Dynamic Modeling and Optimization of Large-Scale Cryogenic Processes

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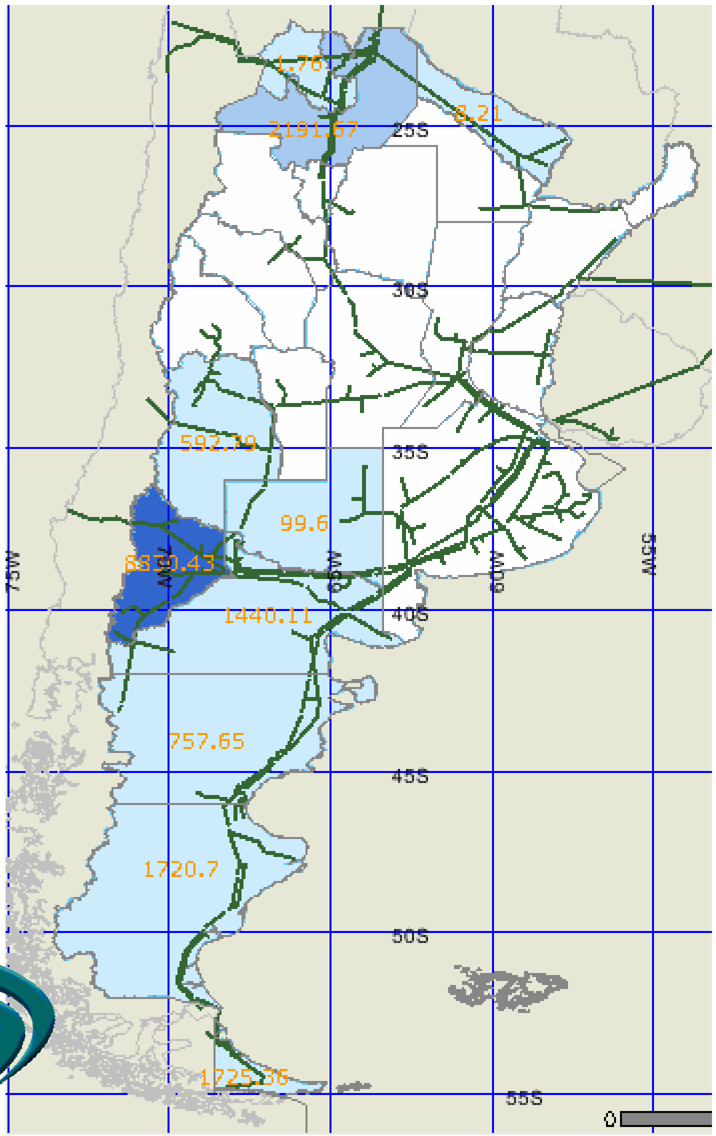
Outline

- Objective
- Natural Gas Processing Plants
- Methodology
- Mathematical Models
- Discussion of Results
- Conclusions and Current Work

Objective

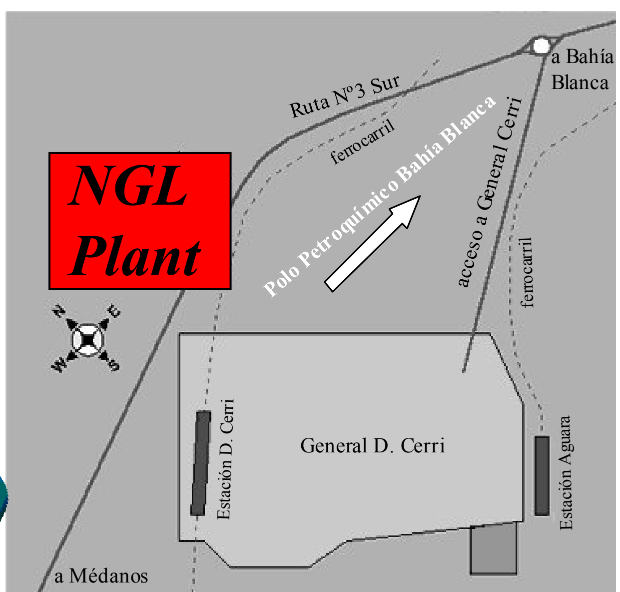
- Dynamic optimization model for natural gas processing plant units
  - Dynamic energy and mass balances
  - Phase equilibrium calculations with cubic equation of state
  - Hydraulic correlations
  - Phase change in countercurrent heat exchanger
  - Carbon dioxide precipitation in column
  - Phase existence in column
- Simultaneous dynamic optimization approach
  - Discretization of state and control variables
  - Resolution of large-scale Nonlinear Programming problem
- Analysis of main variables temporal and spatial profiles

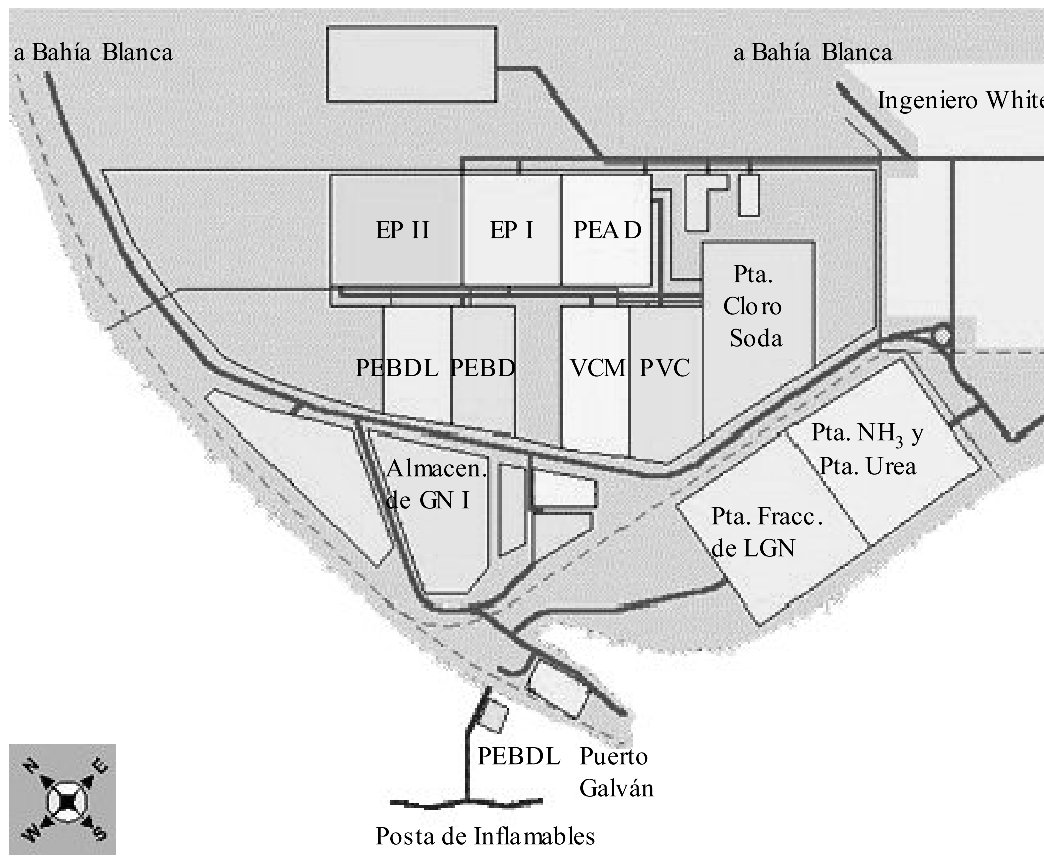
Natural Gas in Argentina



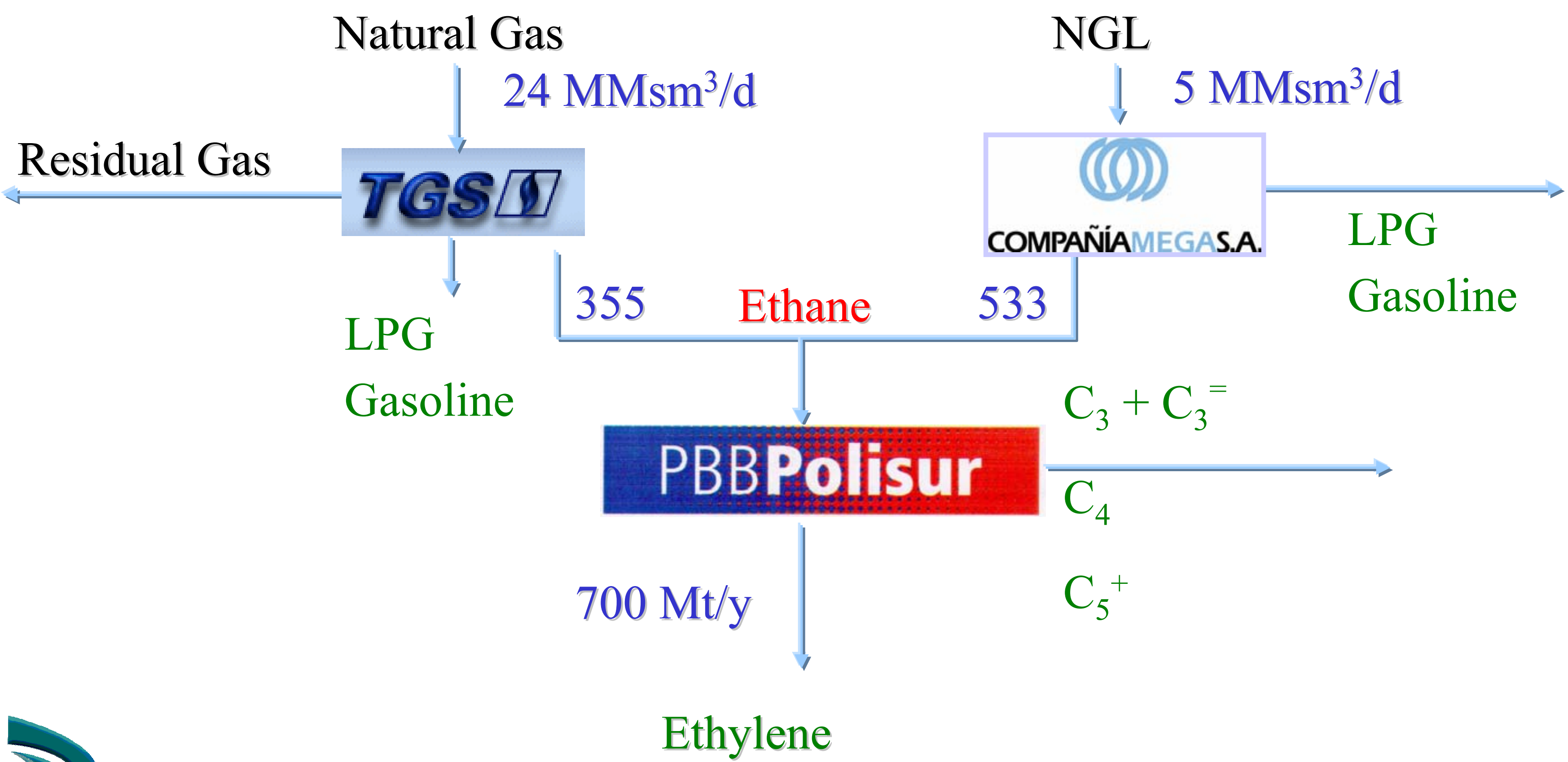
Component	Feed A	Feed B
Nitrogen	1.44	1.37
Carbon dioxide	0.65	1.30
Methane	90.43	89.40
Ethane	4.61	4.43
Propane	1.76	2.04
Butanes	0.77	0.96
Pentanes+	0.34	0.50

- Provide ethane as raw material for olefin plants (ethylene) and petrochemical
- High ethylene yield
- Minimum by-products





