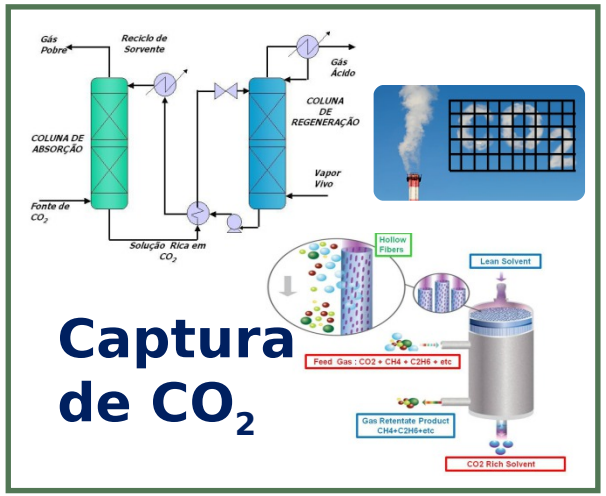
José Luiz de Medeiros
Ofélia Q. F. Araújo

Universidade Federal do Rio de Janeiro

H2CIN

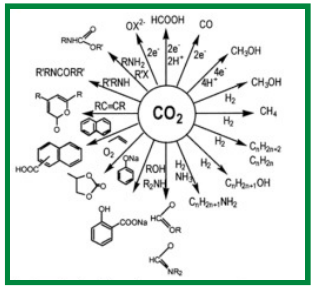
- **Síntese, Simulação, Otimização e Controle de Processos Químicos e Bioquímicos**

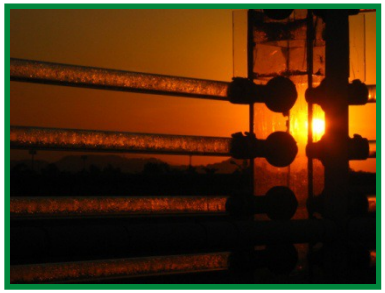
LINHAS DE PESQUISA



Captura de CO_2

Sequestro Químico e Bioquímico de CO_2





Engenharia Verde LCA

Blends

HCC e HDT

Processamento *Offshore*

Simulação e Controle

Transporte

(GN, Óleo, CO_2)

