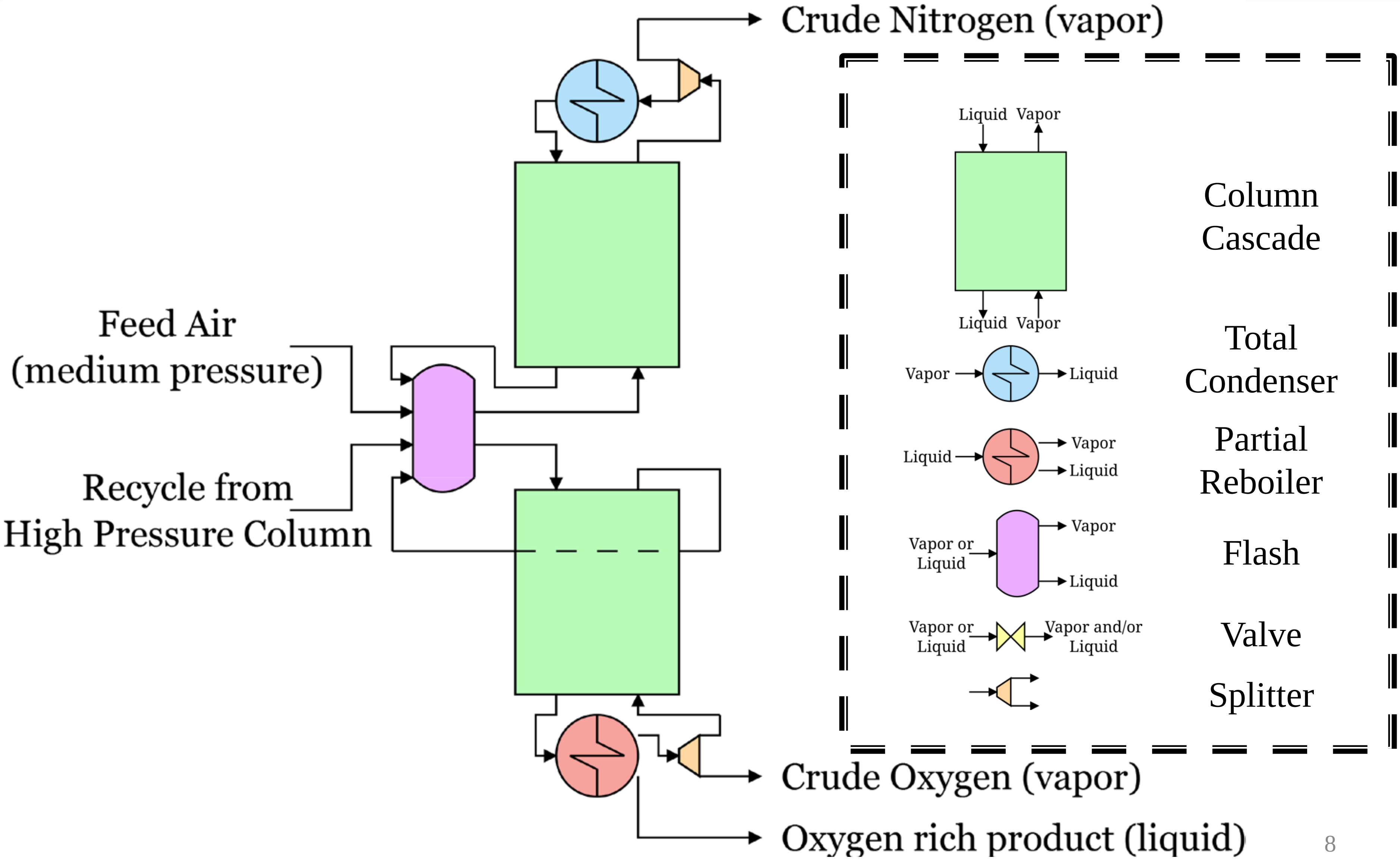
Partial Reboiler

Flash

Valve

Splitter

Low Pressure Column



Crude Nitrogen (vapor)

Feed Air
(medium pressure)

Recycle from
High Pressure Column

Column Cascade

Total Condenser

Partial Reboiler

Flash

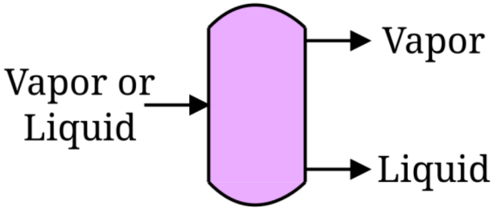
Valve

Splitter

Crude Oxygen (vapor)

Oxygen rich product (liquid)

Flash Model



Mole balance for component c

$$F_{in,c} = F_{out,c}^{(L)} + F_{out,c}^{(V)}$$

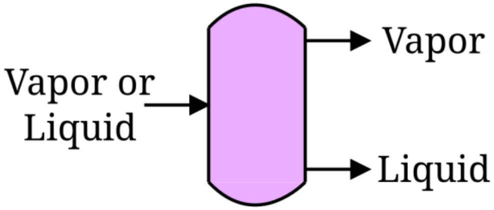
Overall mole balance for stream s

$$F_s = \sum_c F_{s,c}$$

Pressure and Temperature Matching

$$P_{in} = P_{out}^{(V)} = P_{out}^{(L)} \qquad T_{out}^{V} = T_{out}^{L}$$

Flash Model



Energy balance (adiabatic)

$$F_{in}H_{in} = F^{(L)}_{out}H^{(L)}_{out} + F^{(V)}_{out}H^{(V)}_{out}$$

Phase Equilibrium for component c

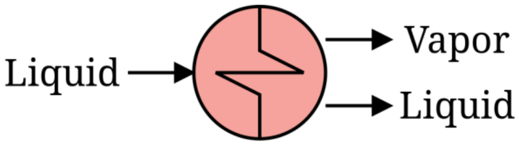
$$\phi^{(V)}_{out,c}\; y_{out,c} = \beta\; \phi^{(L)}_{out,c}\; x_{out,c}$$

Equilibrium Relaxation

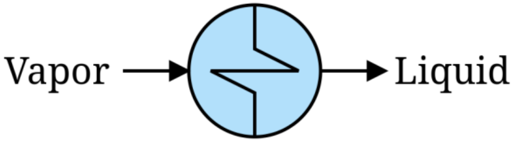
$$-s_L \leq \beta - 1 \leq s_V$$

Units Similar to Flash

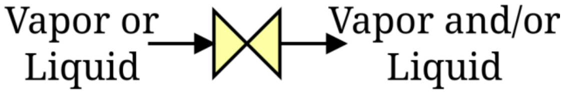
- Partial Reboiler
  - Not adiabatic



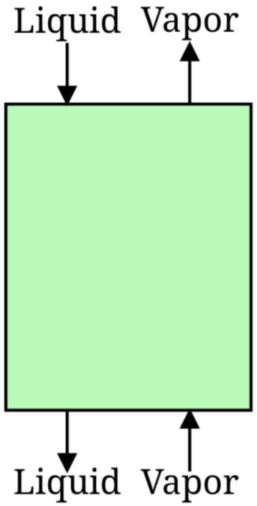
- Total Condenser
  - No exit vapor stream → no equilibrium equation
  - Not adiabatic



- Valve
  - $P_{in} \geq P_{out}$
  - Entropy inequality (optional)



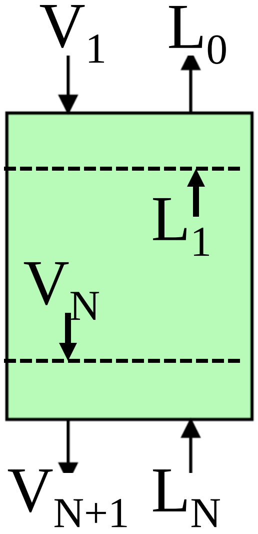
Cascade Model



- Group method
  - Continuous number of ideal stages
  - Based on work of Kremser and Edminster
  - Requires specification of stripping and absorbing section
- Modifications for distillation:
  - Exit streams at dew/bubble point
  - Decrease vapor at bottom = increase liquid at top

Kamath, Grossmann & Biegler (2010). Aggregate models based on improved group methods for simulation and optimization of distillation systems. *Computers & Chemical Engineering*.