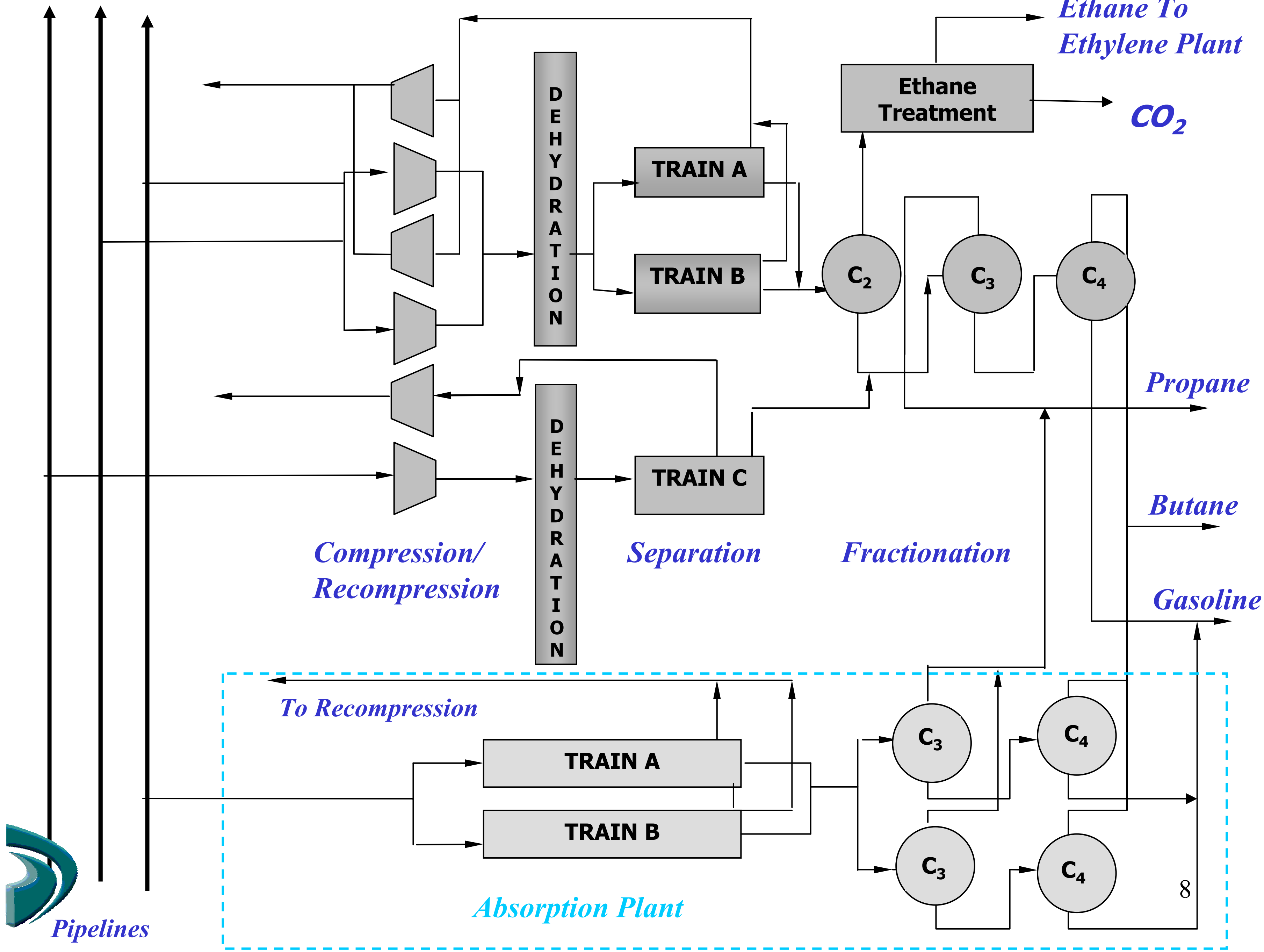
Natural Gas Plants at Bahia Blanca



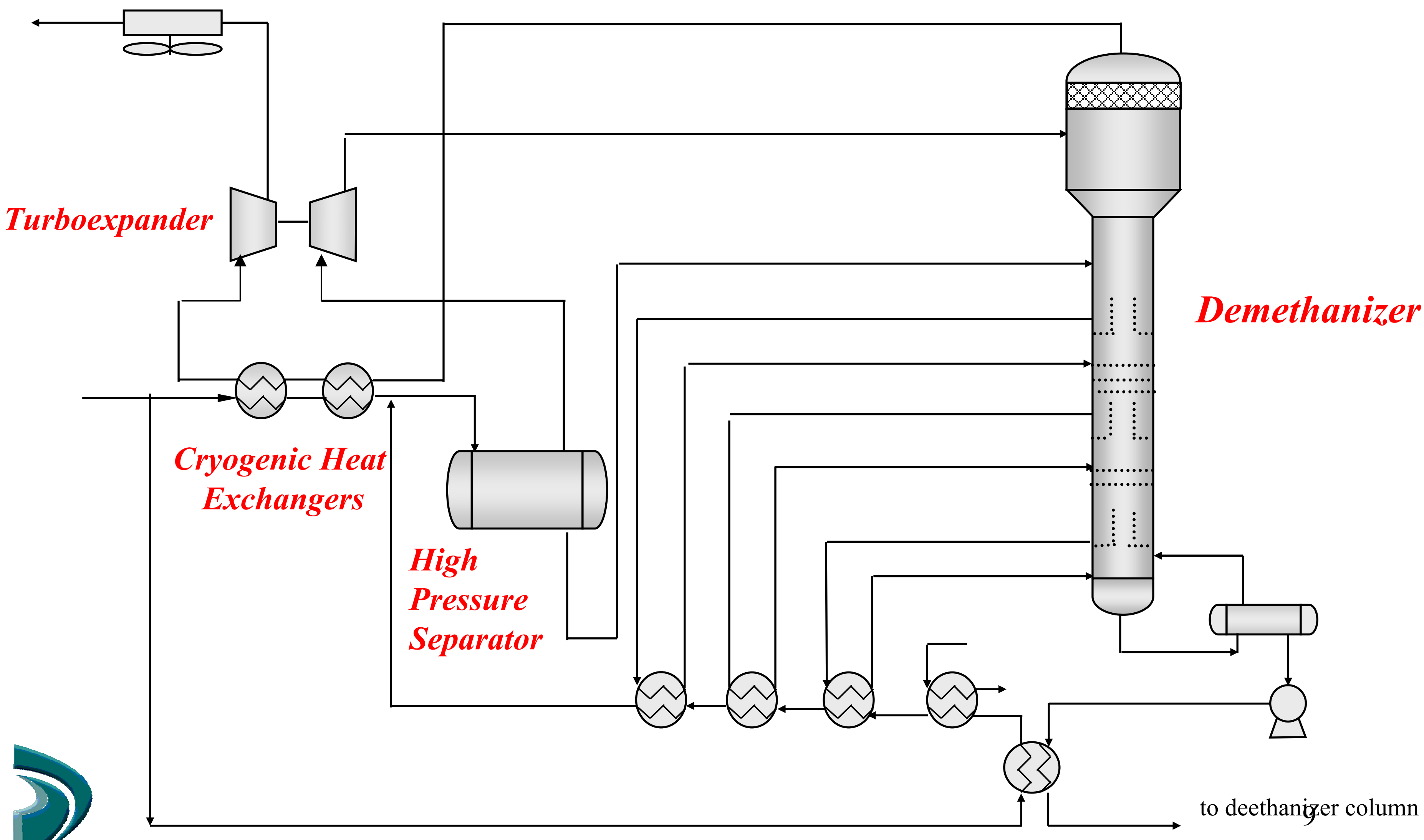
Natural Gas Processing Plants

- Cryogenic sector (demethanizing), Conventional fractionation (deethanizing, depropanizing, debutanizing, gasoline stabilization), CO_2 removal
- Current technology: Turboexpansion (Old technology: Absorption)
- High pressure
- Cryogenic conditions

NATURAL GAS PLANT



Cryogenic Sector



Previous Work

- Operating conditions optimization in natural gas processing plants (NLP) (Diaz, Serrani, Be Deistegui, Brignole, 1995)
- Automatic design and debottlenecking of ethane extraction plants (MINLP) (Diaz, Serrani, Bandoni Brignole, 1997)
- Thermodynamic model effect on the design and optimization of natural gas plants (NLP) (Diaz, Zabaloy, Brignole, 1999)
- Flexibility of natural gas processing plants - Dual mode operation (Bilevel NLP) (Diaz, Bandoni, Brignole, 2002)

General Formulation

$$\min_{z(t), y(t), u(t), tf, p} \Phi(z(tf), y(tf), u(tf), tf, p)$$

st

$$F(dz(t)/dt, (z(t), y(t), u(t), p, t) = 0$$
$$G(z(t), y(t), u(t), p, t) = 0$$

$$z_o = z(0)$$

$$z(t) \in [z^l, z^u] \quad , \quad y(t) \in [x^l, x^u]$$
$$u(t) \in [u^l, u^u] \quad , \quad p \in [p^l, p^u]$$

t, time
z, differential variables
y, algebraic variables

tf, final time
u, control variables
p, time independent parameters

Dynamic Optimization Strategy

Simultaneous Approach Cervantes, Biegler (1998)

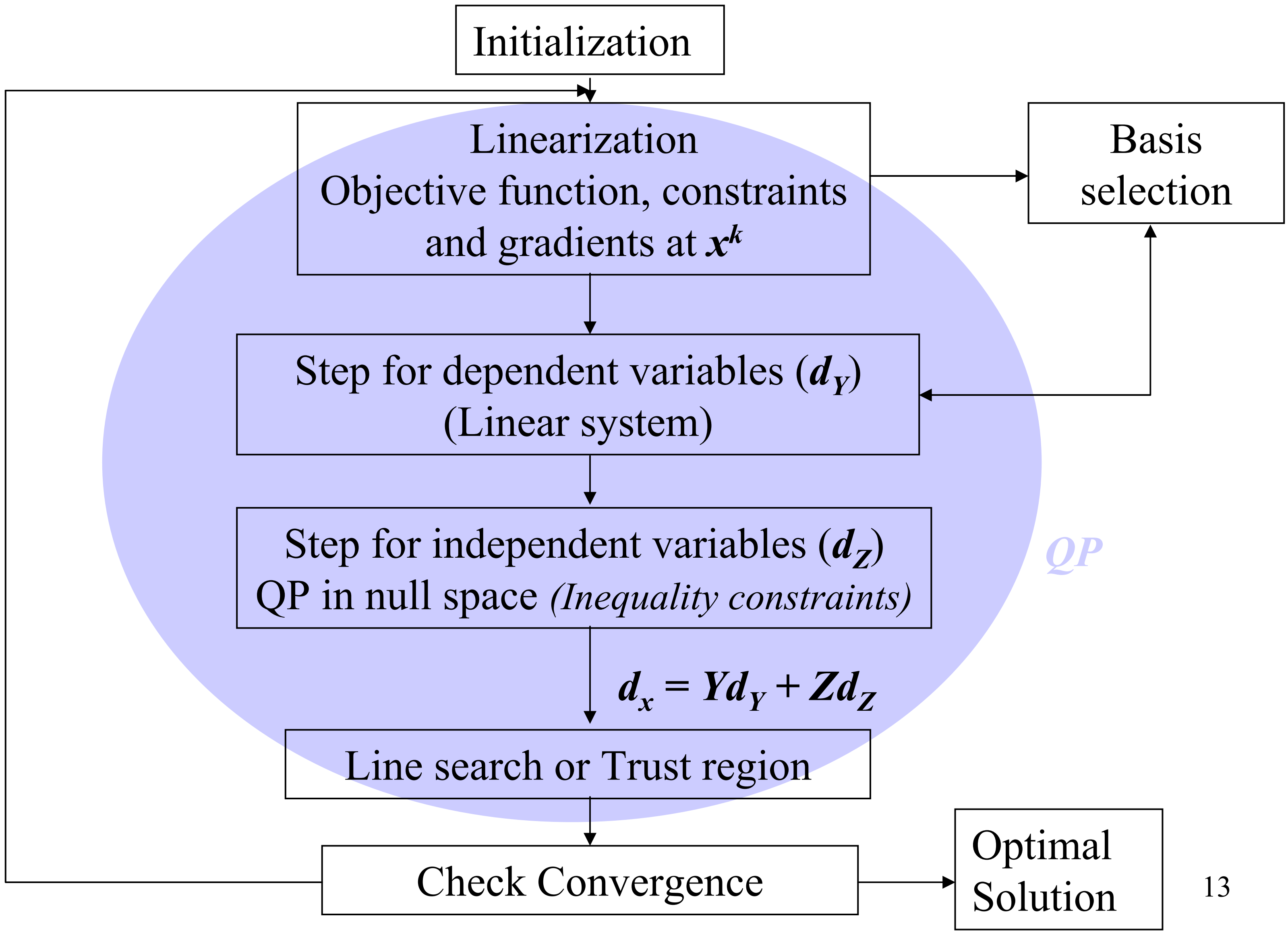
Nonlinear DAE optimization problem

Discretization of Control and State variables

Collocation on finite elements

Large-Scale Nonlinear Programming Problem (NLP)

Interior Point Algorithm Biegler, Cervantes, Waechter (2002)


Initialization
Linearization
Objective function, constraints
and gradients at x^k
Basis
selection
Step for dependent variables (d_Y)
(Linear system)
Step for independent variables (d_Z)
QP in null space *(Inequality constraints)*
QP
$d_x = Yd_Y + Zd_Z$
Line search or Trust region
Check Convergence
Optimal
Solution