Risers & Gas Lift

Dinâmica e Controle

ÓLEO E GÁS

Sistemas via Software para Detecção de Vazamentos em Dutovias

PLANTAS PILOTOS

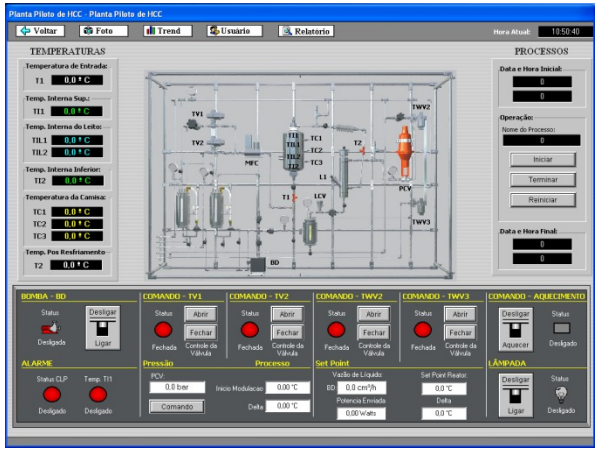
LOOP - GAS LIFT

2” X 12m Plexiglass Pilot Riser System

LOOP - GAS LIFT

HCC DE DIESEL

200 bar



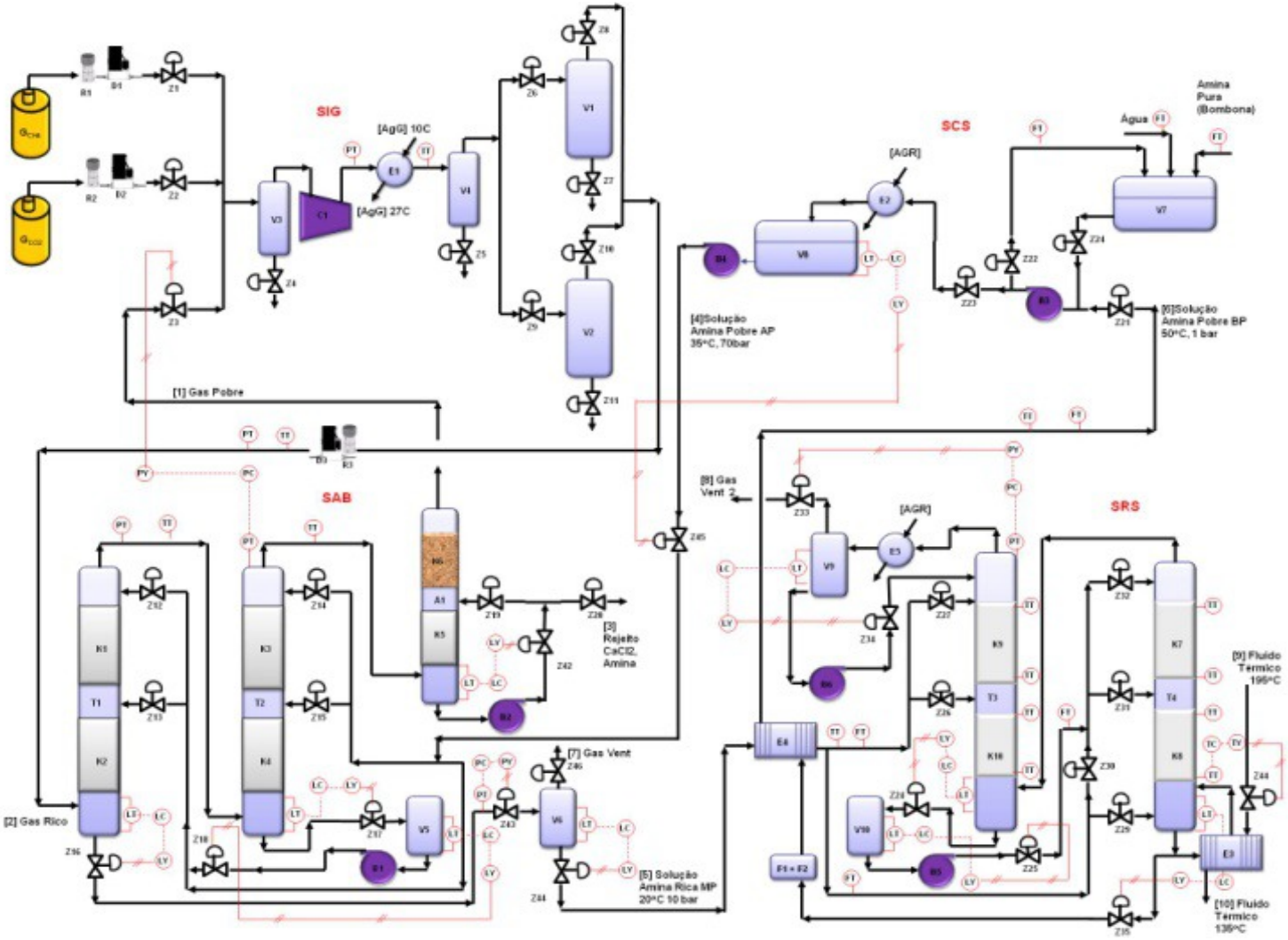
HDT DE PYGAS

50 bar

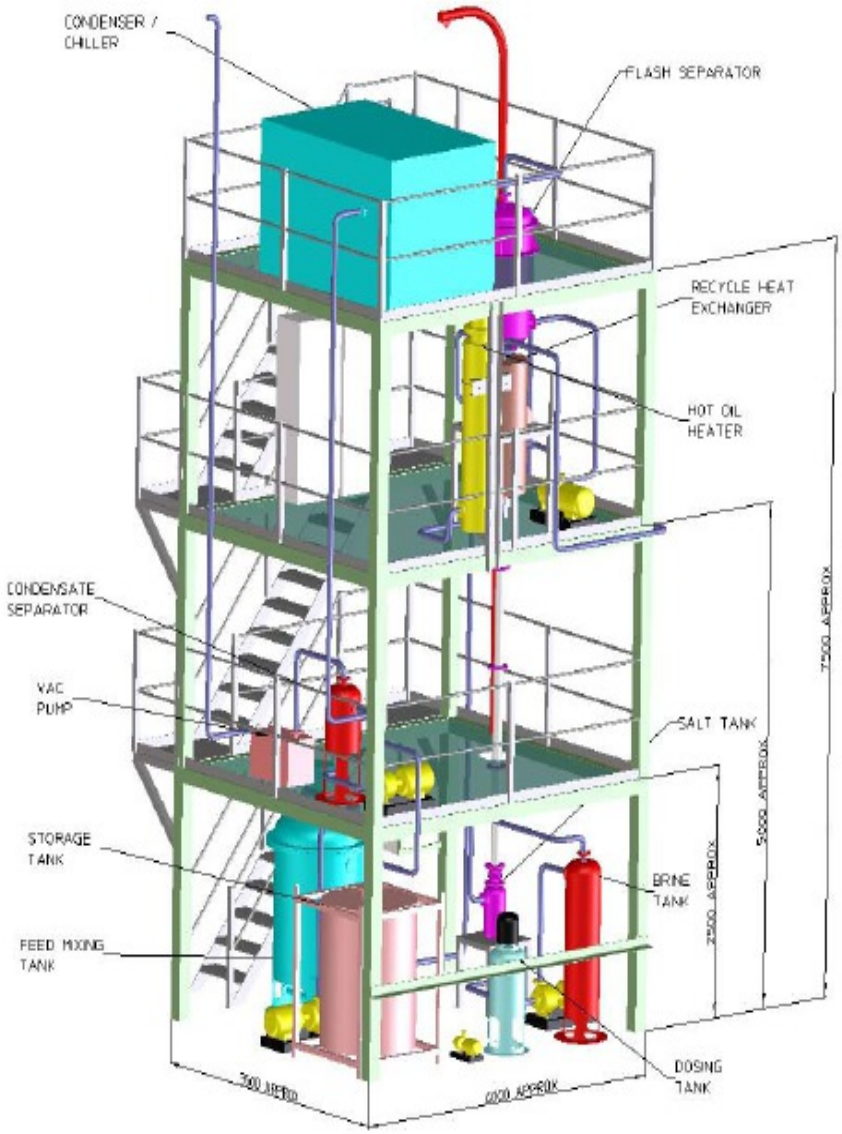
LOOP DE SIMULAÇÃO DE VAZAMENTOS

SEQUESTRO BIOQUIMICO DE CO_2

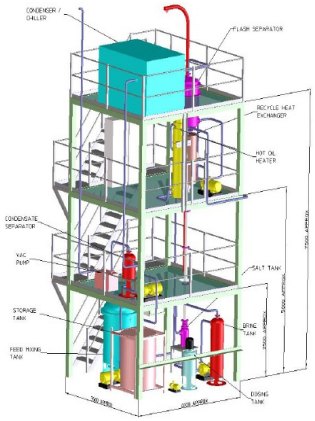
PLANTA PILOTO DE CAPTURA DE CO_2 COM AMINAS - CEGN

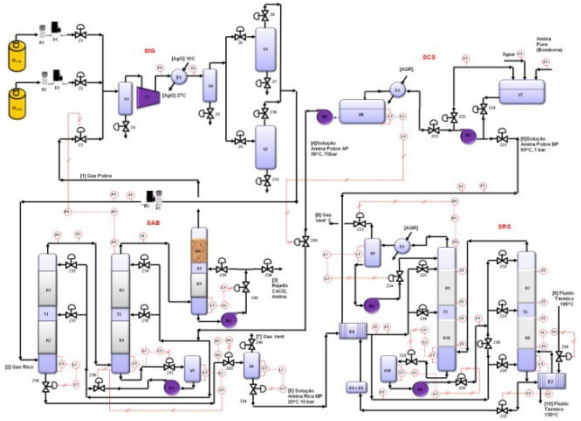


PLANTA DE RECUPERAÇÃO DE MEG - CEGN



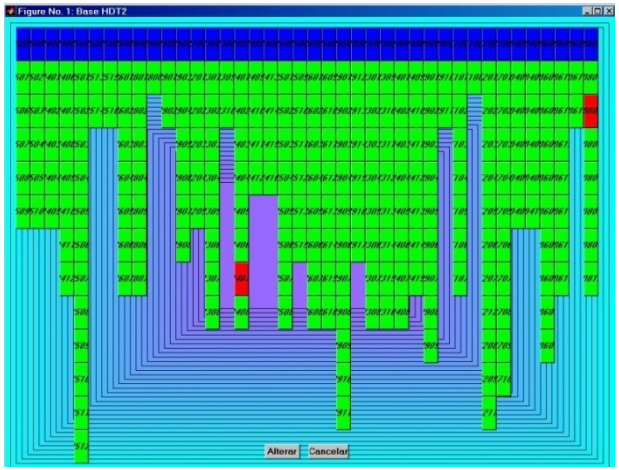
CEGN – CENTRO DE EXCELÊNCIA EM GÁS NATURAL
Parque Tecnológico - UFRJ