Cascade Model



Performance Equation

$$F_{out,c}^{(V)} = F_{in,c}^{(V)}\psi_{A,c} + F_{in,c}^{(L)}(1 - \psi_{S,c})$$

Adsorption and Stripping Factors

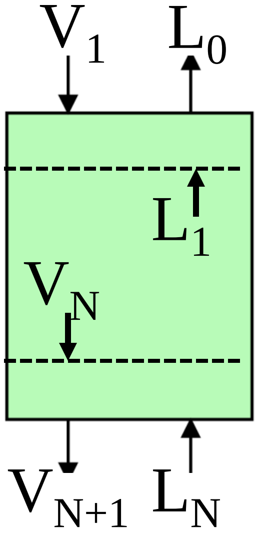
$$\psi_{A,c} = \frac{A_{e,c} - 1}{A_{e,c}^{N+1} - 1} \qquad \psi_{S,c} = \frac{S_{e,c} - 1}{S_{e,c}^{N+1} - 1}$$

Effective Factors

$$A_{e,c} = [A_{N,c}(A_{1,c} + 1) + 0.25]^{0.5} - 0.5$$

$$S_{e,c} = [S_{1,c}(S_{N,c} + 1) + 0.25]^{0.5} - 0.5$$

Cascade Model



Factor Caculations

$$A_{1,c} = \frac{L_1}{K_{1,c}V_1} \qquad A_{N,c} = \frac{L_N}{K_{N,c}V_N}$$

$$S_{1,c} = 1/A_{1,c} \qquad S_{N,c} = 1/A_{N,c}$$

Model Modifications

$$L_1 - L_N = V_1 - V_N$$

$$K_{1,c} = \frac{\phi^V_{BP,c}}{\phi^L_{out,c}} \qquad K_{N,c} = \frac{\phi^V_{out,c}}{\phi^L_{DP,c}}$$

Thermodynamic Model

- Cubic Equation of State (CEOS)

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2}$$

$$Z = \frac{RT}{PV}$$

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

- Properties from departure functions

$$H(T, P, x, y) - H^\circ(T) = \ldots$$

$$S(T, P, x, y) - S^\circ(T) = \ldots$$

$$\phi(T, P, x, y) = \ldots$$

Root Selection Constraints

General CEOS

$$f(r) = ar^3 + br^2 + cr + d$$

Up to 3 Root?!?

Phase	**CEOS**	**1st Derivative**	**2nd Derivative**
Liquid	$f(r_L) = 0$	$f'(r_L) \geq 0$	$f''(r_L) \leq 0$
Vapor	$f(r_V) = 0$	$f'(r_V) \geq 0$	$f''(r_V) \geq 0$

Kamath, Grossmann & Biegler (2010). An equation-oriented approach for handling thermodynamics based on cubic equation of state in process optimization. *Computers & Chemical Engineering*.

Phase Disappearance

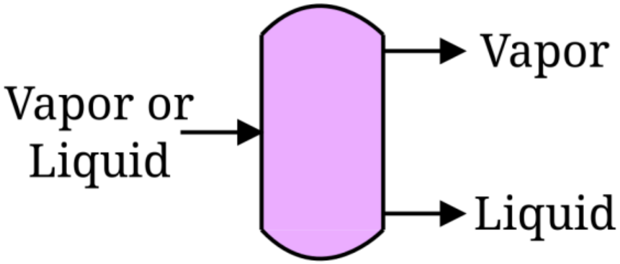
Idea: If a phase disappears, the thermodynamics must also be relaxed.

Thermodynamics Relaxation

$$f''(r_L) \leq M s_L$$
$$f''(r_V) \geq -M s_V$$

Complementarity Condition

$$0 \leq F^{(V)} \perp s_V \geq 0$$
$$0 \leq F^{(L)} \perp s_L \geq 0$$



Phase Disappearance

Complementarity Condition

$$0 \leq F^{(V)} \perp s_V \geq 0$$

$$0 \leq F^{(L)} \perp s_L \geq 0$$

Phase Equilibrium for component c

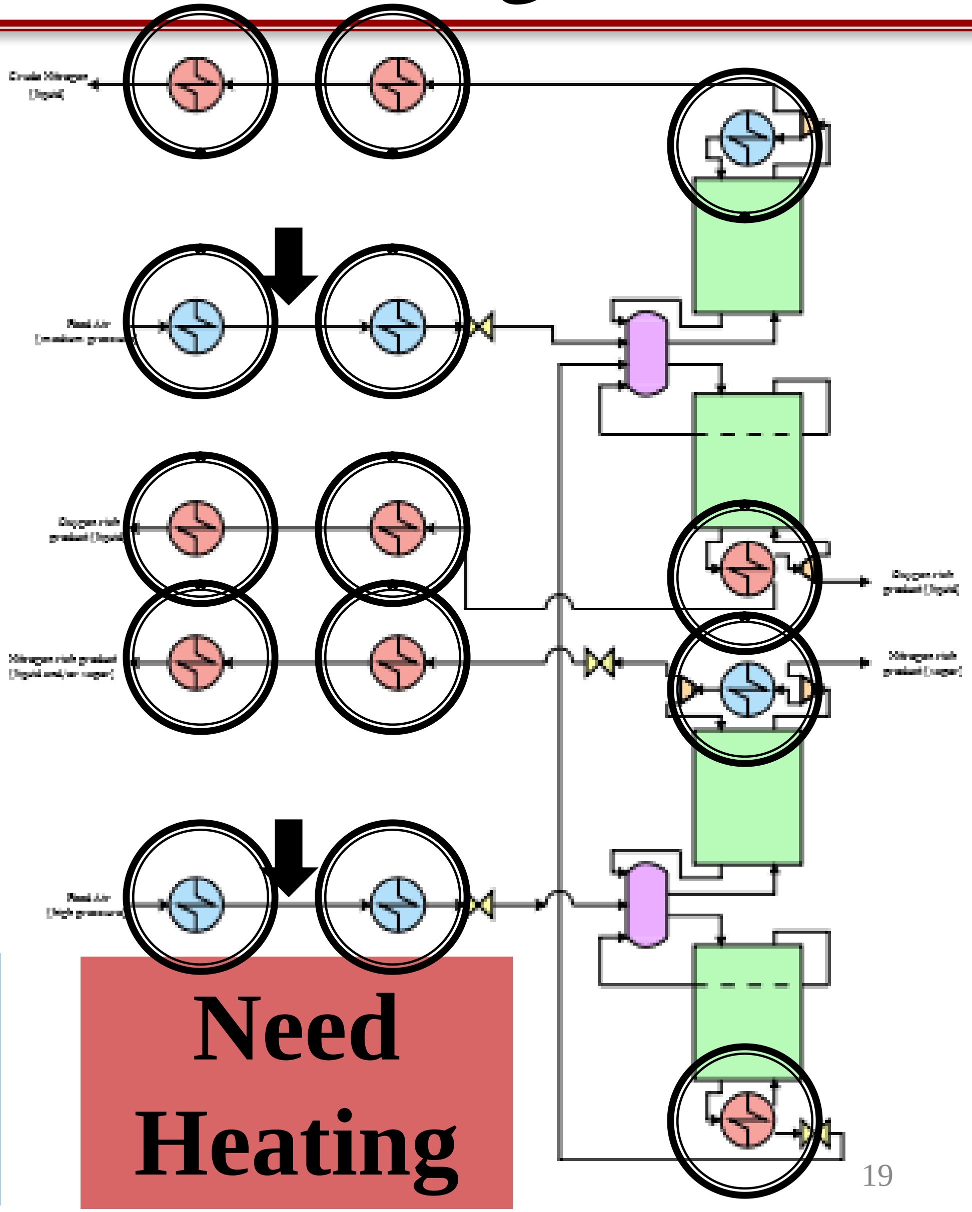
$$\phi_{out}^{(V)} \; y_{out,c} = \beta \; \phi_{out}^{(L)} \; x_{out,c}$$

Equilibrium Relaxation

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

Pinch Location Heat Integration

- No utility heating or cooling
- Constant heat capacity assumed for each unit
- Require 2 phase flow for select intermediate streams



Need Cooling

Need Heating

Heat Integration Model

Pinch candidates

Based on work of Duran & Grossmann (1986)

$$T^p = \begin{cases} T_p^{in} & \text{if candidate } p \text{ is a hot stream} \\ T_p^{in} + \Delta T_{min} & \text{if candidate } p \text{ is a cold stream} \end{cases}$$