Application of Barrier method

$$\min f(x)$$

$$\text{s.t} \quad c(x) = 0$$

$$x \geq 0$$

$$\Rightarrow$$

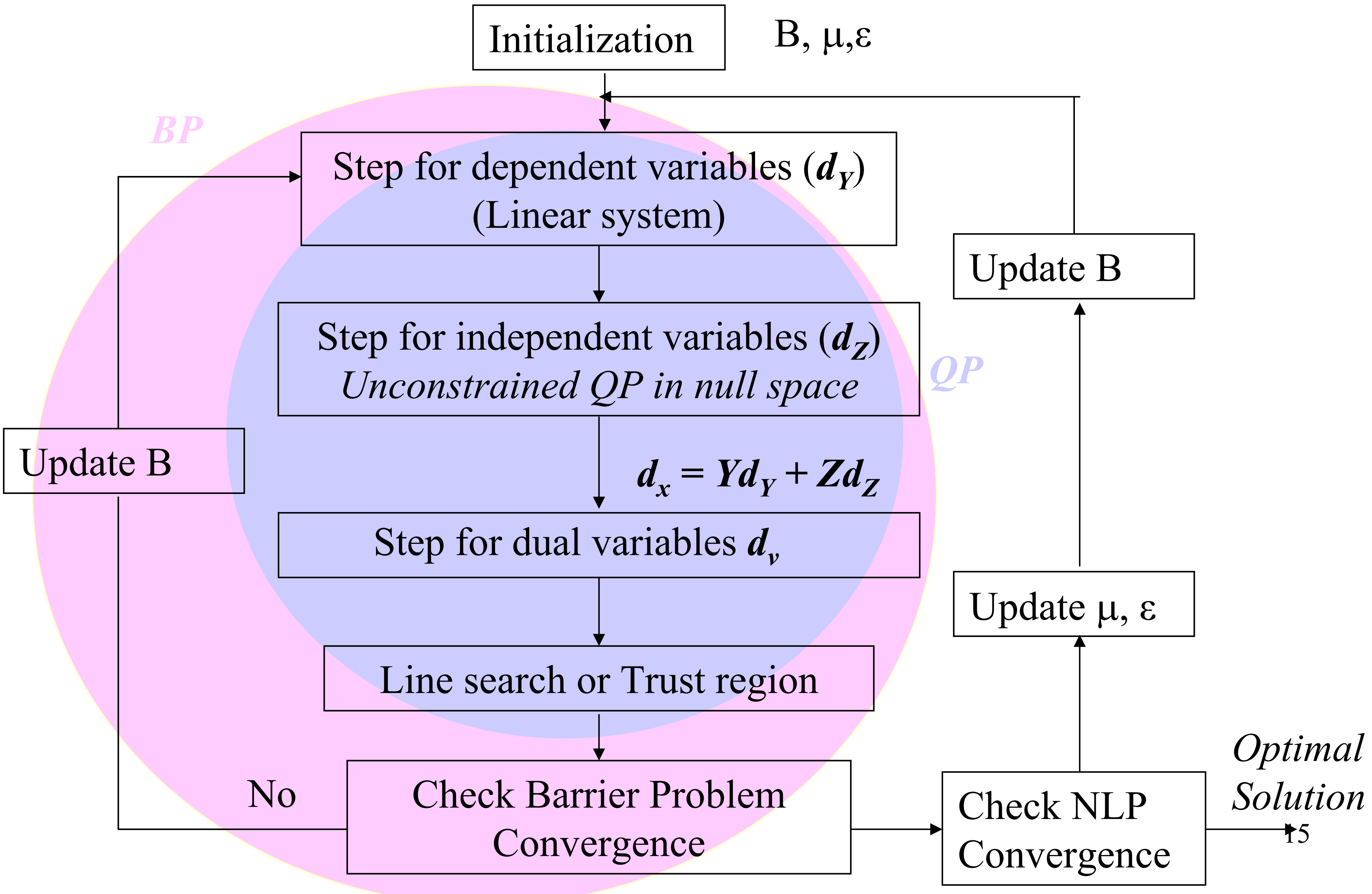
$$\min f(x) - \mu \sum_{j=1}^{n} \ln x_j$$

$$\text{s.t} \quad c(x) = 0$$

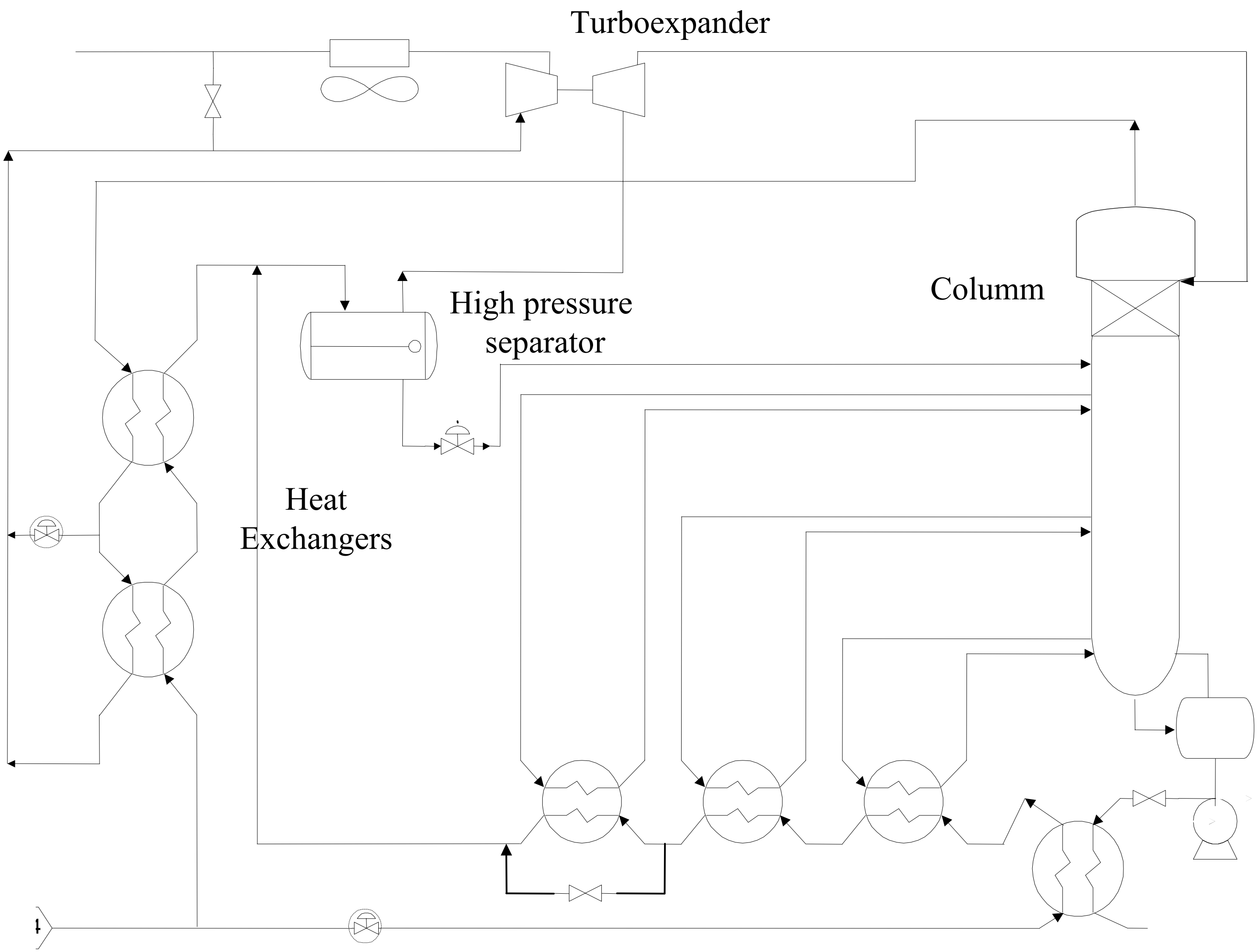
As $\mu \rightarrow 0$, $x^*(\mu) \rightarrow x^*$

Sequence of barrier problems for decreasing μ values

Barrier Method Algorithm: Primal-Dual Approach

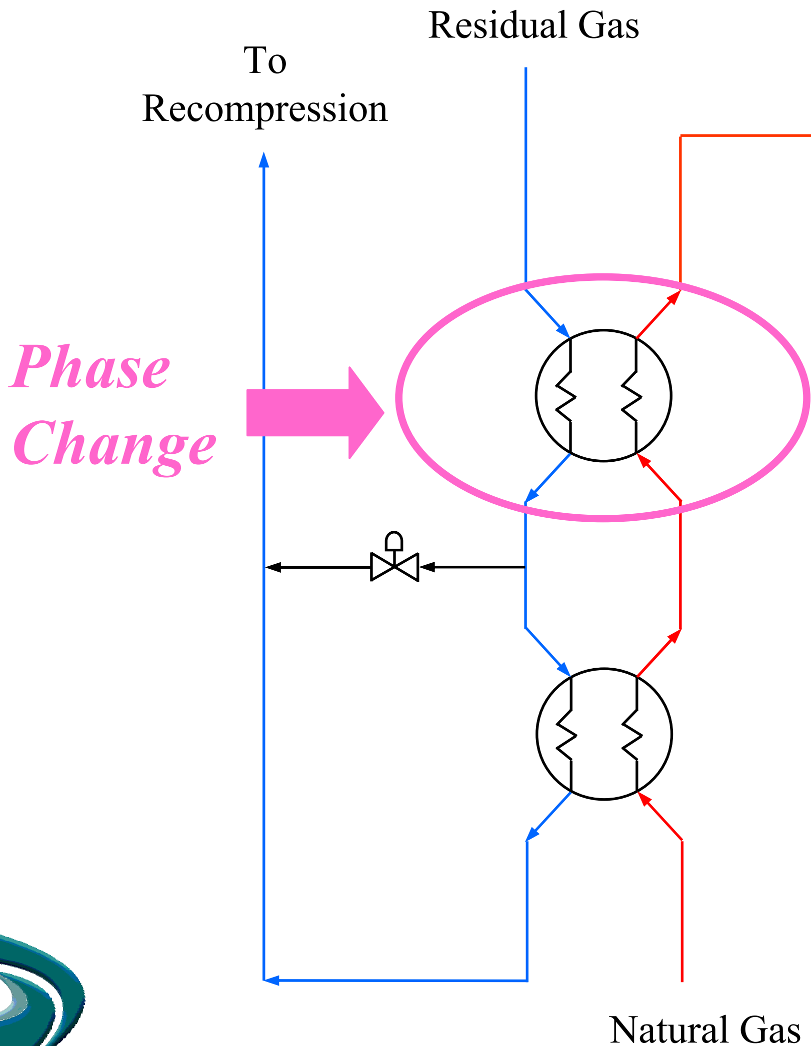


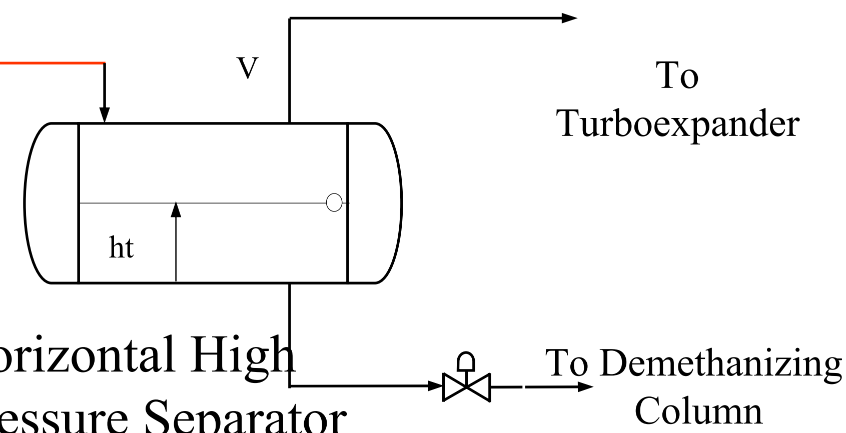
Cryogenic Sector



Cryogenic Heat Exchangers and HP Separator

Rodriguez, Bandoni, Diaz (2004)





Horizontal High Pressure Separator

Baffled shell-and-tube single-pass countercurrent heat exchangers

Tubes: residual gas

Shell: natural gas feed

Partial condensation: Second heat exchanger

HE Model (no Phase Change)