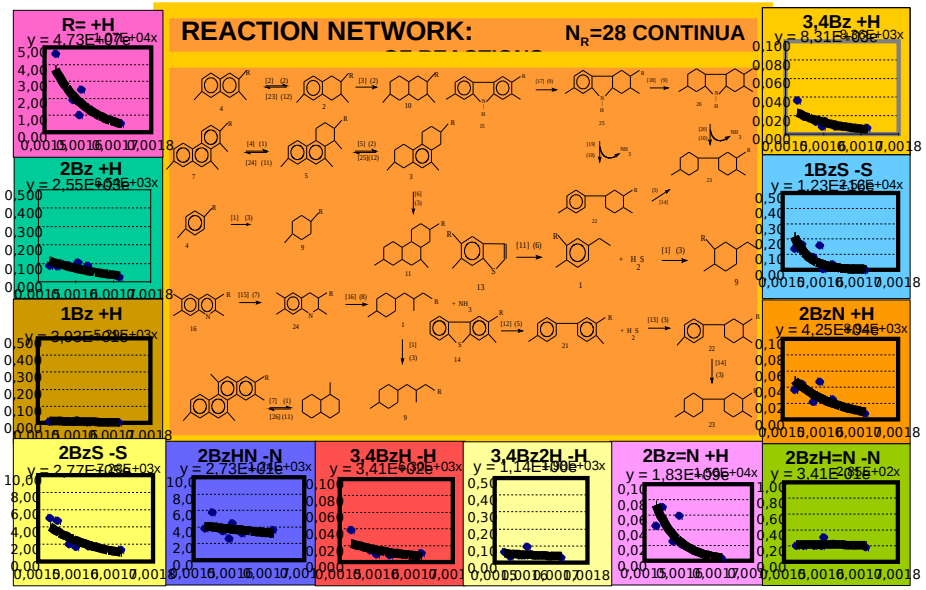


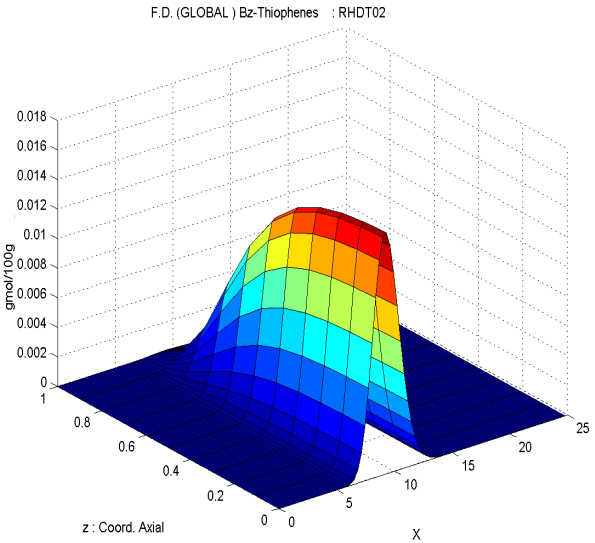


SIMULADORES DESENVOLVIDOS

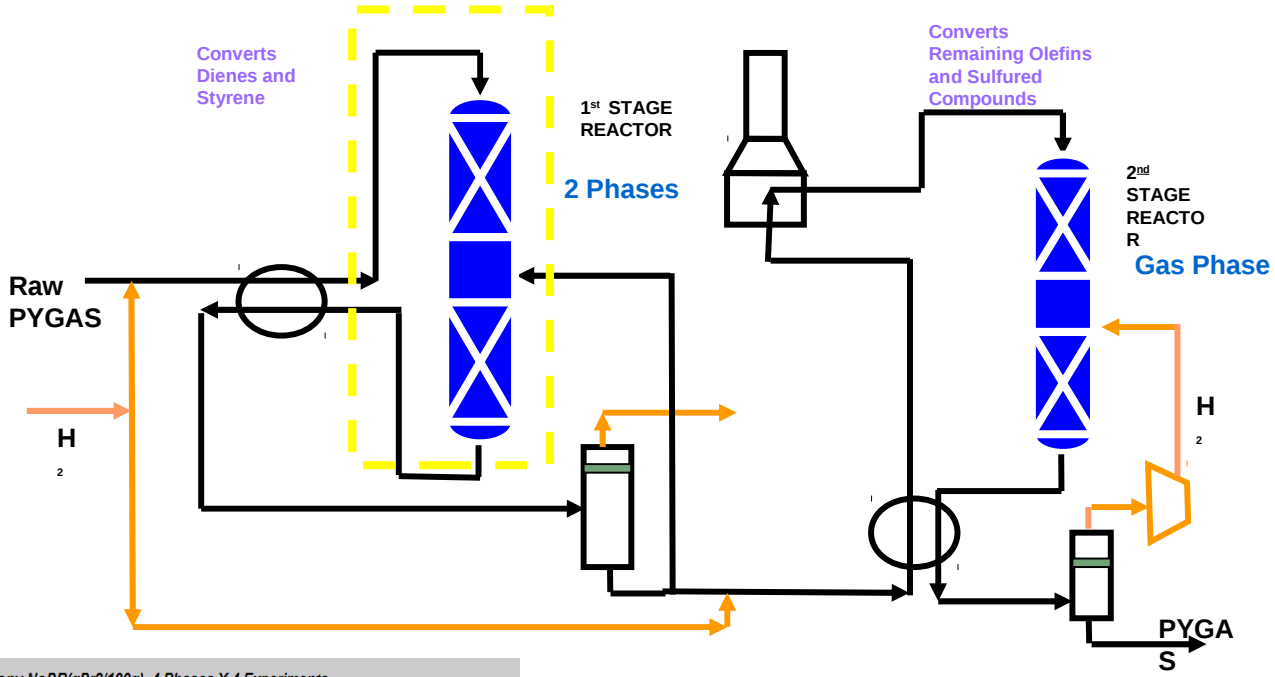
HDT DE DIESEL

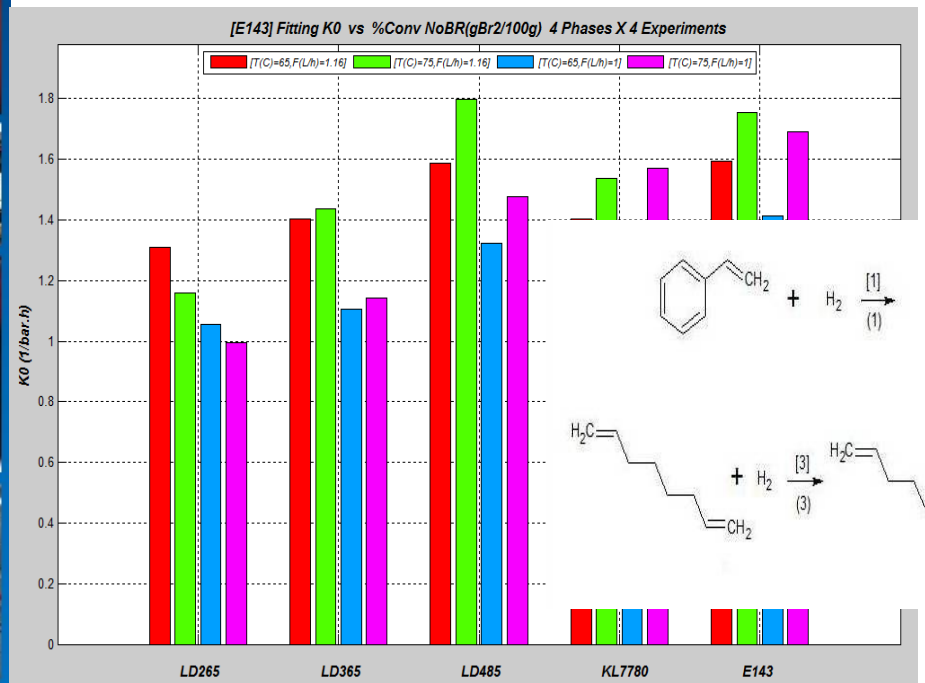


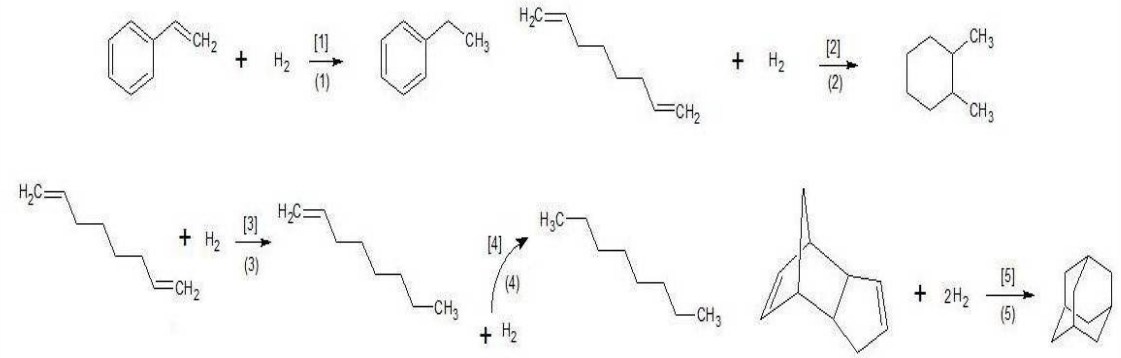




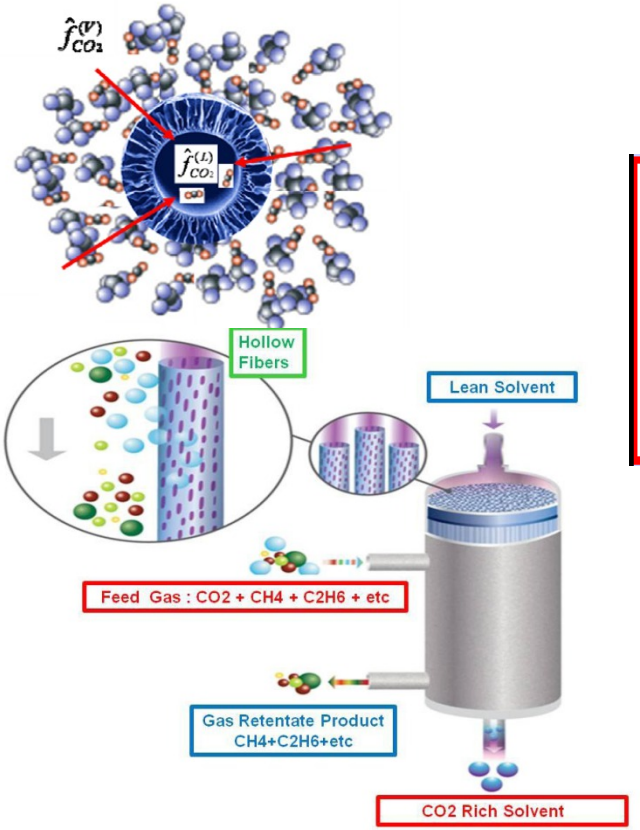
HDT PYGAS


Converts Dienes and Styrene
1st STAGE REACTOR
2 Phases
Converts Remaining Olefins and Sulfured Compounds
2nd STAGE REACTOR
Gas Phase
Raw PYGAS
H2
H2
PYGAS


[E143] Fitting K0 vs %Conv NoBR(gBr2/100g) 4 Phases X 4 Experiments
[T(C)=65,F(L/h)=1.16]
[T(C)=75,F(L/h)=1.16]
[T(C)=65,F(L/h)=1]
[T(C)=75,F(L/h)=1]