Available heating and cooling above each pinch candidate

$$QA_H^p = \sum_{i \in \{Hot\}} FCp_i \left[max(0, T_i^{in} - T^p) - max(0, T_i^{out} - T^p) \right]$$

$$QA_C^p = \sum_{j \in \{Cold\}} FCp_j \left[max(0, T_j^{out} - T^p + \Delta T_{min}) - max(0, T_j^{in} - T^p + \Delta T_{min}) \right]$$

Utility calculations

$$Q_s \geq QA_C^p - QA_H^p \quad \text{for all } p$$

$$Q_w = Q_s + \sum_{j \in \{Cold\}} Q_j^{in} - \sum_{i \in \{Hot\}} Q_i^{out}$$

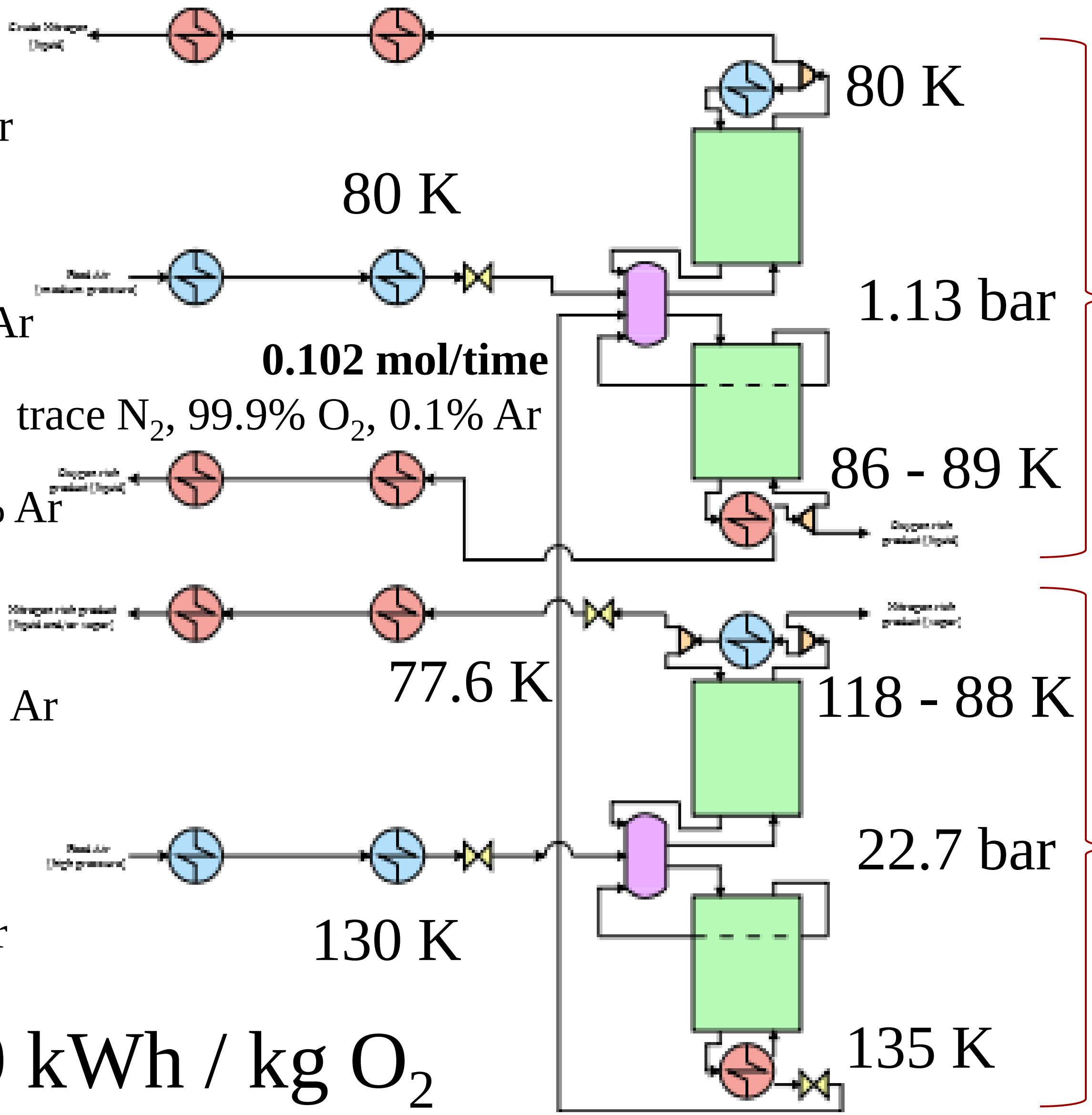
Optimization Problem

Minimize Specific Compression Energy

s.t. O_2 purity $\geq$ 90 mol %
Unit Models
Connectivity Equations
Variable Bounds

Variables / Equations:	2,660 / 2,993
Solver:	CONOPT3 in GAMS
Solution Time:	87.9 seconds
	(with init: 163.4 s)