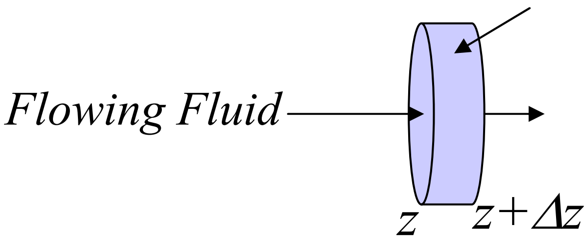
Energy Balances: Partial Differential Equations System

Tube side
$$\frac{\partial Tt(z,t)}{\partial t} + vt\frac{\partial Tt(z,t)}{\partial z} = \frac{h_t * A_{sup}}{\rho t * Cp_t * A_t * L}\left(Ts(z,t) - Tt(z,t)\right)$$

Shell side
$$\frac{\partial Ts(z,t)}{\partial t} - vs\frac{\partial Ts(z,t)}{\partial z} = \frac{h_s * A_{sup}}{\rho s * Cp_s * A_s * L}\left(Tt(z,t) - Ts(z,t)\right)$$

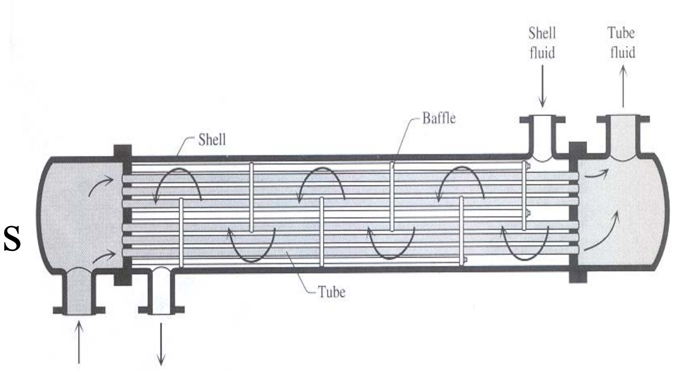
$$Tt(0,t) = Tto(t)$$
$$Ts(L,t) = Tso(t)$$
$$Tt(z,0) = Tt^*(z)$$
$$Ts(z,0) = Ts^*(z)$$

First-order hyperbolic PDE



Method of Lines

Spatial Discretization: Backward Finite Differences for Convection Term → ODE System

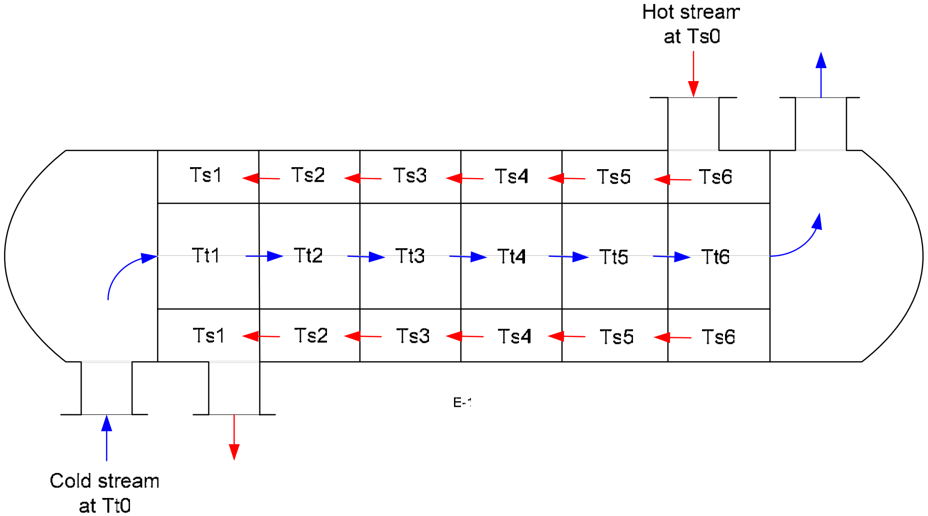


HE Model (no Phase Change)

Energy Balance at cell i

Tube side
$$\frac{dTt_i}{dt} = -\frac{vt_i}{\Delta z}(Tt_i - Tt_{i-1}) + \frac{h_t * A_{sup}}{\rho t_i * Cp_t * A_t * L}(Ts_i - Tt_i)$$

Shell side
$$\frac{dTs_i}{dt} = \frac{vs_i}{\Delta z}(Ts_i - Ts_{i-1}) + \frac{h_s * A_{sup}}{\rho s_i * Cp_s * A_s * L}(Tt_i - Ts_i)$$



Multicell model

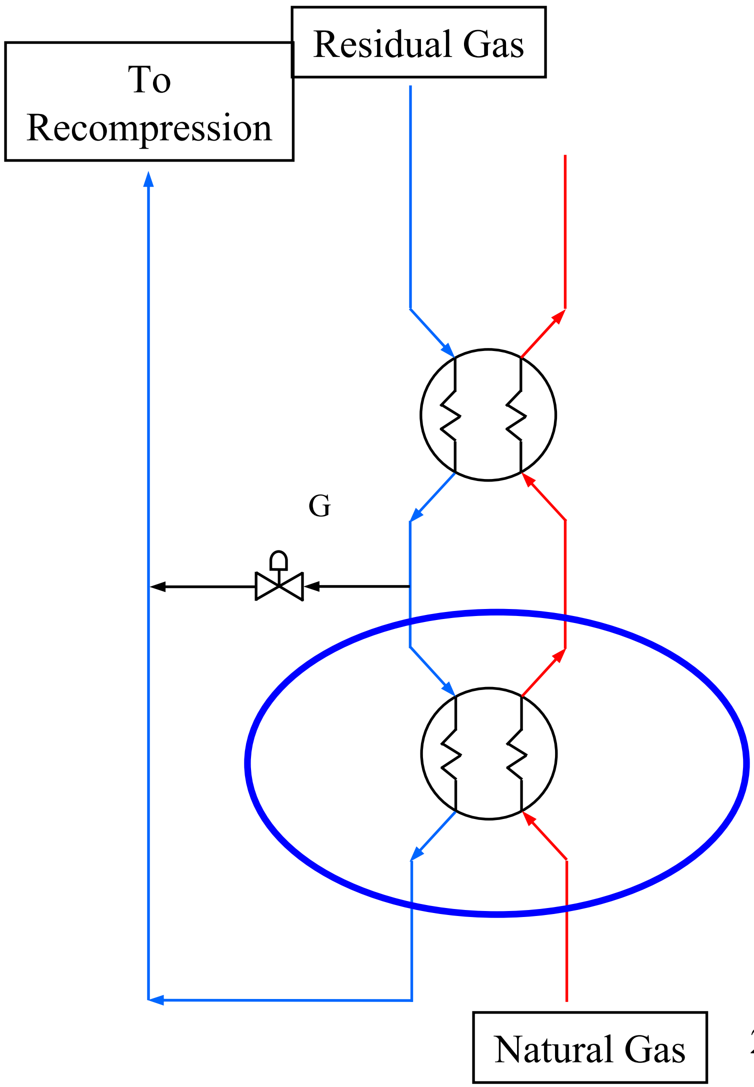
Algebraic Equations (no Phase Change)

$$\rho_{j,i} = \frac{M * P}{z_{j,i} * R * T_{j,i}}$$

$$v_{j,i} = \frac{F_j}{\rho_{j,i} * A_j}$$

i = 1, …, N (cells)
j = tube or shell side

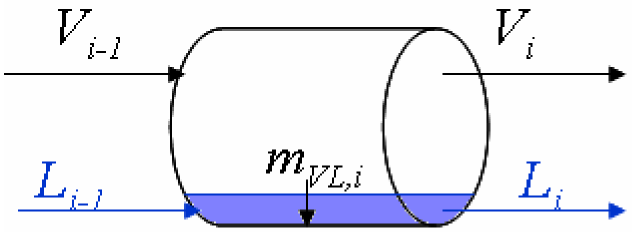
HE model ➡ ***DAE System***



HE Model (Partial Phase Change on Shell Side)

Rodriguez, Bandoni, Diaz (2005)

Mass Balance at cell i



Vapor Phase $$\frac{dM_{V,i}}{dt} = V_{i-1} - V_i - m_{VL,i}$$

Liquid Phase $$\frac{dM_{L,i}}{dt} = L_{i-1} - L_i + m_{VL,i}$$

$m_{VL,i}$: interfacial mass-transport rate from vapor to liquid phase

Component $$\frac{dm_{ij}}{dt} = V_{i-1}y_{i-1,j} + L_{i-1}x_{i-1,j} - V_i y_{i,j} - L_i x_{i,j}$$

Energy Balance at cell i

$$\frac{dE_i}{dt} = L_{i-1} {*} h_{i-1} + V_{i-1} {*} H_{i-1} - L_i {*} h_i - V_i {*} H_i + Q_i^t$$

HE Model (Partial Phase Change on Shell Side)

Momentum Balance at cell i

Vapor Phase $$\frac{d(M_{V,i}v_{V,i})}{dt} = V_{i-1}v_{V,i-1} - V_i v_{V,i} + F_{P,i} - F_{inter,i} - m_{VL,i}v_{L,i}$$

Liquid Phase $$\frac{d(M_{L,i}v_{L,i})}{dt} = L_{i-1}v_{L,i-1} - L_i v_{L,i} + F_{P,i} + F_{inter,i} + m_{VL,i}v_{L,i} - F_{w,i}$$

Algebraic Equations at cell i

$$\theta_i = \frac{A_{V,i}}{A_T}$$ Void fraction based on cross-section area

$$M_{V,i} = A_T Le_i \theta_i \rho_{V,i} \qquad v_{V,i} = \frac{V_i}{A_{V,i}\rho_{V,i}}$$

$$M_{L,i} = A_T Le_i (1-\theta_i)\rho_{L,i} \qquad v_{L,i} = \frac{L_i}{(1-A_{V,i})\rho_{L,i}}$$

HE Model (Partial Phase Change on Shell Side)

Driving Force

$$F_{P,i} = \left(Ps_{i-1}\theta_{i-1} - Ps_i\theta_i\right)A_T$$

Interfacial shear stress

$$F_{inter,i} = \frac{4\sqrt{\theta_i}}{D} f_{f,i} \frac{\rho_{L,i}}{2}\left(v_{V,i} - v_{L,i}\right)^2$$

Interfacial friction factor

$$f_{f,i} = f_v\left[1 + 24\left(\frac{\rho_{L,i}}{\rho_{V,i}}\right)^{1/3}\frac{\delta}{D}\right]$$

Friction resistance on wall surface

$$F_{w,i} = \frac{4}{D}\tau_w$$

$$f_v = \begin{cases} 0.079\,Re^{-0.25}, 4000 \le Re \le 30000 \\ 0.046\,Re^{-0.20}, Re > 30000 \end{cases}$$

HE Model (Partial Phase Change on Shell Side)

Internal Energy $$E_i = M_{V,i} H_i + M_{L,i} h_i$$

Summation Eqns $$\sum_j y_{i,j} - \sum_j x_{i,j} = 0$$

Equilibrium ratio $$K_{i,j} = \frac{\phi_{i,j}^L}{\phi_{i,j}^V} \qquad y_{i,j} = K_{i,j} x_{i,j}$$

$$h_i = h_i^{ideal} - \Delta h_i, \qquad h_i^{ideal} = \sum_{j=1}^{nc} h_{i,j}^{ideal}(T_i) x_{i,j}$$

$$H_i = H_i^{ideal} - \Delta H_i, \qquad H_i^{ideal} = \sum_{j=1}^{nc} H_{i,j}^{ideal}(T_i) y_{i,j}$$

HE Model (Partial Phase Change on Shell Side)

$$
\left.
\begin{array}{l}
\text{Compressibility factor} \\
z_i^V = z^V(Ts_i, Ps_i, y_{i,j}) \\
z_i^L = z^L(Ts_i, Ps_i, x_{i,j}) \\
\text{Residual enthalpies} \\
\Delta H_i = \Delta H(Ts_i, Ps_i, y_{i,j}) \\
\Delta h_i = \Delta h(Ts_i, Ps_i, x_{i,j}) \\
\text{Fugacity coefficients} \\
\phi_{i,j}^V = \phi^V(Ts_i, Ps_i, y_{i,j}) \\
\phi_{i,j}^L = \phi^L(Ts_i, Ps_i, x_{i,j})
\end{array}
\right\}
\quad \textbf{\textit{Soave-Redlich-Kwong EoS}}
$$

$$Ps_i = \frac{\rho_{L,i} * z_i^L * R * Ts_i}{Pmols_i^L} \qquad Ps_i = \frac{\rho_{V,i} * z_i^V * R * Ts_i}{Pmols_i^V}$$