K0 (1/bar.h)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
LD265
LD365
LD485
KL7780
E143


CH2
+ H2
[1]
(1)
CH3
H2C
CH2
+ H2
[2]
(2)
CH3
CH3
H2C
CH2
+ H2
[3]
(3)
H2C
CH3
[4]
(4)
+ H2
H3C
CH3
+ 2H2
[5]
(5)

SEPARAÇÃO DE CO_2 DE GN – MEMBRANAS (contactora)



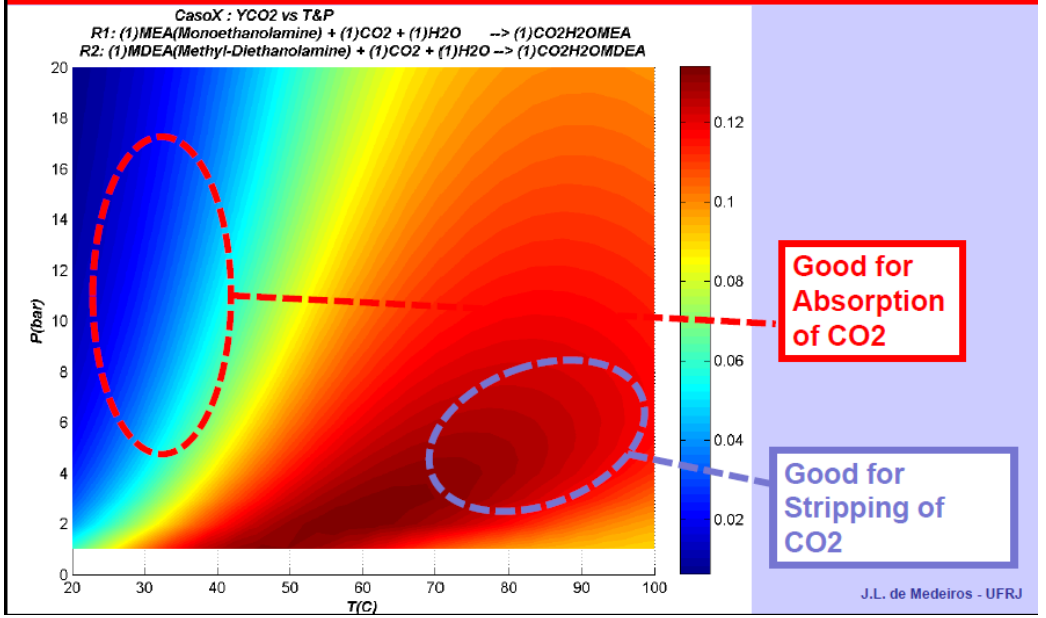
Same AGWA Reactive Model for Two-Phase Permeate = ChE + VLE
(AGWA = Acid Gas + Water + Amine)

ChE Reactions forming Non Volatile Complex Species

Conventional EOS (PR, SRK, etc) for property prediction in the Two-Phase Permeate & in Gas Retentate

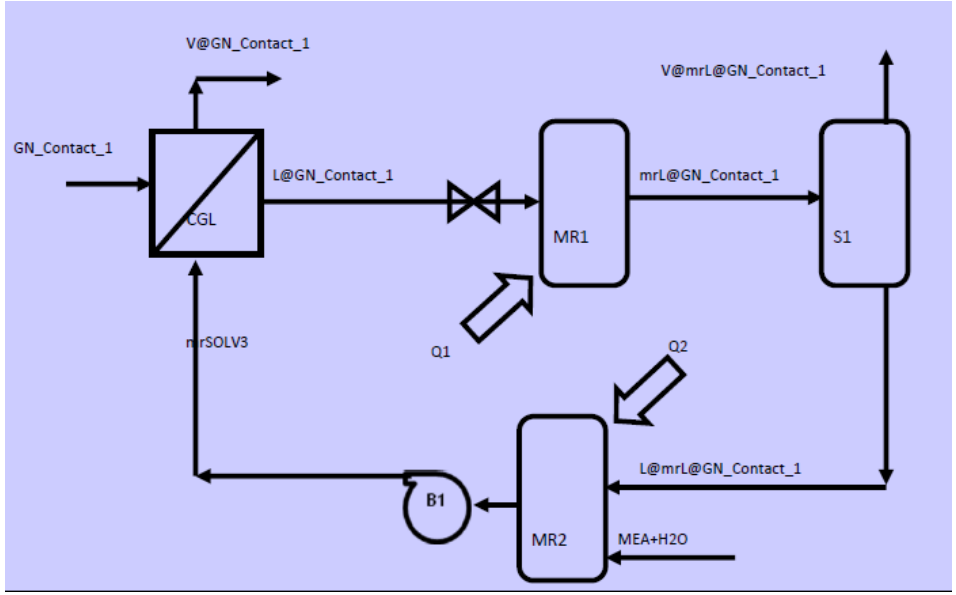
ChE Constants estimated with a Database from the Literature