Optimization Results



1.225 mol/time
1.13 bar, 298 K
94.4% N_2, 5.3% O_2, 0.3% Ar

1.518 mol/time
1.3 bar, 300 K
78% N_2, 21% O_2, 1% Ar

0.394 mol/time
1.13 bar, 298 K
7.1% N_2, 90.0% O_2, 2.9% Ar

0.381 mol/time
1.01 bar, 298 K
98.8% N_2, trace O_2, 1.2% Ar

0.482 mol/time
41.3 bar, 300 K
78% N_2, 21% O_2, 1% Ar

80 K

0.102 mol/time
trace N_2, 99.9% O_2, 0.1% Ar

77.6 K

130 K

80 K

1.13 bar

86 - 89 K

14.5
Thr.
Stages

118 - 88 K

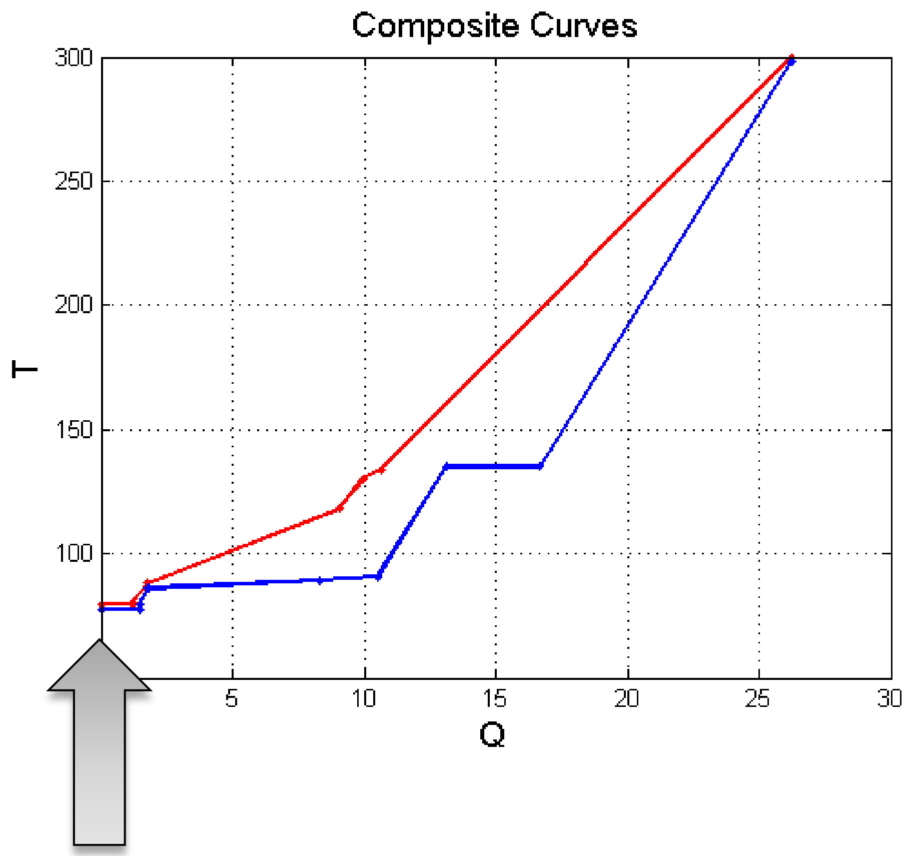
22.7 bar

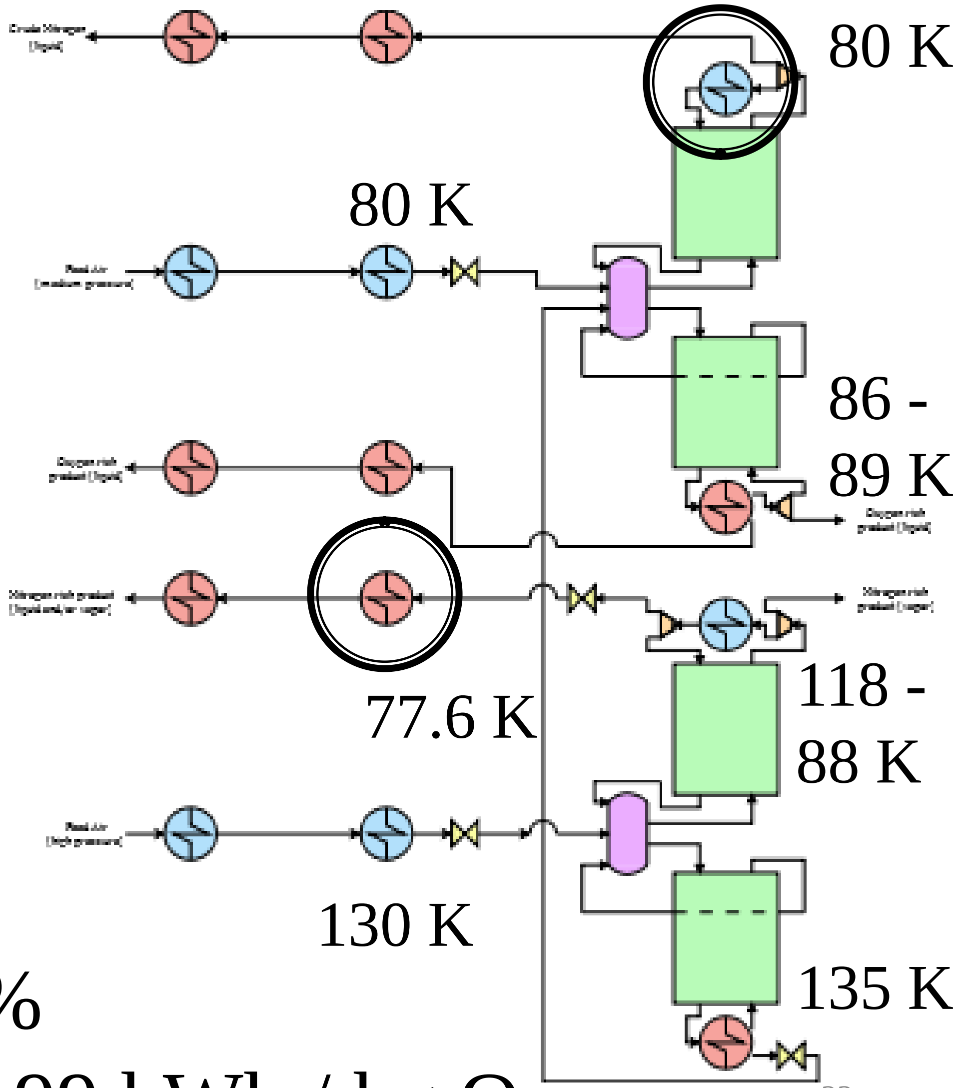
135 K

36.6
Thr.
Stages

0.199 kWh / kg O_2

Optimization Results





80 K

80 K

86 - 89 K

77.6 K

118 - 88 K

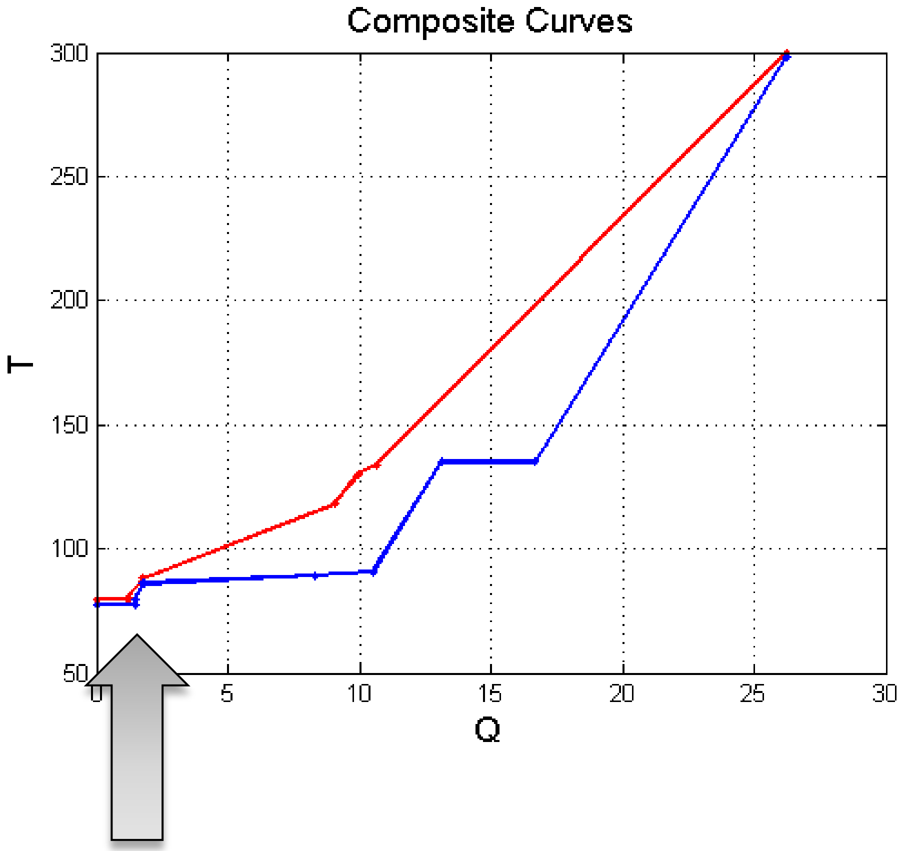
130 K

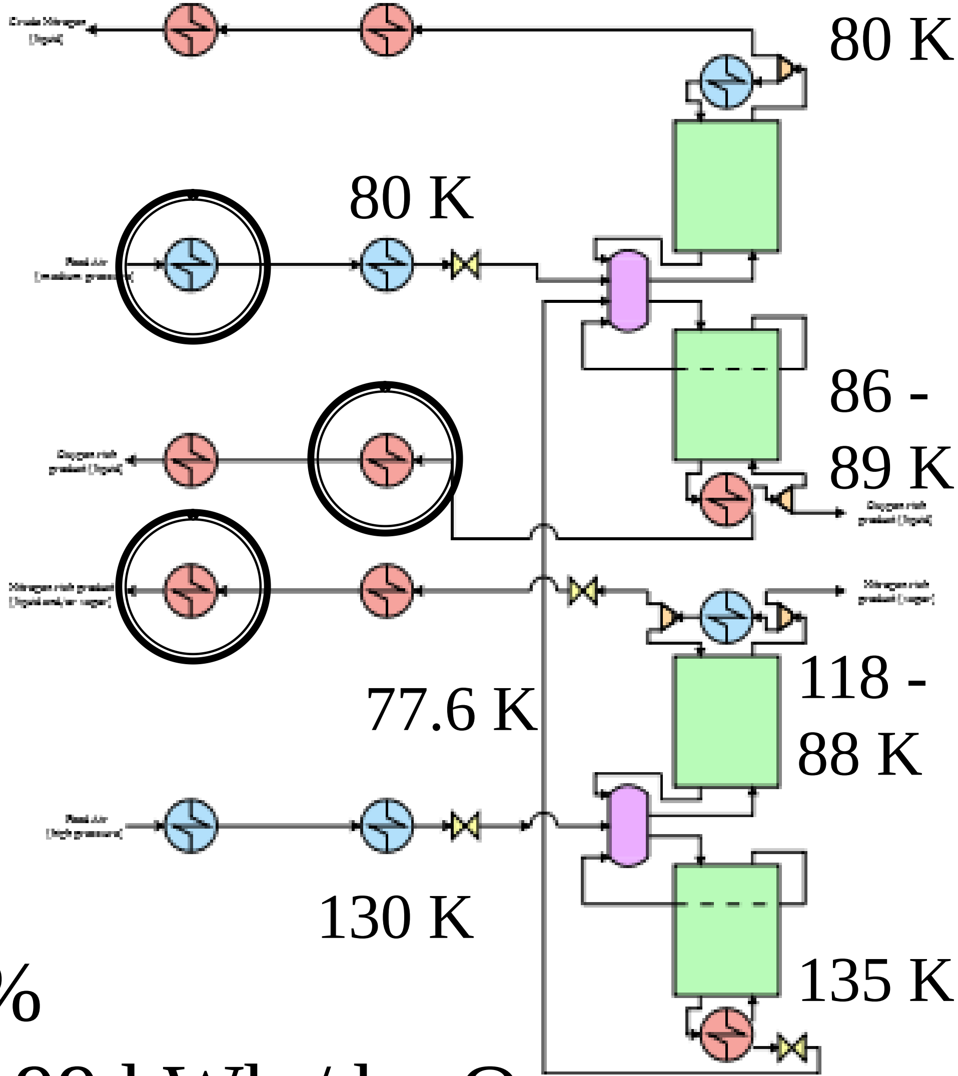
135 K

O_2 purity: 90.0 mol%

Air Compressor: 0.199 kWh / kg O_2

Optimization Results





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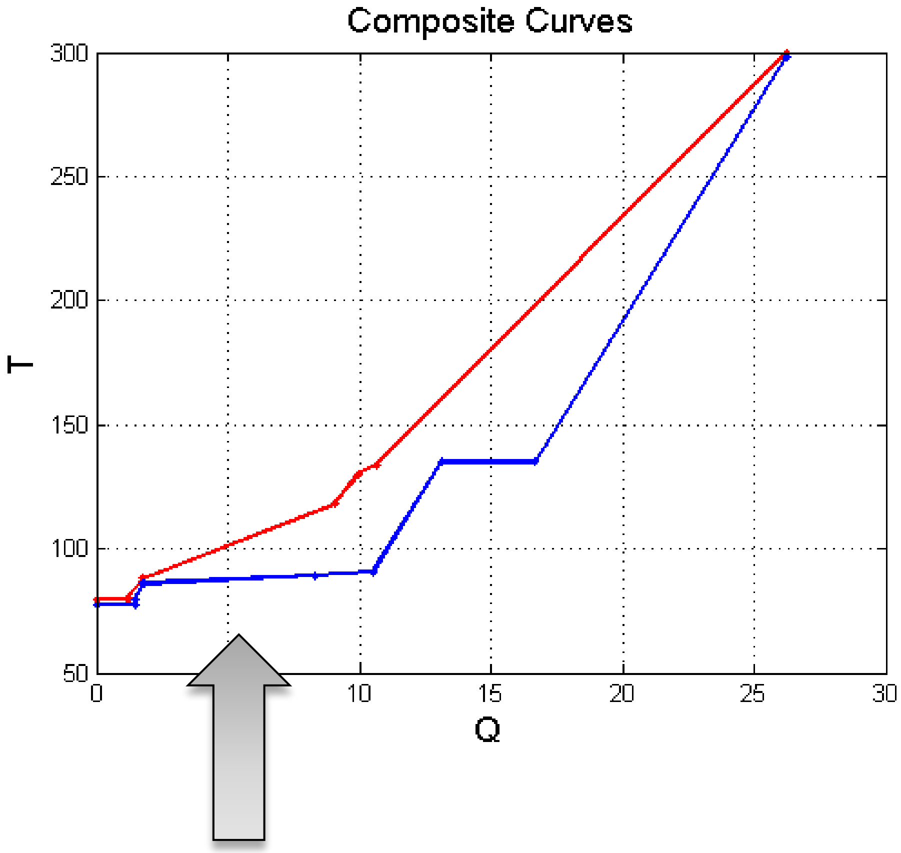