High Pressure Separator

$$\frac{dM}{dt} = Lp + Vp - L - V$$

Horizontal tank

$$Vol_V = \pi r^2 Long - \frac{M_L}{\rho_L}$$

$$L = C_v x \sqrt{\frac{(P_t - P_s) + g\ \rho_L (h_t + r)}{\rho_L / \rho_w}}$$

$$M_V = \rho_V Vol_V \qquad M = M_V + M_L$$

$$M_L = \frac{\rho_L Long}{Pmol_L}\left(\pi r^2 - r^2 \arccos\left(\frac{h_t}{r}\right) + h_t \sqrt{r^2 - h_t^{\,2}}\right)$$

Turboexpander

- Feed: vapor from High Pressure Separator
- Polytropic expansion (η = 1.26, natural gas)

$$\frac{T_s}{T_e} = \left(\frac{P_s}{P_e}\right)^{\frac{\eta-1}{\eta}}$$

- Assumption: Static mass and energy balances
- Thermodynamic predictions: Soave-Redlich-Kwong
- Algebraic equations: Same as Flash
- Outlet partially condensed stream: to Demethanizing column

Demethanizing Column

Diaz, Tonelli, Bandoni, Biegler (2003)

Differential Equations at stage i (1 ≤ i ≤ N)

$$\frac{dM_i}{dt} = F_i + V_{i+1} + L_{i-1} - V_i - L_i$$

$$\frac{dm_{ij}}{dt} = F_i z_{i,j} + V_{i+1} y_{i+1,j} + L_{i-1} x_{i-1,j} - V_i y_{i,j} - L_i x_{i,j} \qquad j=1,\ldots,ncomp$$

$$\frac{dE_i}{dt} = V_{i+1} H_{i+1} + L_{i-1} h_{i-1} - V_i H_i - L_i h_i - F_i \left[\varphi_i H_{Fi} + (1-\varphi_i) h_{Fi} \right] + Qsr_i$$

$$N = 8; \;\; ncomp = 10$$

Algebraic Equations

Compressibility factor (z_i^V , z_i^L)

Residual enthalpies (ΔH_i, Δh_i)

Fugacity coefficients ($\phi_{i,j}^V$, $\phi_{i,j}^L$)

$\Bigg\}$ ***SRK***

$$K_{i,j} = \frac{\phi_{i,j}^L}{\phi_{i,j}^V} \qquad y_{i,j} = K_{i,j} x_{i,j}$$

$$\sum_j y_{i,j} - \sum_j x_{i,j} = 0$$

$$H_i = H_i^{ideal} - \Delta H_i$$

$$h_i = h_i^{ideal} - \Delta h_i$$

Algebraic Equations

Vapor volume

$$Vol_i^V = \pi \left(\frac{D_i}{2} \right)^2 H_{plate,i} - \frac{M_i^L}{\rho_i^L}$$

Vapor and liquid holdup

$$M_i^V = \rho_i^V Vol_i^V$$

$$M_i = M_i^V + M_i^L$$

Component holdup

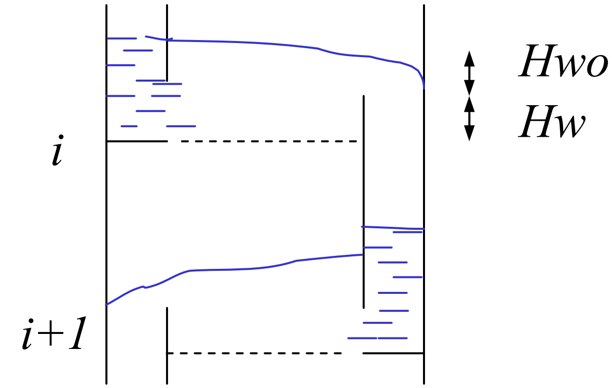
$$m_{i,j} = M_i^V y_{i,j} + M_i^L x_{i,j}$$

Internal energy holdup

$$E_i = M_i^V (H_i - \frac{p_i}{\rho_i^V}) + M_i^L (h_i - \frac{p_i}{\rho_i^L})$$

Demethanizing Column

Liquid holdup and hydraulic correlations



$$M_i^L = 0.896\pi\left(\frac{D_i}{2}\right)^2 (Hw_i + Hwo_i)\rho_i^L$$

$$Hwo_i = 30(0.01495)^{2/3} Fw_i \left(\frac{L_i}{\rho_i^L Weirl_i}\right)^{2/3}$$

Equivalent height of vapor free liquid

$$Hldrop_i = \beta(Hw_i + Hwo_i)$$

Pressure drop through aerated liquid

$$Ho_i = 5.56.10^{-4}\left(\frac{V_i}{\rho_i^V Ahole_i Co_i}\right)^2 \left(\frac{\rho_i^V Pmol_i^V}{\rho_i^L Pmol_i^L}\right)$$

Dry hole pressure drop

Pressure drop

$$P_1 = P_{TOP} - KK\rho_1^V V_1^2$$

$$P_i = P_{i-1} + 0.24917.10^{-5}(Ho_i + Hldrop_i)\rho_i^L Pmol_i^L$$

Demethanizing Column

Carbon dioxide solubility constraints

Phase Equilibrium $\mu^{V}_{i,CO2} = \mu^{L}_{i,CO2} = \mu^{S}_{i,CO2}$

$$\overline{f^{V}_{i,CO2}} = \overline{f^{L}_{i,CO2}} = \overline{f^{S}_{i,CO2}}$$

Assumption

No hydrocarbon in solid phase $\overline{f^{S}_{i,CO2}} = f^{S}_{i,CO2}$

To avoid CO_2 precipitation $\overline{f^{V}_{i,CO2}} \leq f^{S}_{i,CO2}$

$$\overline{f^{L}_{i,CO2}} \leq f^{S}_{i,CO2}$$

But $\overline{f^{L}_{i,CO2}} = \overline{f^{V}_{i,CO2}}$ from VLE calculations at each stage

Carbon dioxide solubility constraints

$$\overline{f_{i,CO2}^{V}} \leq f_{i,CO2}^{S}$$

Solid phase

$$f_{i,CO2}^{S} = P_{i,CO2}^{S}\phi_{i,CO2}^{V}$$

$$ln\left(\frac{P_{i,CO2}^{S}}{P_{CO2}^{t}}\right) = 14.568\left(1-\frac{T_{CO2}^{t}}{T_i}\right) - 14.480\,ln\left(\frac{T_i}{T_{CO2}^{t}}\right) + 65.356\left(\frac{T_i}{T_{CO2}^{t}}-1\right)$$
$$-47.146\left[\left(\frac{T_i}{T_{CO2}^{t}}\right)^{2}-1\right] + 14.540\left[\left(\frac{T_i}{T_{CO2}^{t}}\right)^{3}-1\right]$$

Vapor phase

$$\overline{f_{i,CO2}^{V}} = y_{i,CO2}P_i\overline{\phi_{i,CO2}^{V}}$$

Demethanizing Column: Phase Existence

Raghunathan, Diaz, Biegler (2004)

Gibbs Free Energy minimization at stage i

⬇

Karush Kuhn Tucker conditions

⬇ Raghunathan, Biegler (2003)

MPECs (Mathematical Program with Equilibrium Constraints)

as additional constraints ($x.y = 0$; $x,y \geq 0$)

⬇

IPOPT-C under AMPL

($x.y \leq \delta\mu$)

Demethanizing Column: Phase Existence

Relaxed Equilibrium Conditions

$$y_{i,j} = \gamma_i K_{i,j}(T_i, P_i, x_{i,j}, y_{i,j})x_{i,j}$$

$$\sum_j y_{i,j} - \sum_j x_{i,j} = 0$$

$$\gamma_i - 1 = s_i^V - s_i^L$$

$$\left.\begin{array}{l} 0 \le M_i^L \perp s_i^L \ge 0 \\ 0 \le M_i^V \perp s_i^V \ge 0 \end{array}\right\} \text{Complementarity Constraints}$$

$$\Rightarrow$$

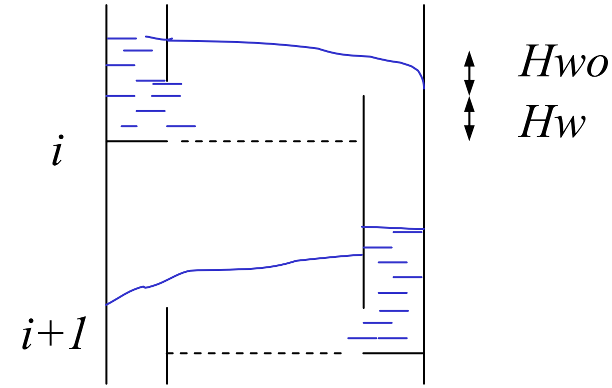
$$\gamma = 1 \Rightarrow M_i^L > 0, M_i^V > 0$$

$$\gamma < 1 \Rightarrow M_i^L = 0, M_i^V > 0$$

$$\gamma > 1 \Rightarrow M_i^L > 0, M_i^V = 0,$$

Demethanizing Column: Phase Existence

Liquid Holdup and Hydraulic correlations



$$M_i^L = 0.896\pi\left(\frac{D_i}{2}\right)^2 Hw_i\rho_i^L + M_i^{L+} - M_i^{L-}$$

$$M_i^{L+} = 0.896\pi\left(\frac{D_i}{2}\right)^2 Hwo_i\rho_i^L$$

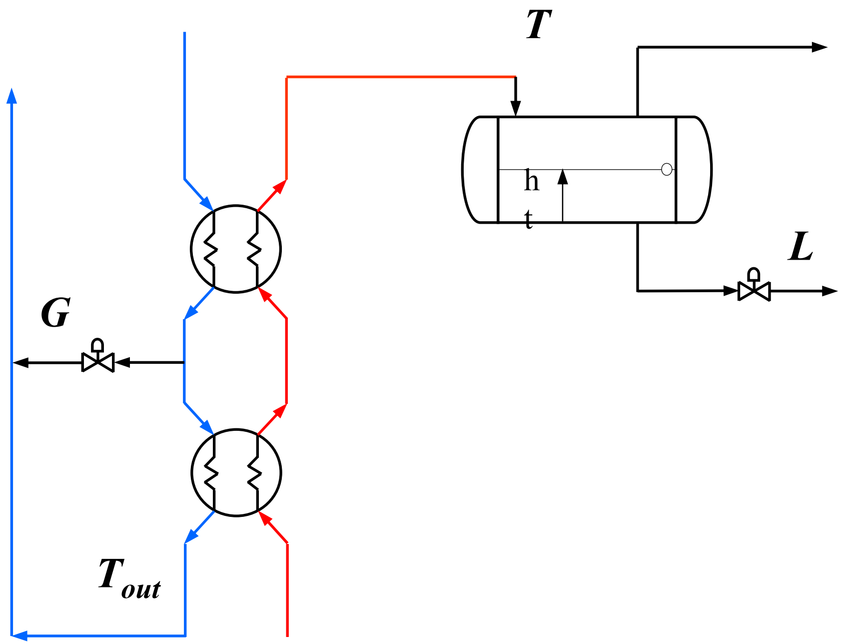
$$Hwo_i = 30(0.01495)^{2/3} Fw_i\left(\frac{L_i}{\rho_i^L Weirl_i}\right)^{2/3}$$

$$\left(L_i = k_d(M_i^{L+})^{\frac{3}{2}}\right)$$

$$0 \le M_i^{L+} \perp M_i^{L-} \ge 0$$

Numerical Results

Optimization Problem: HEs + HPS



$$\min \int_0^{tf} \left(T - T_{SP}\right)^2 dt$$

$$st.$$

$$\{DAE\ System\}$$

$$60 \le L \le 80 (kmol / min)$$

$$5 \le G \le 80 (kmol / min)$$

$$303 \le T_{out} \le 306 (K)$$

(8+6 cells in HEs)