Typical ChE Behavior of *YCO2* vs *T&P* in the Two-Phase Reactive Permeate

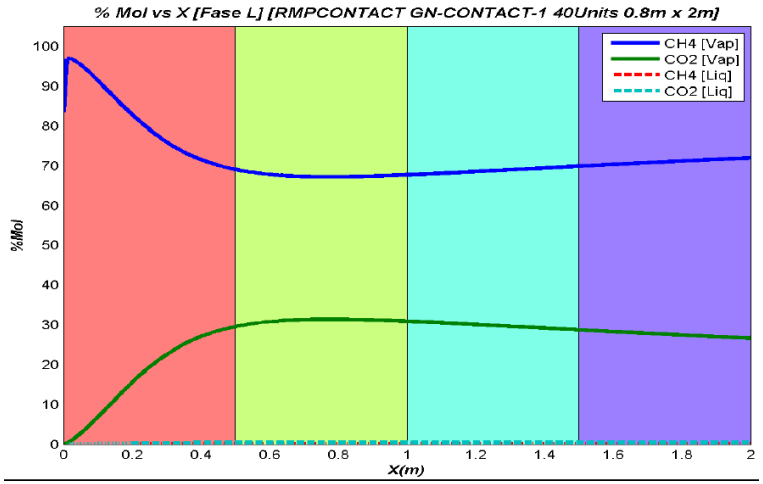


SEPARAÇÃO DE CO_2 DE GN – MEMBRANAS (contactora)

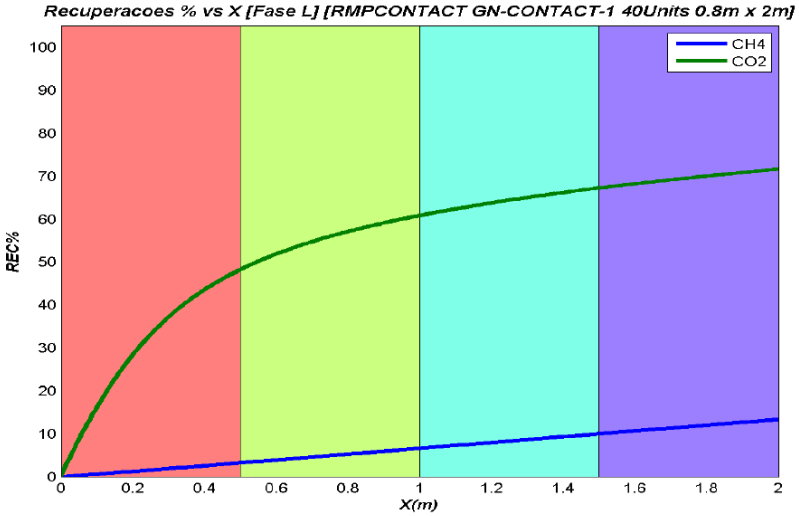
- Rigorous Component Balances for Permeate (Two-Phase) & Retentate (Gas)
- Permeation Fluxes Expressed in Terms of Fugacity Gradients
- Rigorous Momentum Balances for Permeate (Two-Phase) & Retentate (Gas)
- Rigorous Energy Balances for Permeate (Two-Phase) & Retentate (Gas)
- Temperature Profiles of Permeate & Retentate are Accessed
- Temperature Increases along Permeate & Retentate Flows
  No Risk of Gas Condensation