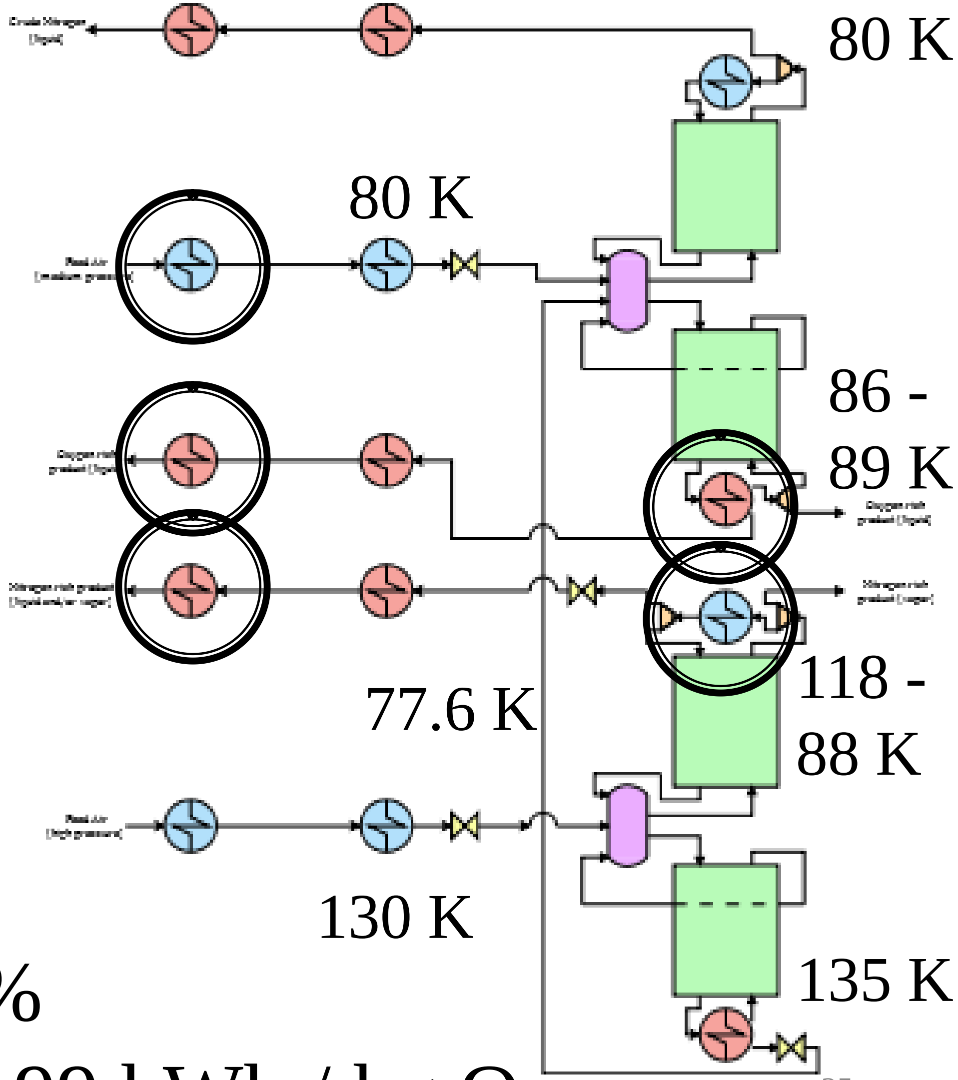

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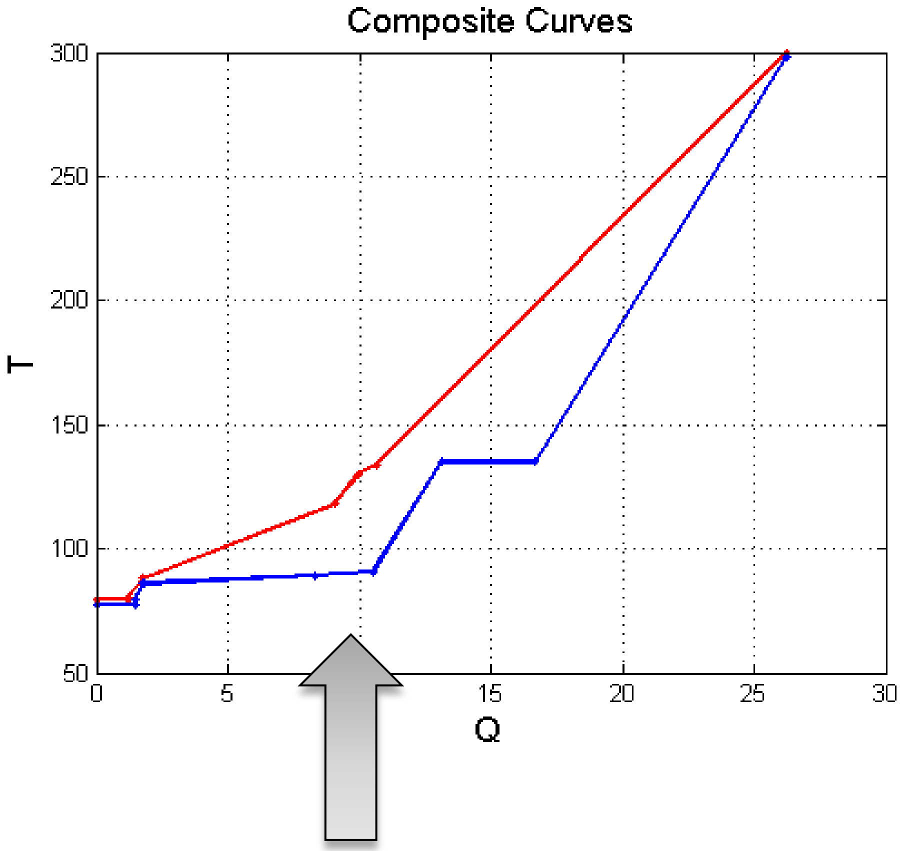

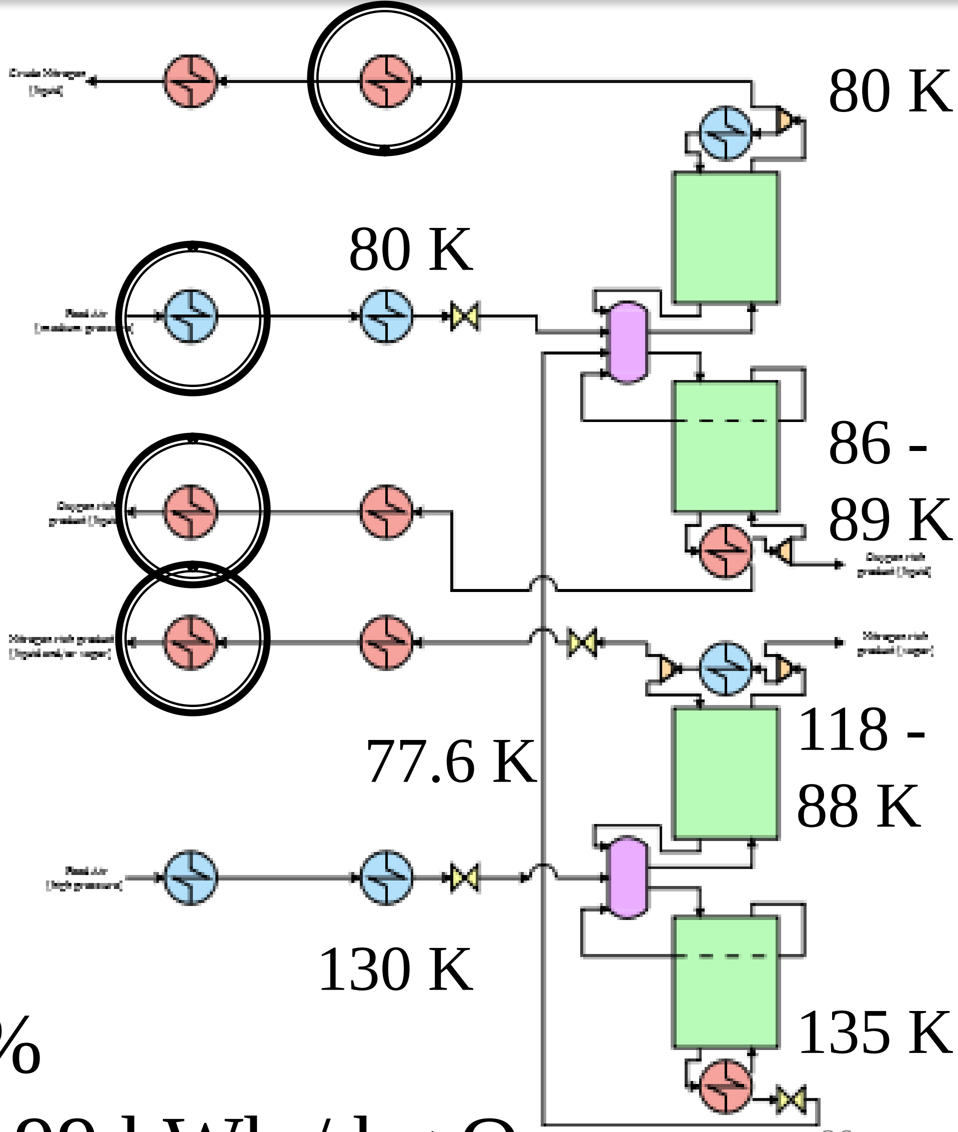
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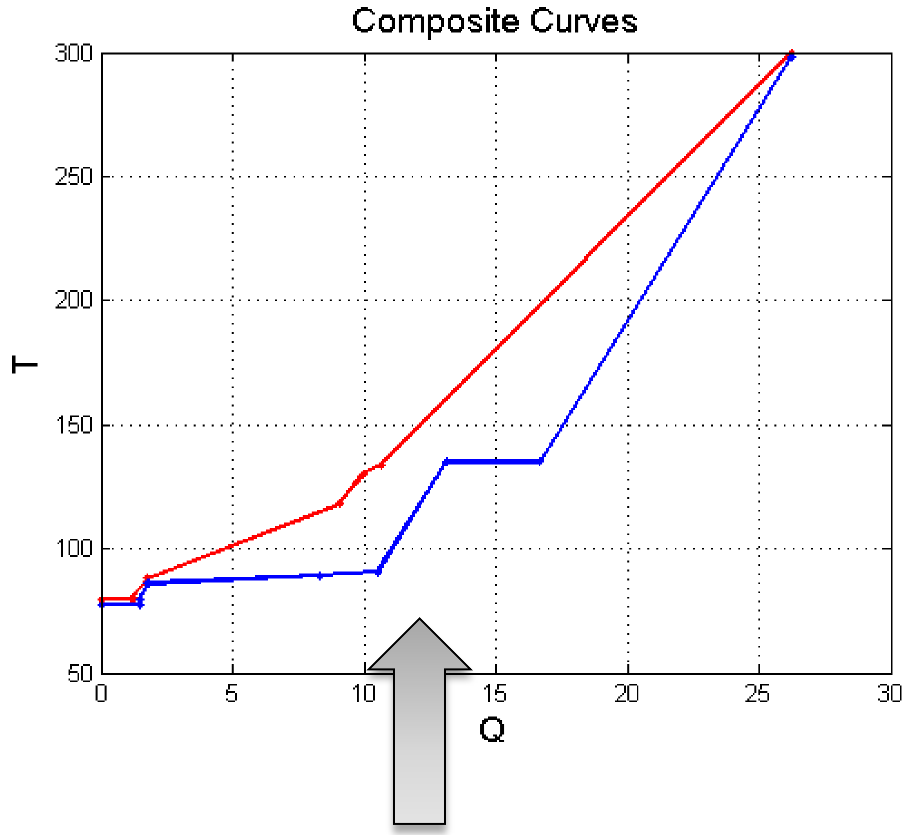