Numerical Results: HEs + HPS

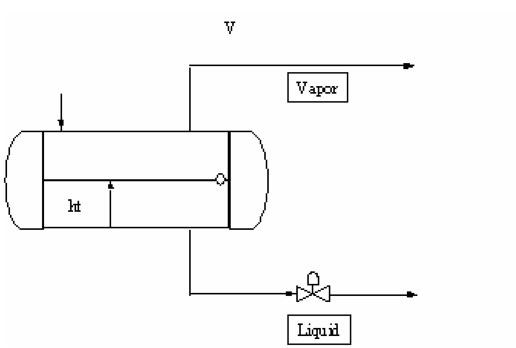
Optimization variables: G, L

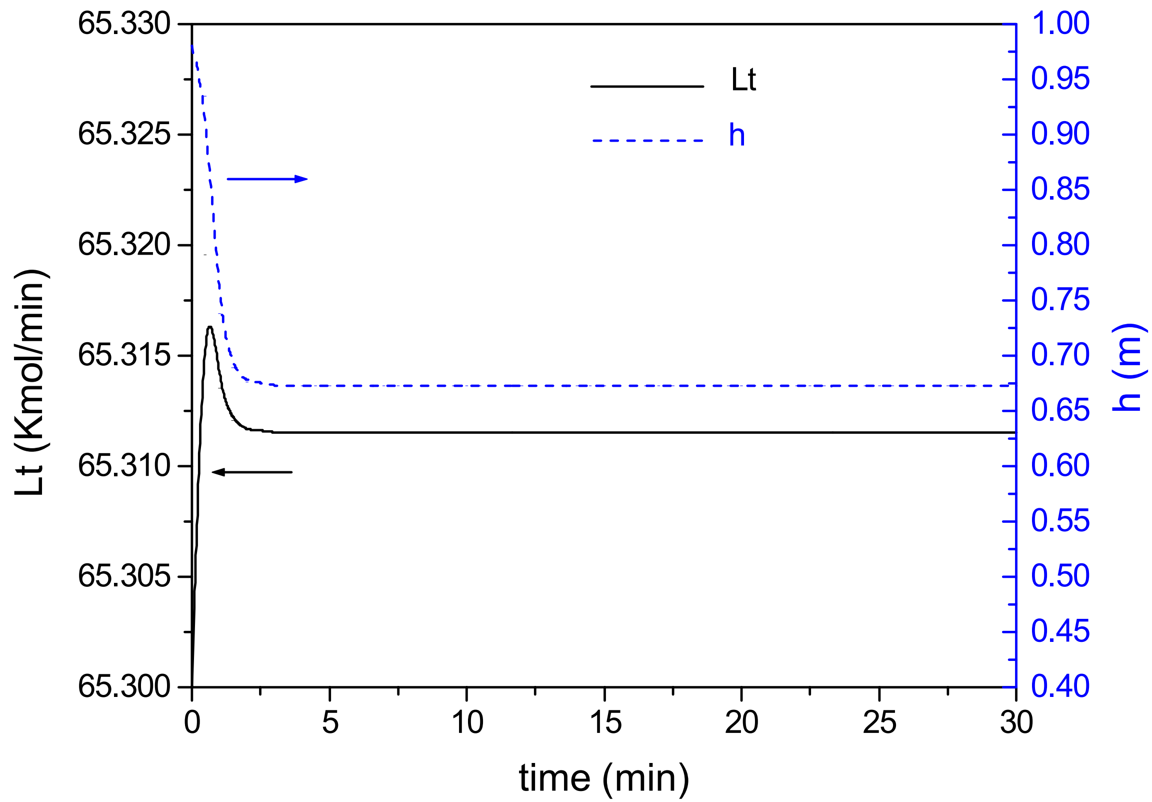
20 elements

2 collocation points

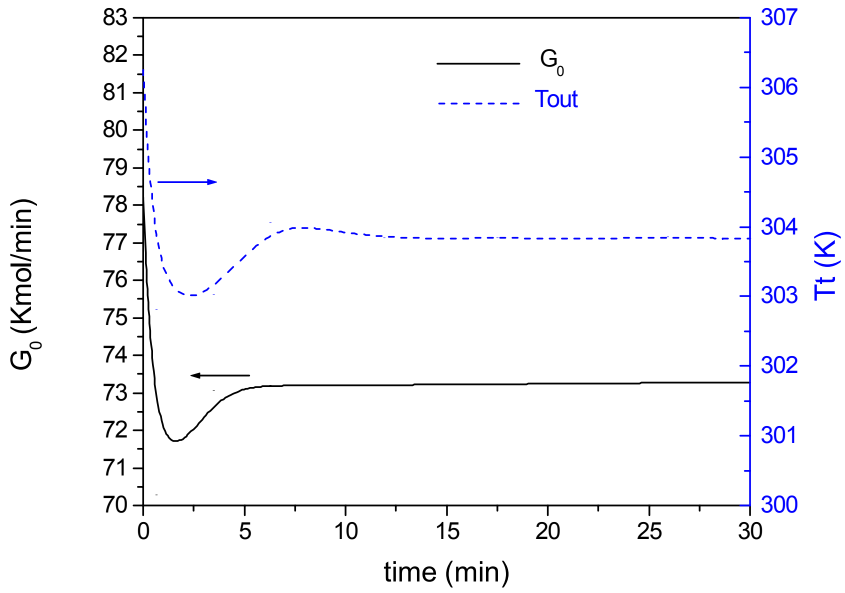
18274 disc. variables

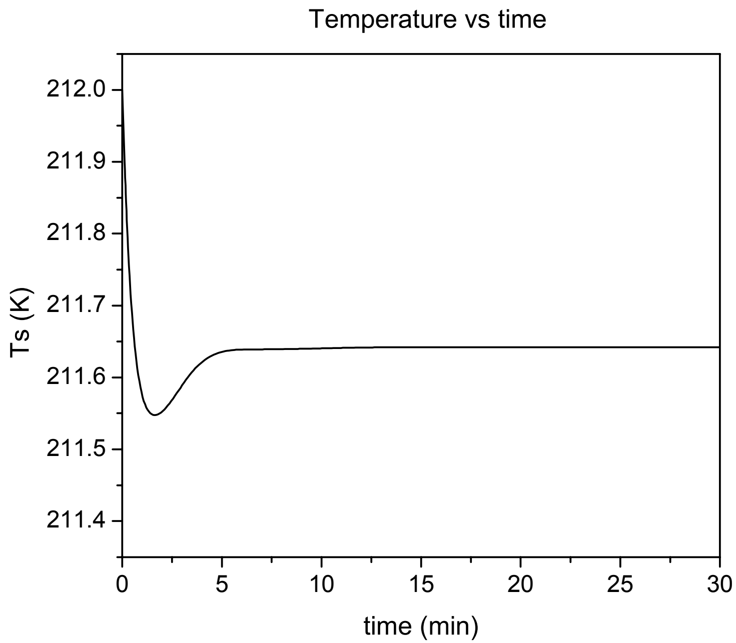
18 iter. (3 barrier problems)



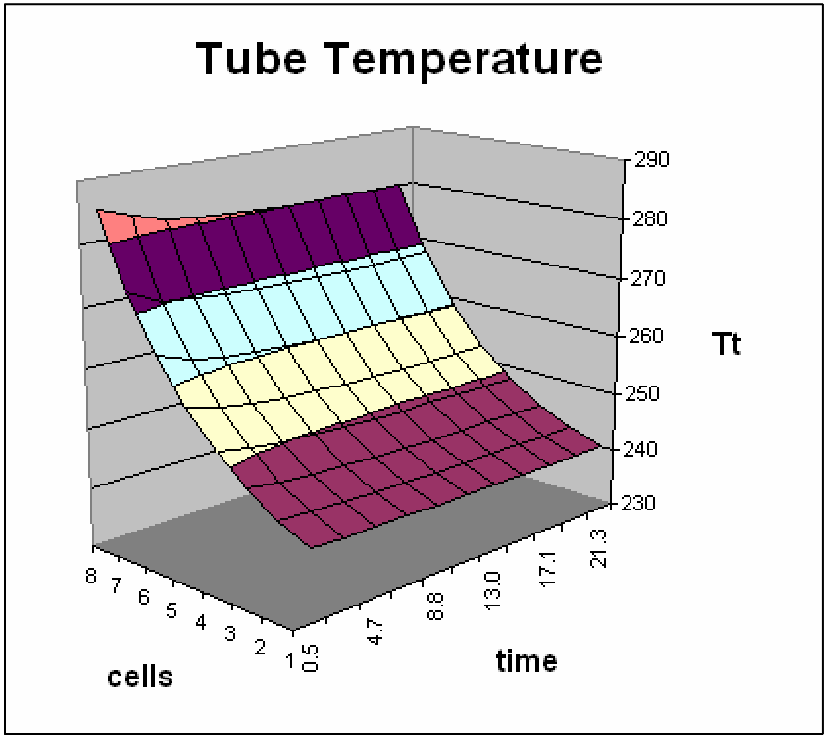


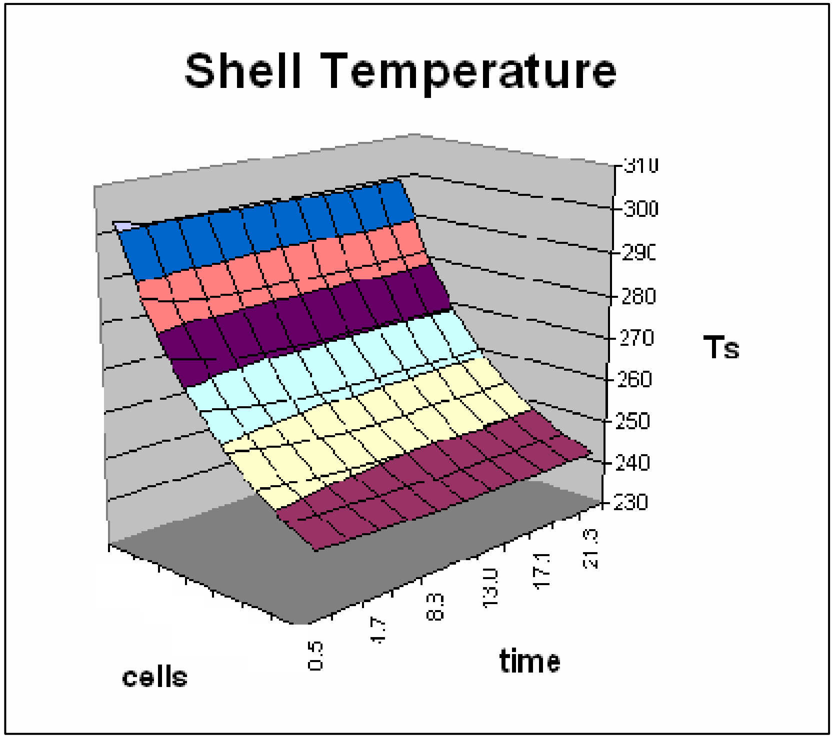
Optimization variables: G, L





Numerical Results: HEs + HPS

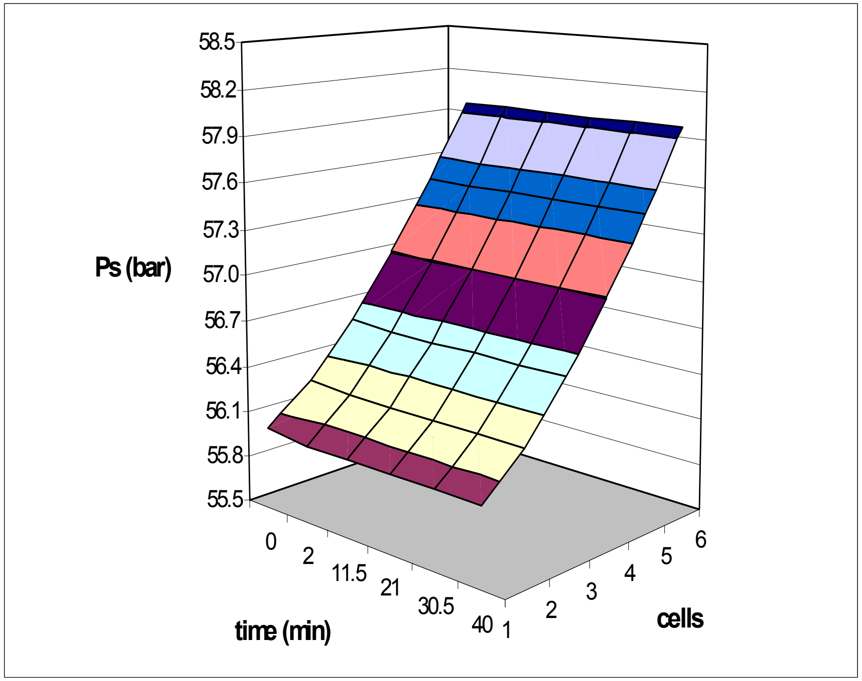




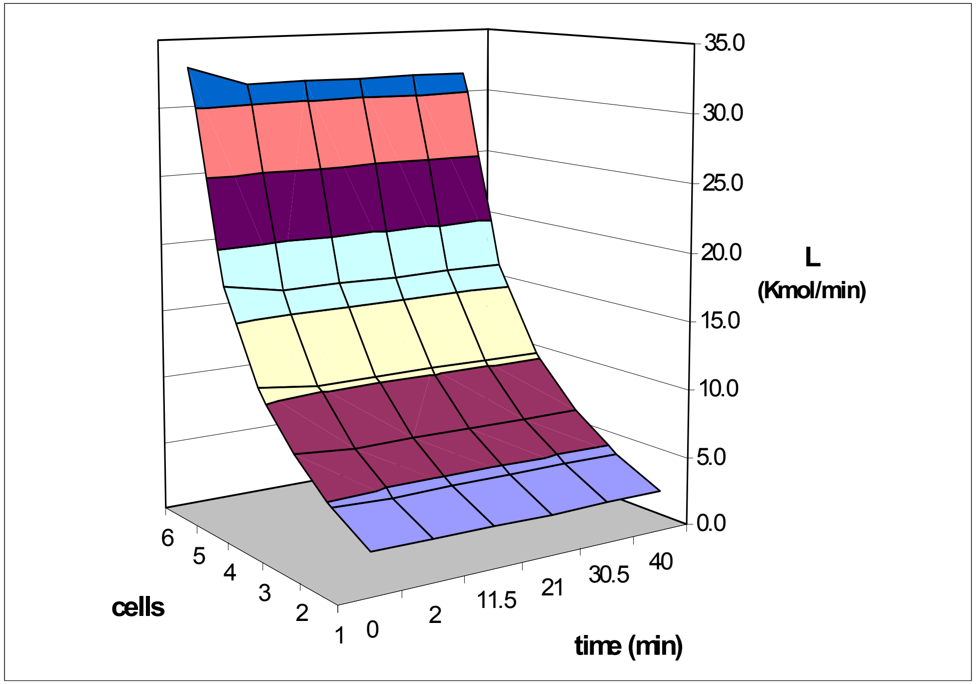
Temp. profile, tubes side

Temp. profile, shell side (no phase change)