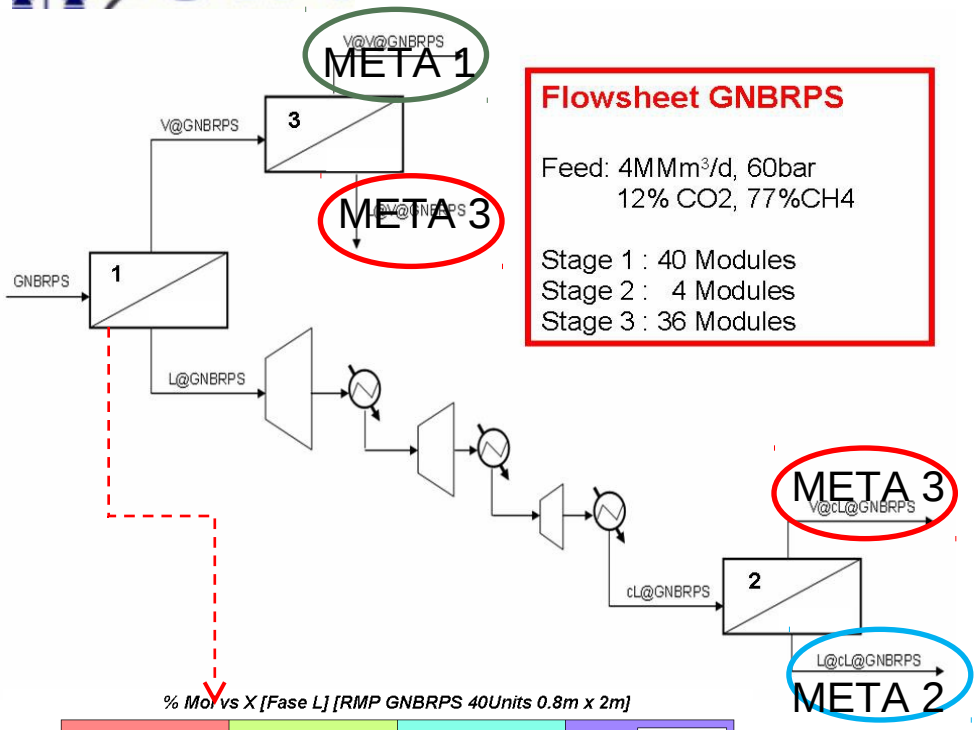
Permeate %mol for Liquid & Vapor Phases



Profiles of %Recovery in the Permeate



SEPARAÇÃO DE CO_2 DE NG –MEMBRANAS

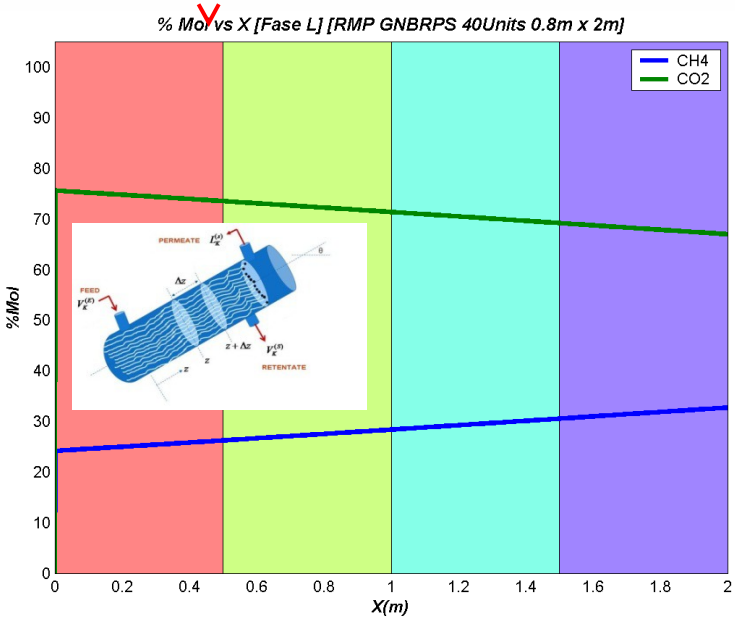


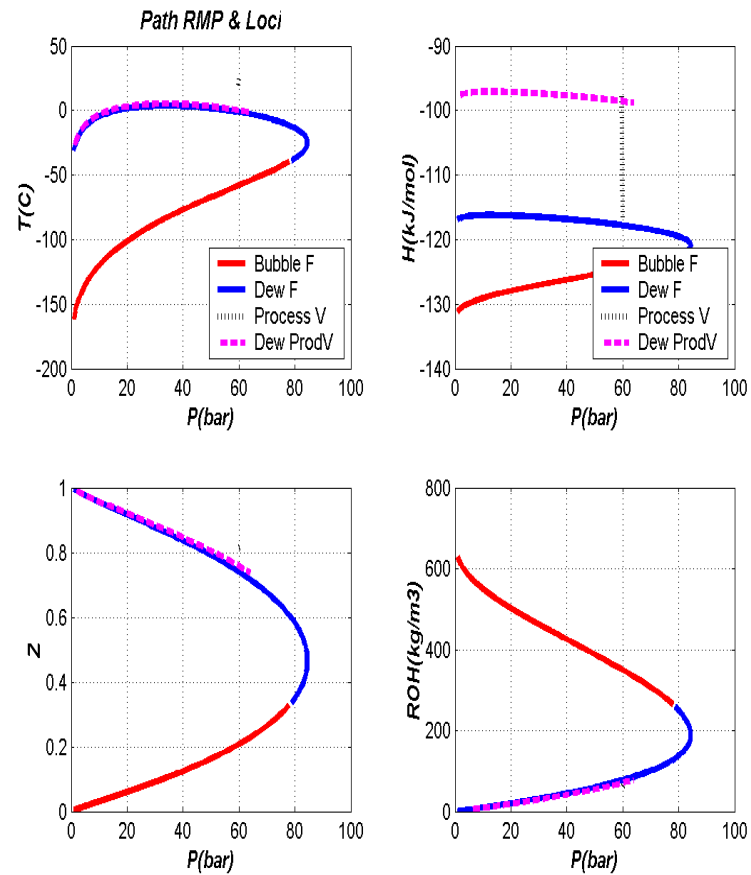
Flowsheet GNBRPS

Feed: 4MMm³/d, 60bar
12% CO2, 77%CH4

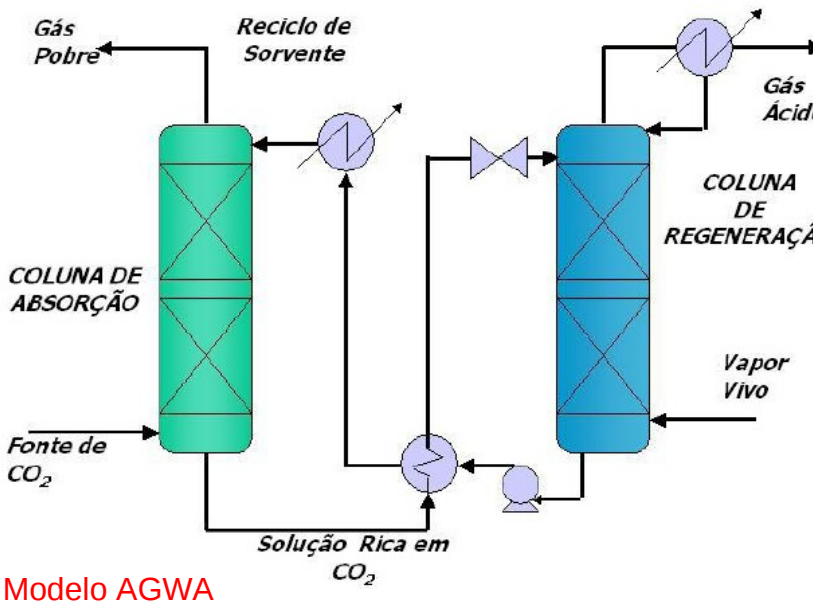
Stage 1 : 40 Modules
Stage 2 : 4 Modules
Stage 3 : 36 Modules

	$\%CO_2$
META 1	**3.2**
META 2	**96.2**
META 3	**37.6/47.1**

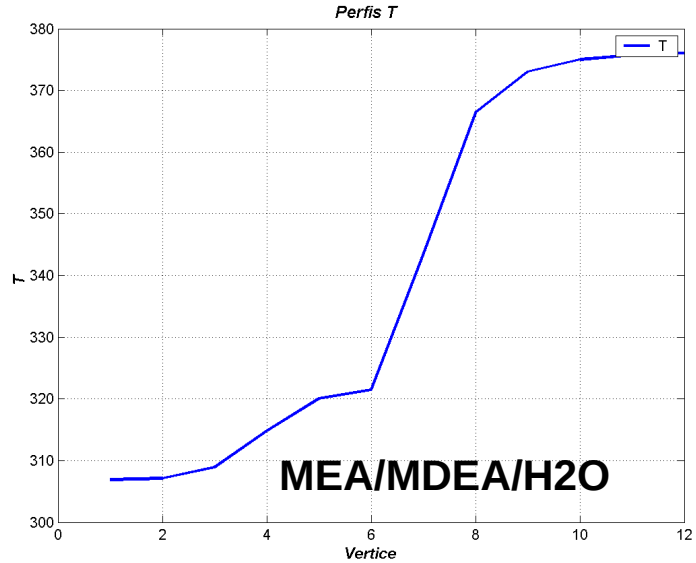


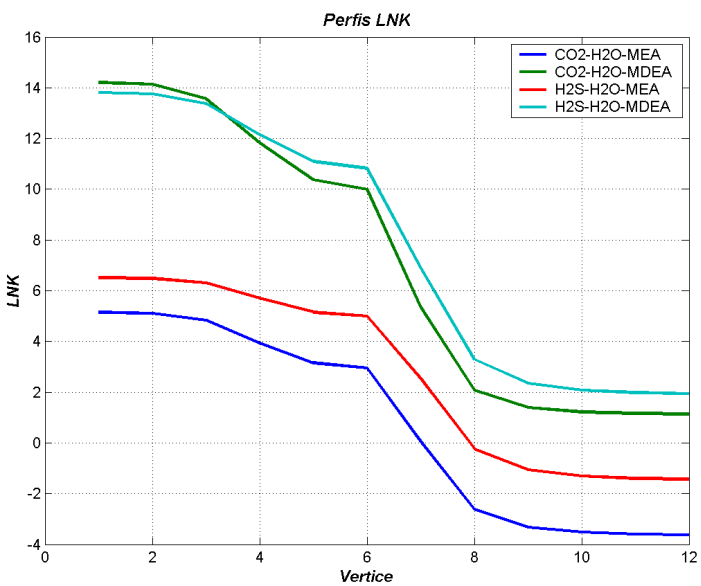


SEPARAÇÃO DE CO_2 DE GN - AMINAS



Modelo AGWA



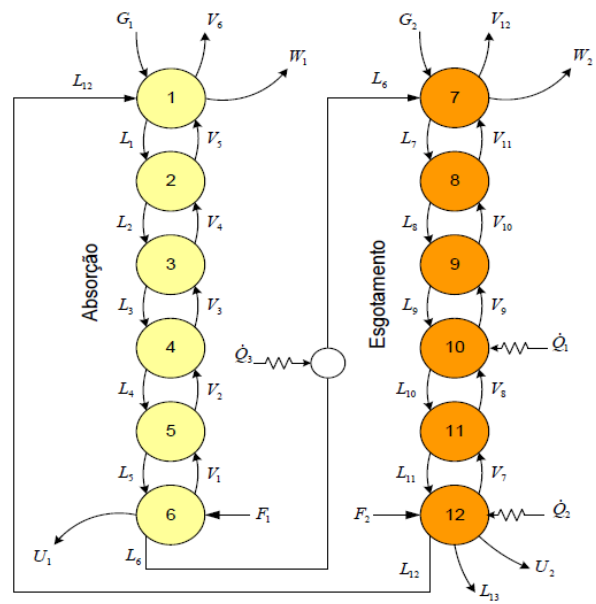


Representation of a Process with Absorption & Stripping Columns for AGWA Systems

Digraph Framework

Vertices : VLE-ChE Stages

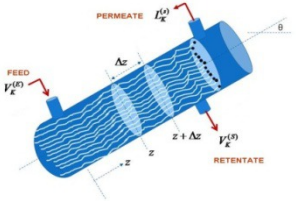
Edges : Connecting Streams, Feeds & Products