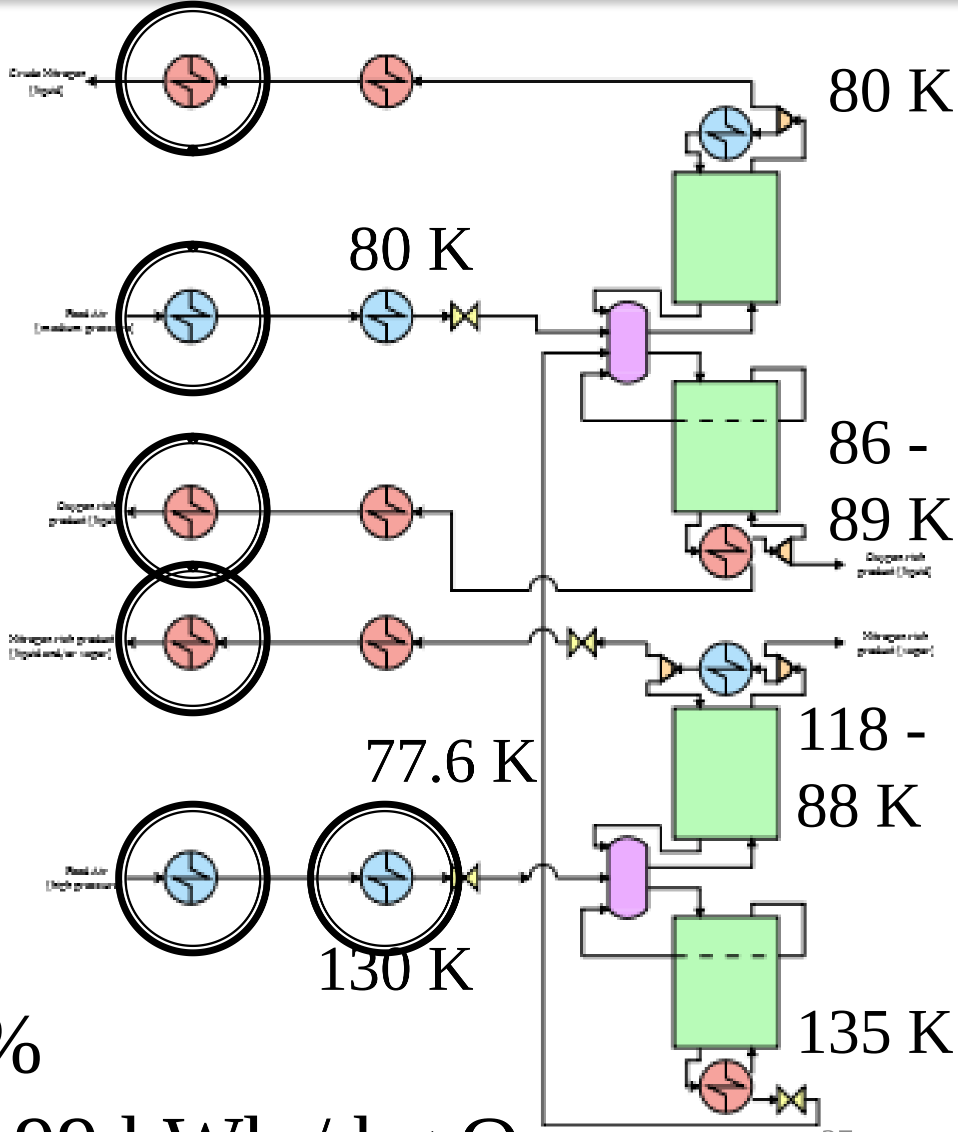

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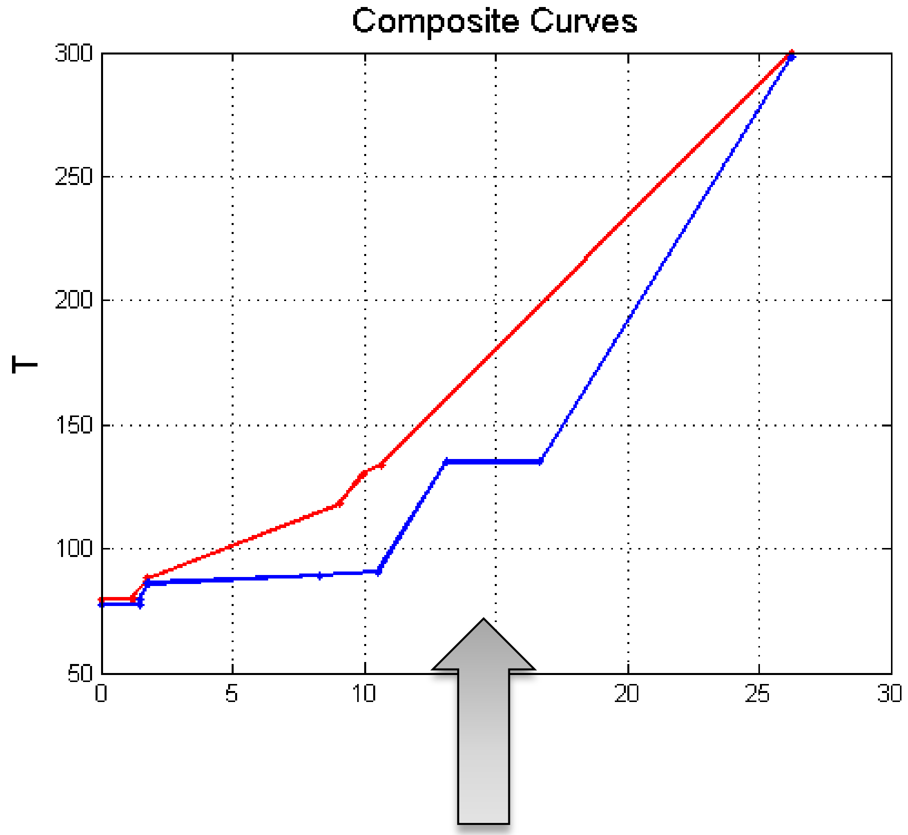