Numerical Results: HEs + HPS



Pressure profile, shell side



Liquid flowrate, shell side

Optimization Problem: Demethanizing Column

$$min \int_0^{tf} \left(\eta_{ethane} - \eta_{SP}\right)^2 dt$$

$$st.$$

$$\{DAE\ System\}$$

$$15 \le P_{TOP} \le 22(bar)$$

$$99 \le Q_{REB} \le 200(kJ/min)$$

$$0 \le x_{B,CH4} \le 0.008$$

$$\overline{f_{i,CO2}^{V}} \le 0.90 f_{i,CO2}^{S}$$

Alg. Eqns = 385
Differ. Eqns = 97

Numerical Results: Demethanizer

Feed A: Low CO_2 content (0.65%)

Optimization variable: P_{TOP}

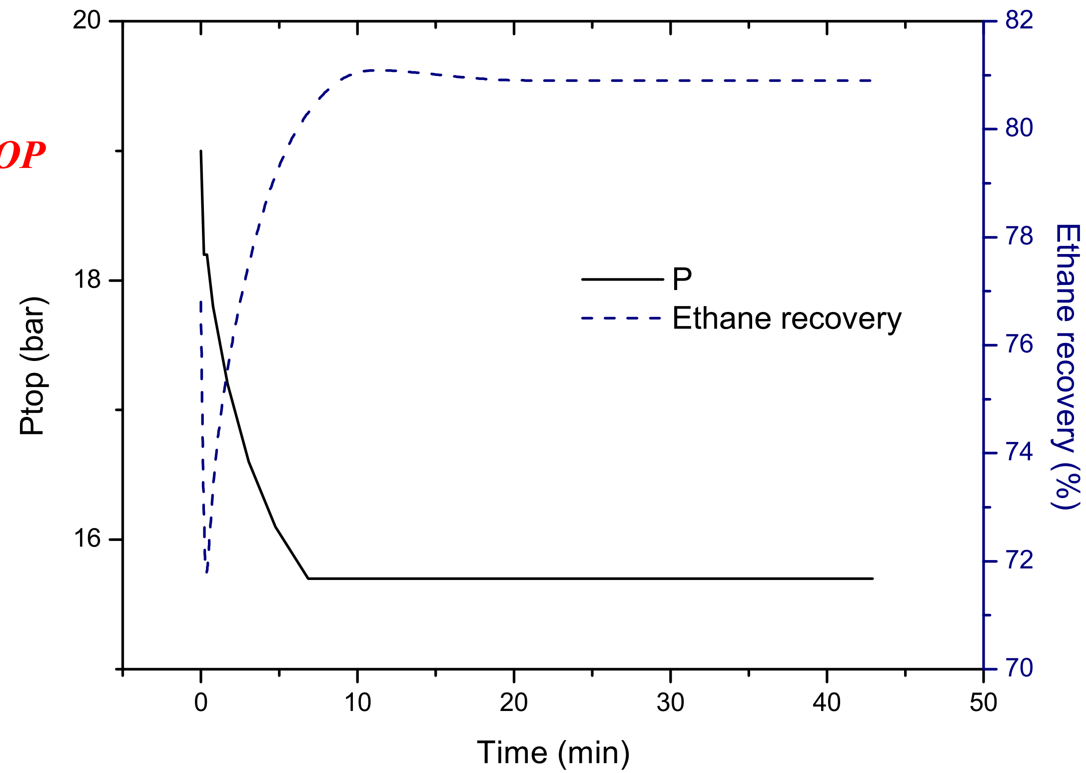
20 finite elements

2 collocation points

21357 discretized variables

40 iter. (3 barrier problems)

ηss = 80.9 %



Numerical Results: Demethanizer

Feed B: High CO_2 content (2%)

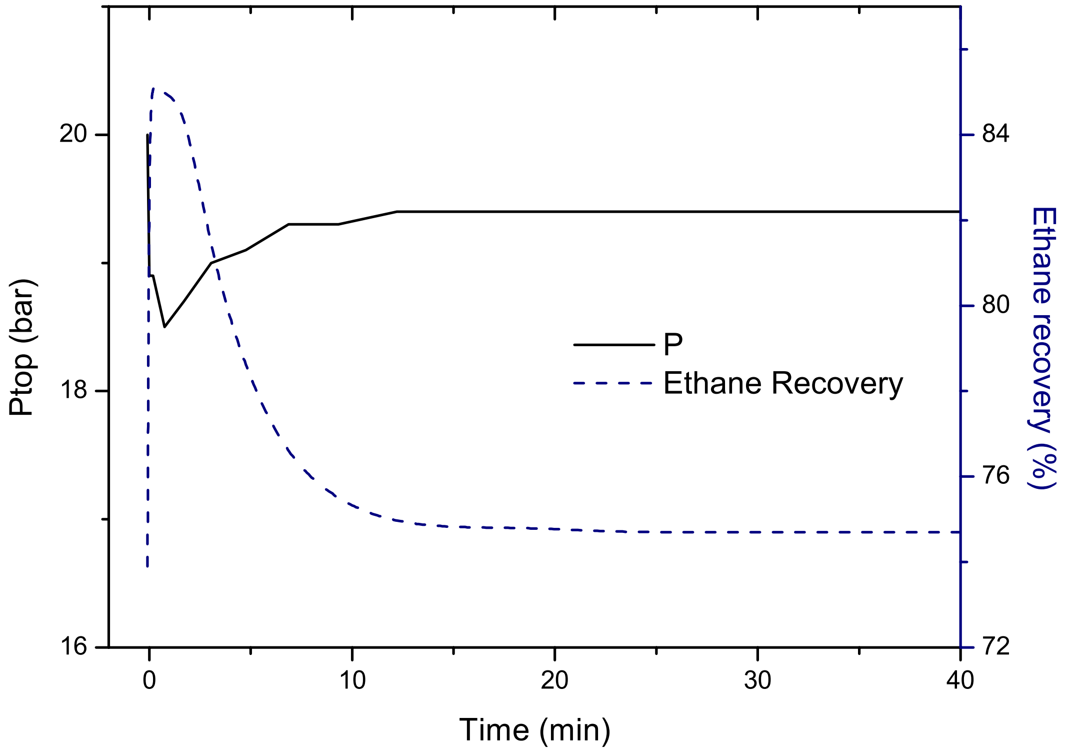
Optimization variable: P_{TOP}

20 finite elements

2 collocation points

43 iter. (3 barrier problems)

ηss = 74.5 %

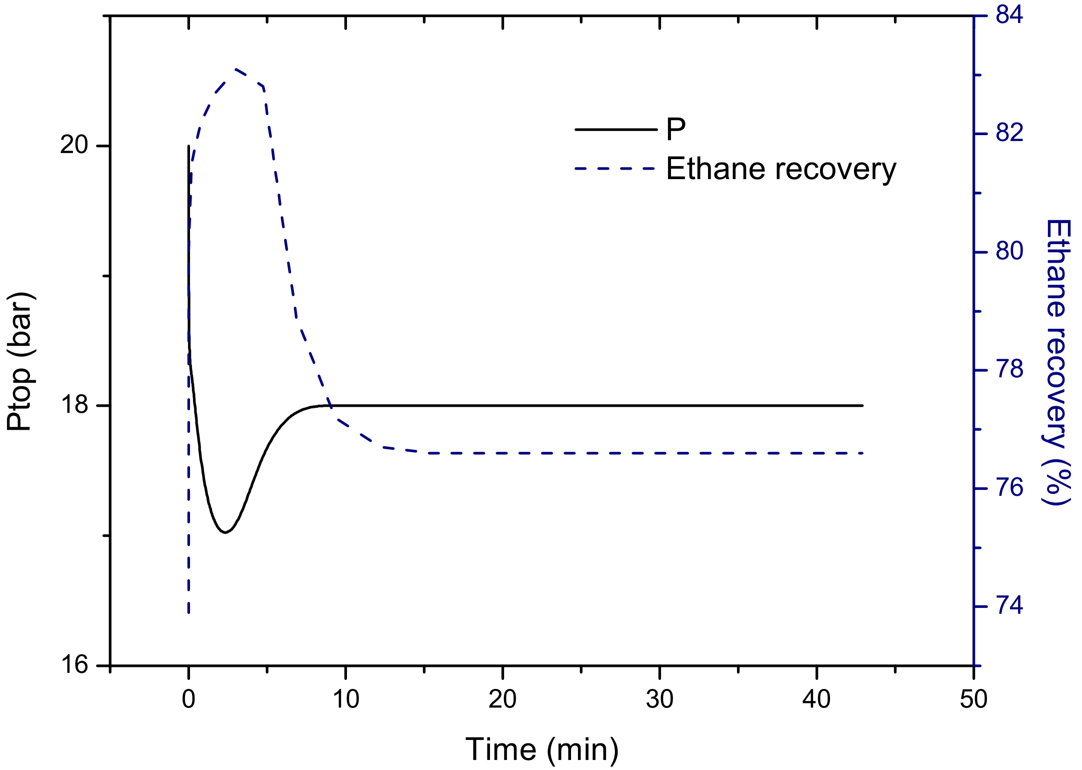


Numerical Results: Demethanizer

Feed B (high CO_2 content)

No solubility constraints

Optimization variable: P_{TOP}



20 finite elements

2 collocation points

59 iter. (4 barrier problems)

$\eta_{ss} = 76.6\ \%$

Numerical Results: Demethanizer

Feed A

Optimization variable:

Reboiler Heat Duty (Q_R)

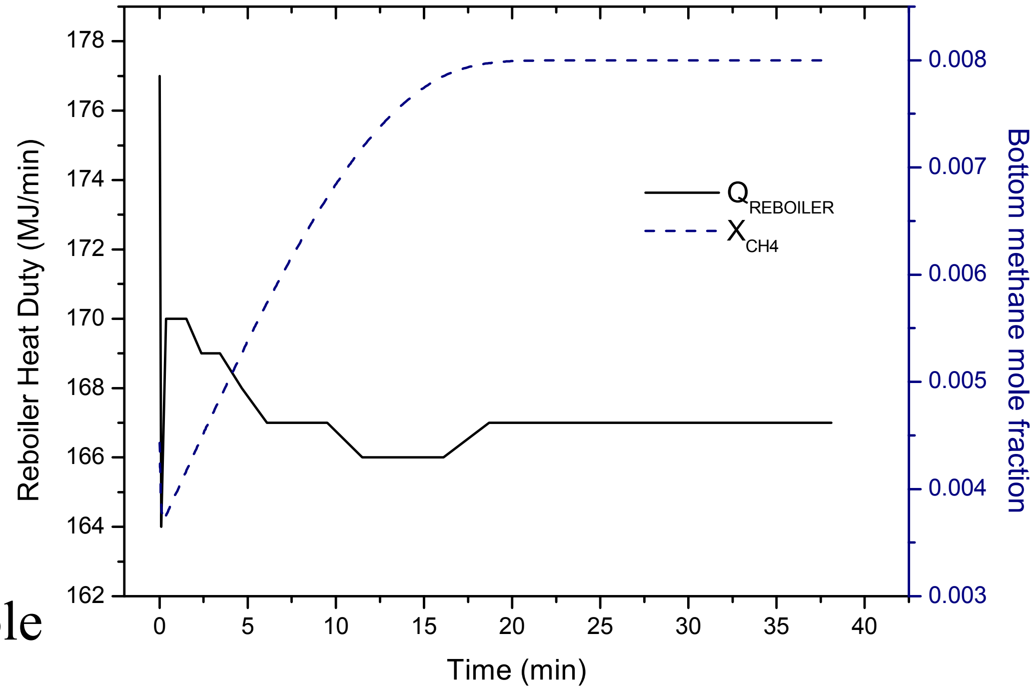
20 finite elements

2 collocation points

57 iter. (5 barrier problems)