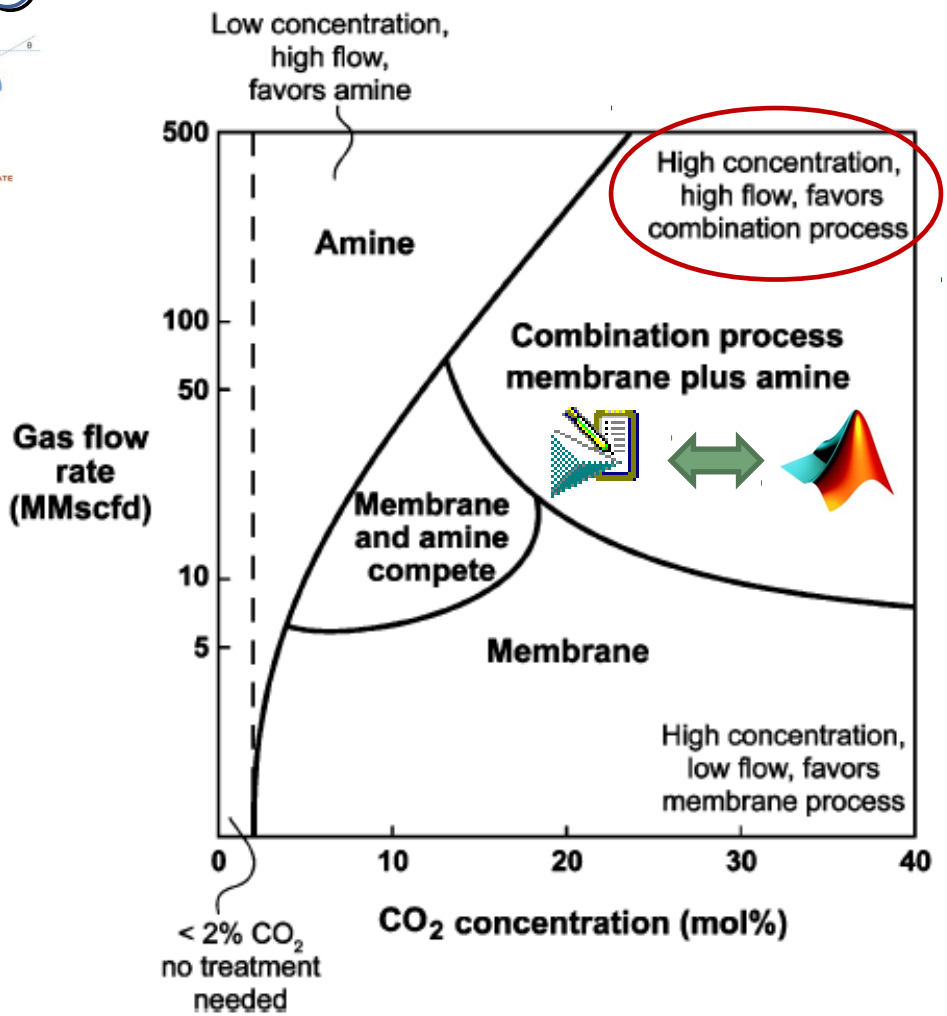


SEPARAÇÃO DE CO_2 DE GN – MEMBRANAS (permeador)