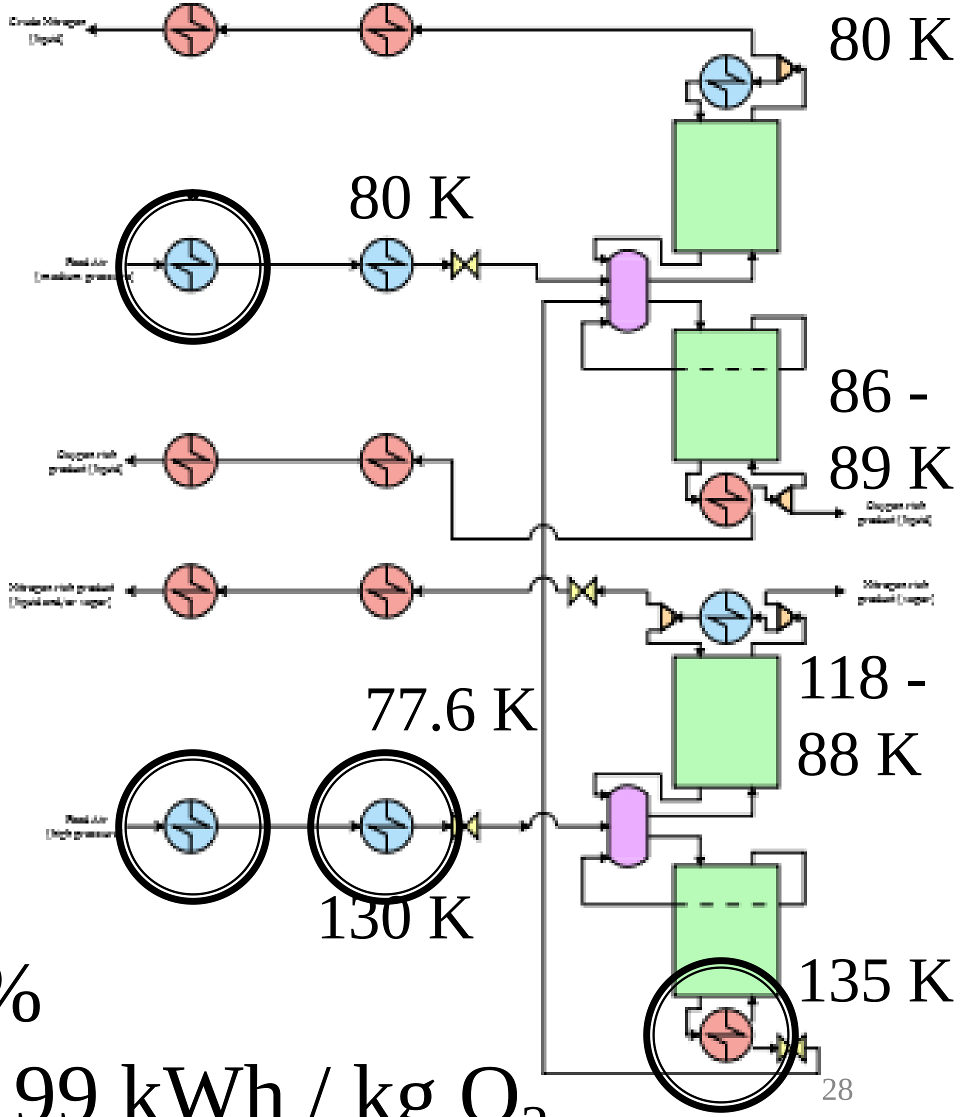

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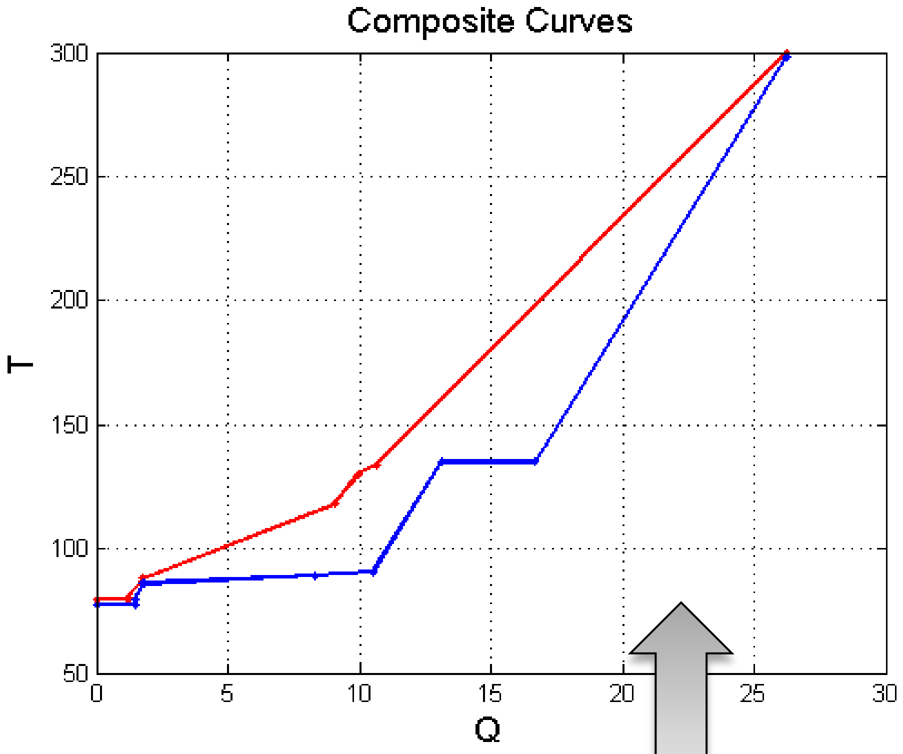

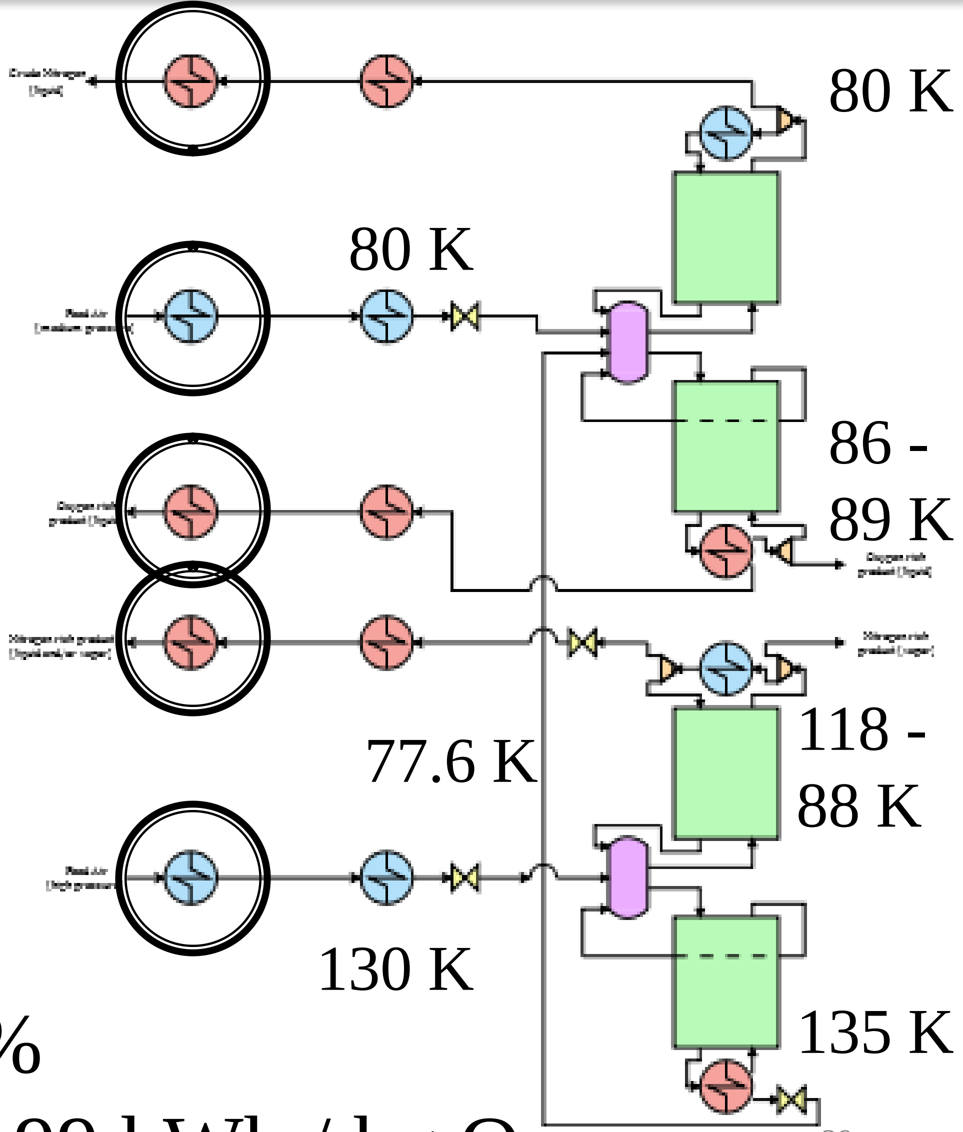

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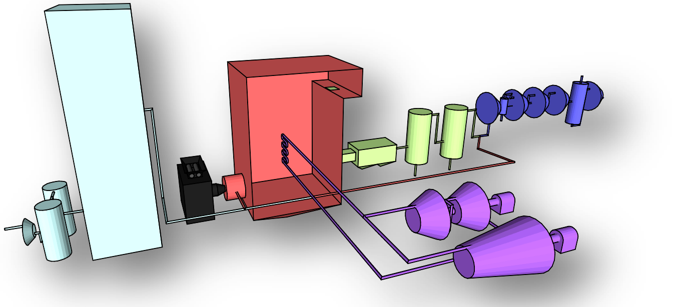
Future ASU Work

- Compare results with Aspen®
  - Adjust thermodynamic coefficients as needed
  - Further validate group method cascade model
- Pareto analysis: energy vs. O_2 purity
- Add capital costs to objective function

Future Flowsheet Work

- Integrate ASU model with remaining flowsheet sections

- Explore potential heat integration synergies
  - ASU with post combustion cryogenics
  - ASU with compression train
  - Compression train with boiler



Conclusions

Optimized ASU with equation-based model:

- Cubic equation of state with accurate derivatives
- Pinch location heat integration
- Pure nonlinear program – no discrete variables

Acknowledgements:

National Energy Technology Laboratory

Yannic Vaupel, RWTH Aachen University

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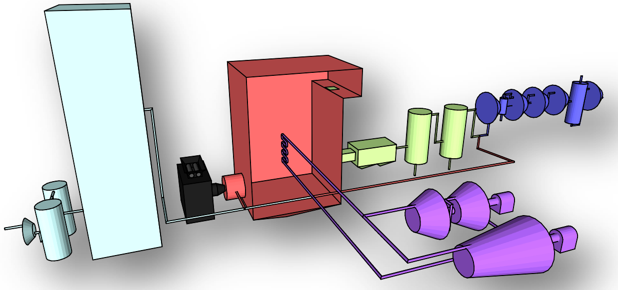

Initialization Procedure

Solve successive optimization problems

1. Mass balances only
2. Simple thermo ASU w/ heat integration
3. CEOS equations only (T, P, x, y, fixed)
4. CEOS ASU w/ heat integration