η_{ss} = 77.8 % (P_{TOP}=19bar)

Active constraint: Methane mole fraction in bottoms



Numerical Results: Demethanizer Start Up

MPECs

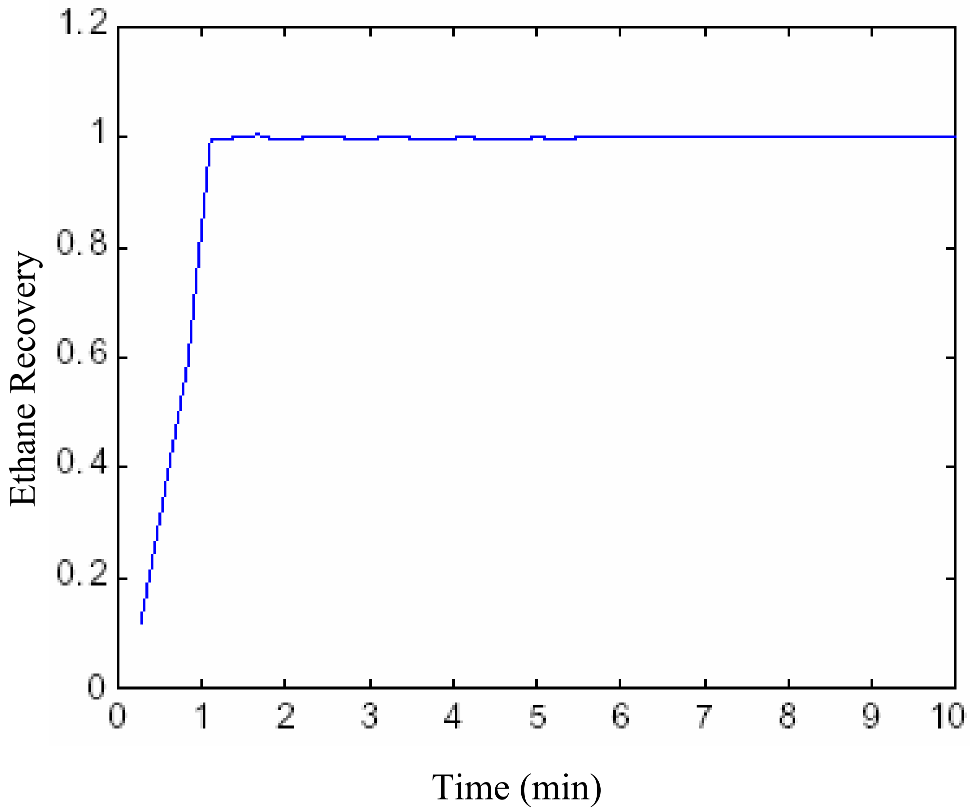
Optimization variable:

P_{TOP}, Q_R

Three time periods

Ideal Gas, Ideal solution

Solved in AMPL with IPOPT-C (Raghunathan, Biegler, 2003)



Numerical Results: Demethanizer Start Up

MPECs

Optimization variable:

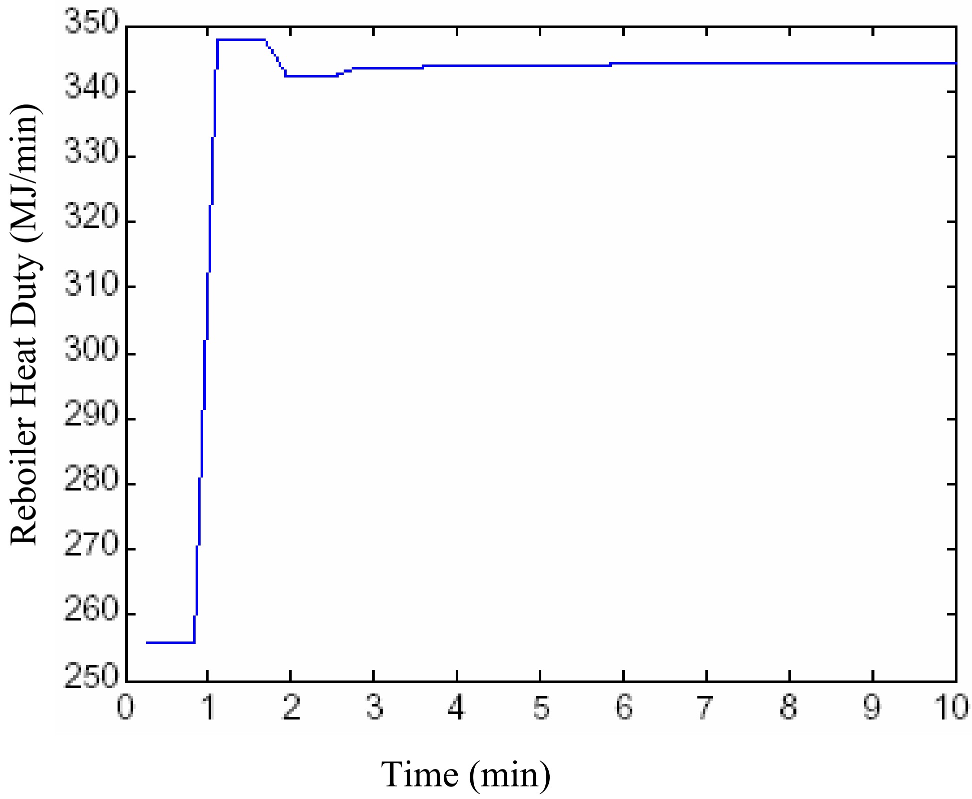
P_{TOP}, Q_R

3rd time period

17944 discretized variables

576 complementarity constraints

97 iterations



Boiler Dynamic Optimization

Rodriguez, Bandoni, Diaz (2005b)

Dynamic optimization model to determine controller parameters

Boiler

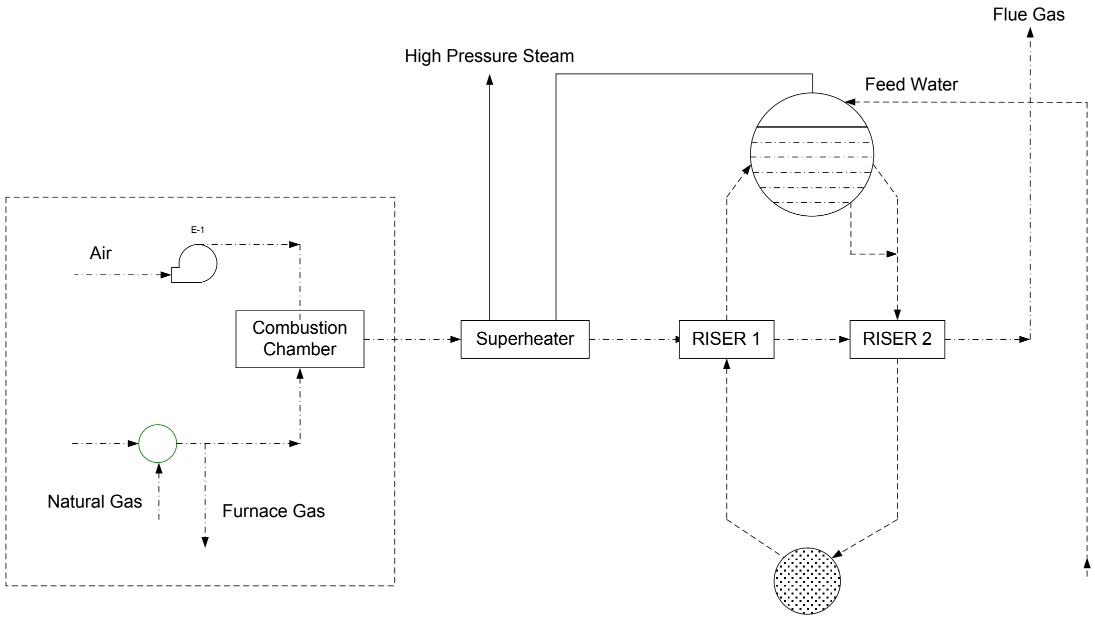
Combustion chamber

Risers

Superheater

Steam drum

Gas path



PI Controller

(Liquid level in drum)

Manipulated: Feed water flowrate

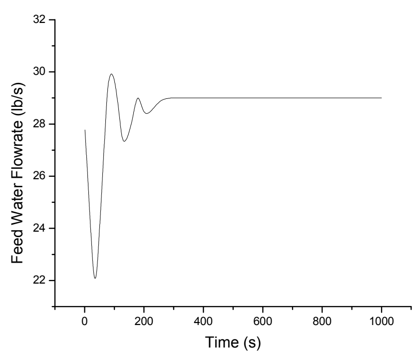
DAE Optimization model

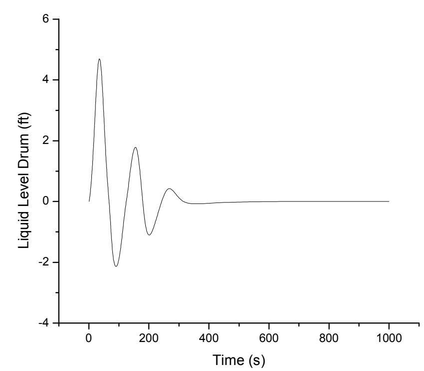
- Differential equations
  - Momentum and energy balances in risers and superheater
  - Mass and energy balances in drum
  - Integral part of controller and valve equation
- Algebraic equations
  - Friction loss
  - Mixture properties
  - Vapor holdup in drum
  - Gas – temperature distribution equations in furnace, risers ans superheaters (6 eqns.)
  - Air / fuel ratio
  - Drum geometric relations (5 eqns.)
  - Steam tables correlations for saturated and high pressure steam density, pressure and enthalpy

DAE Optimization model

- Optimization variables
  - PI controller parameters

- Step change in high pressure steam demand





- Additional PI controllers (current work)
  - Outlet steam pressure (fuel gas flowrate)
  - Superheated steam temperature (air excess)

Conclusions

- Rigorous dynamic optimization models for cryogenic train in Natural Gas Processing plant within a simultaneous approach
- Thermodynamic models with cubic equation of state
- Carbon dioxide solubility addressed in both liquid and vapor phases as path constraints, at each column stage
- Phase detection through the first order optimality conditions for Gibbs free energy minimization (MPECs)
- Boiler dynamic model for controller parameters
- Simultaneous approach provides efficient framework for the formulation and resolution of DAE optimization problems for large-scale real plants

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Appendix: Soave Redlich Kwong Equation of State

Compressibility factor for a mixture (z_i^L, z_i^V)

$$z = \frac{V}{V-b} - \frac{a\alpha}{R_g T(V+b)}$$

$$a\alpha = \sum x_j^* z_j^*; x_j^* = x_j a_j \alpha_j; z_j = \sum_k x_k^* (1 - k_{j,k})$$

$$b = \sum_j b_j; b_j = 0.08664 R_g T_{cj} / P_{cj}$$

$$a_j = \left(\frac{0.42747 R_g^2 T_{cj}^2}{P_{cj}} \right)^{0.5}; \alpha_j = 1 + m_j \left[1 - \left(\frac{T}{T_{cj}} \right)^{0.5} \right]$$

Soave modification (Temperature dependence)

$$m_j = 0.48 + 1.574\omega_j - 0.176\omega_j^2$$

Appendix: Soave Redlich Kwong Equation of State

Fugacity Coeff. for component *j* in mixture $(\phi^V_{i,j}, \phi^L_{i,j})$

$$ln\,\phi_j = \frac{b_j}{b}(z-1) - ln(z-B) - \frac{A}{B}\left[\frac{2a_j\alpha_j z^*_j}{a\alpha} - \frac{b_j}{b}\right] ln\left(1+\frac{B}{z}\right)$$

Residual enthalpy in mixture $(\Delta H_i, \Delta h_i)$

$$-\frac{\Delta H}{R_g T} = -1 - \frac{1}{bR_g T} ln\left(1+\frac{B}{z}\right)\sum_j x^*_j z^*_j \left(\frac{1+m_j}{\alpha_j}\right)$$

$$A = \frac{a\alpha P}{R_g^2 T^2}; B = \frac{bP}{R_g T}$$