MATLAB®

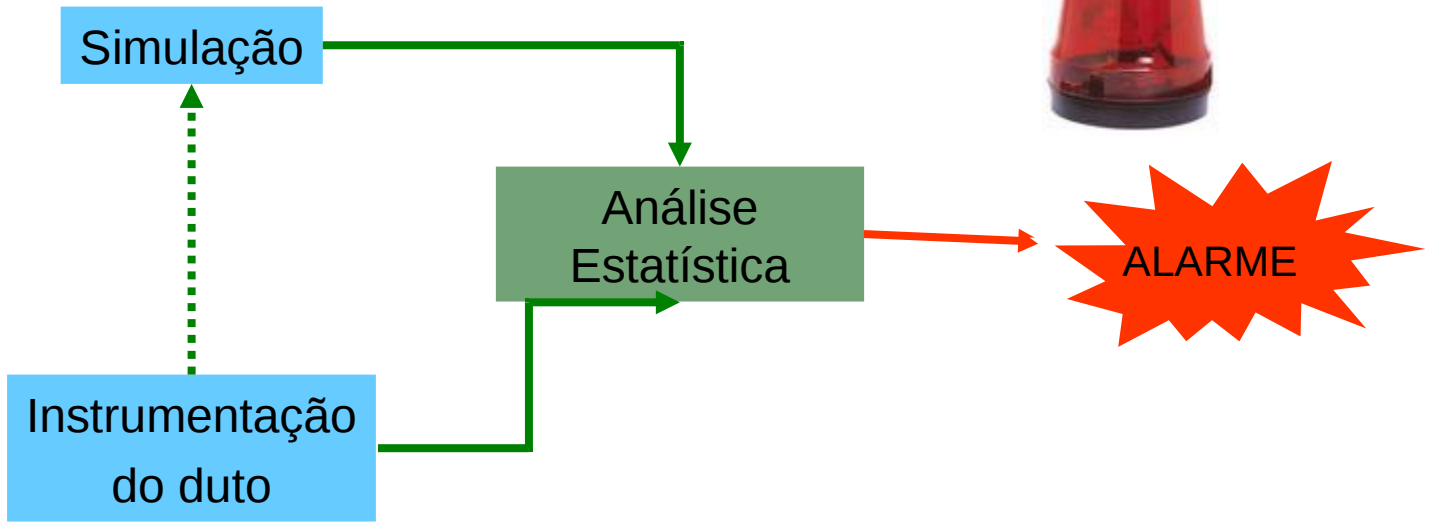
MODELO DE PERMEADOR



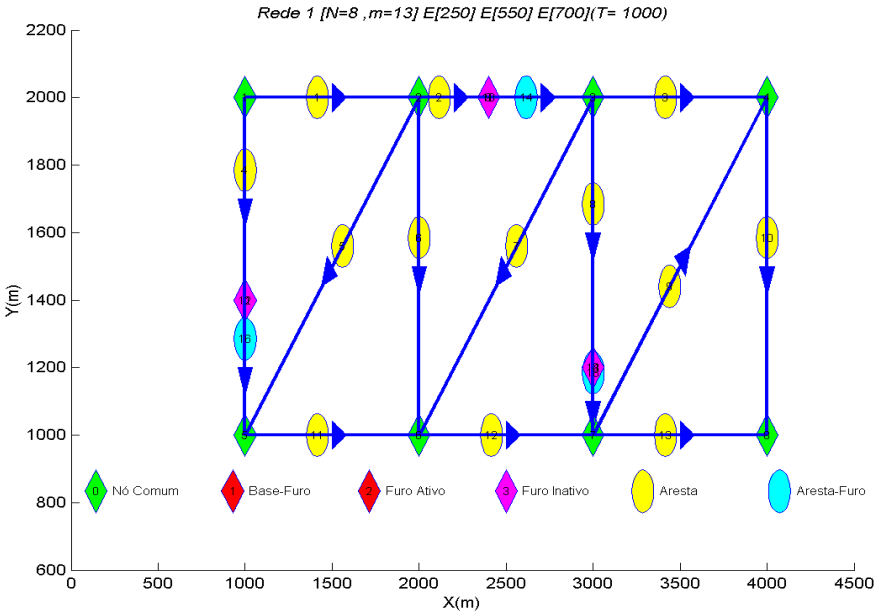


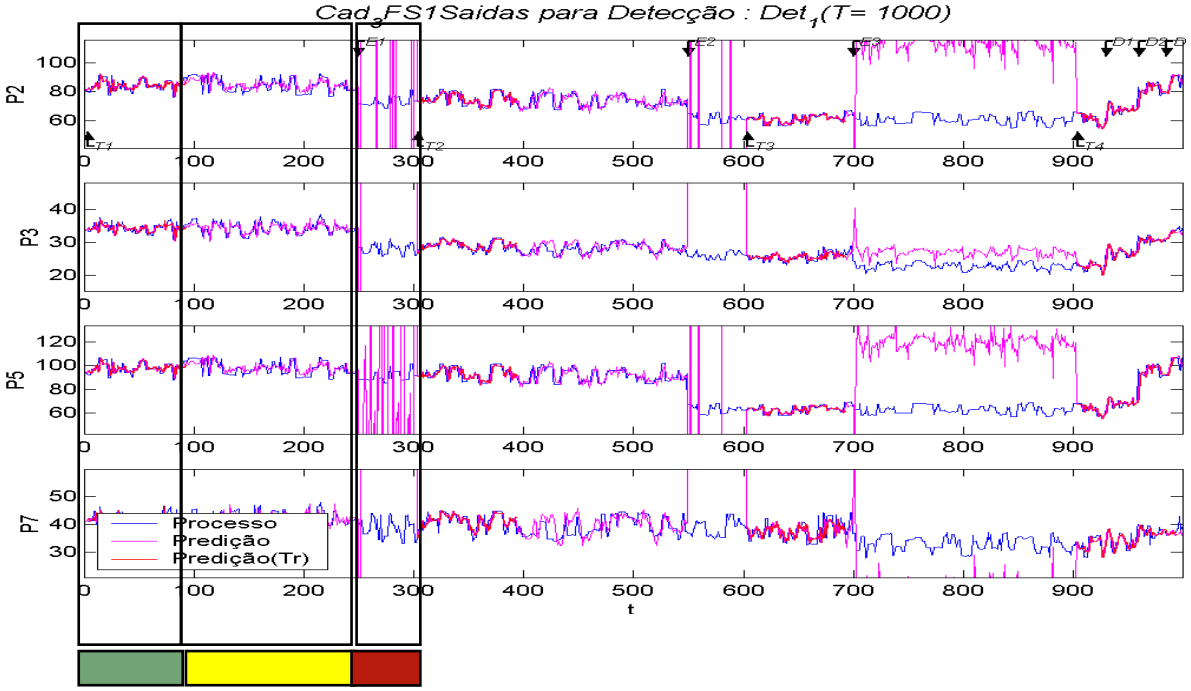
DETECÇÃO DE VAZAMENTOS EM DUTOVIAS

Monitoramento de integridade de dutos rastreando predições de balanço de massa em tempo real capturado por instrumentos



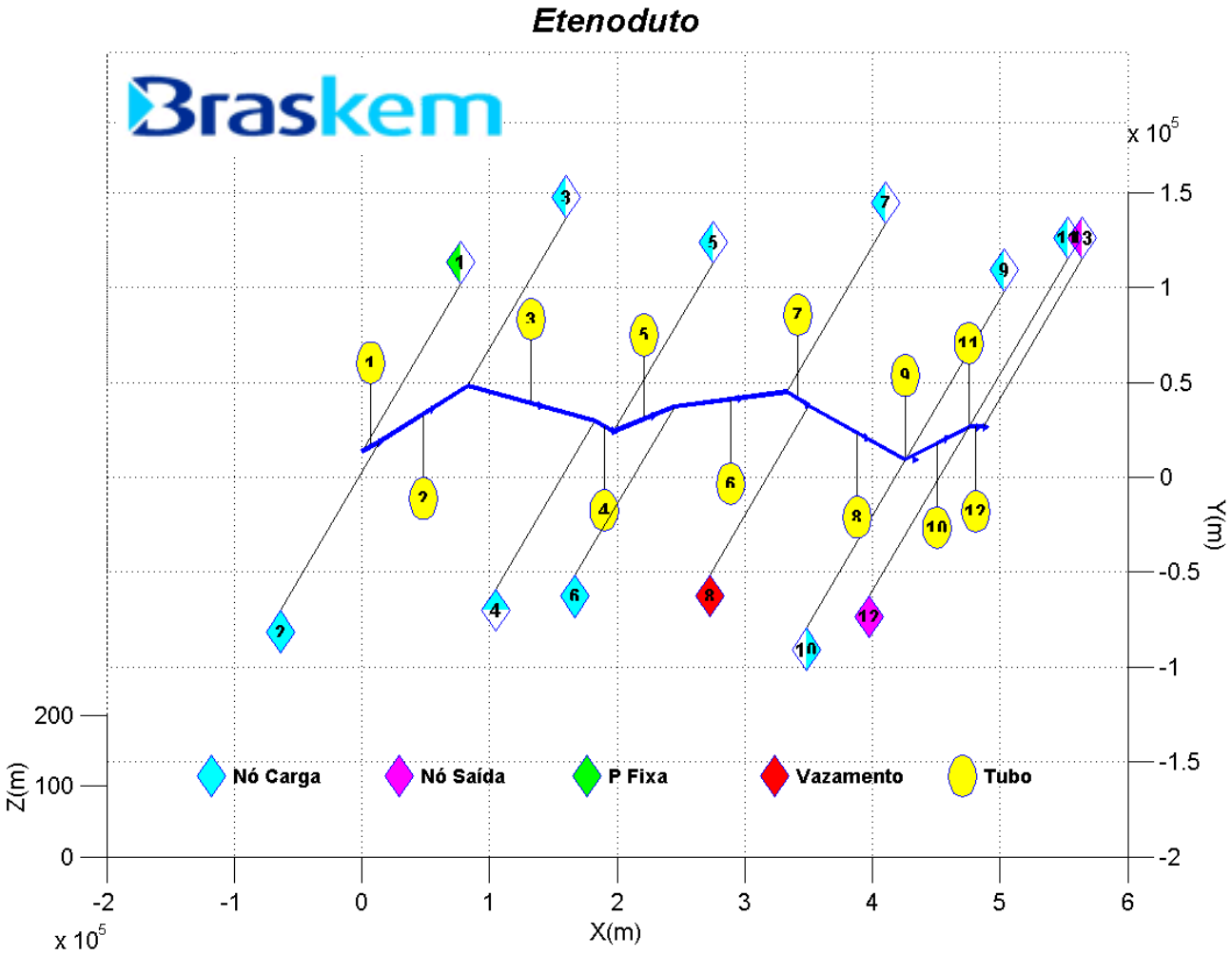
DETECÇÃO DE VAZAMENTOS EM DUTOVIAS



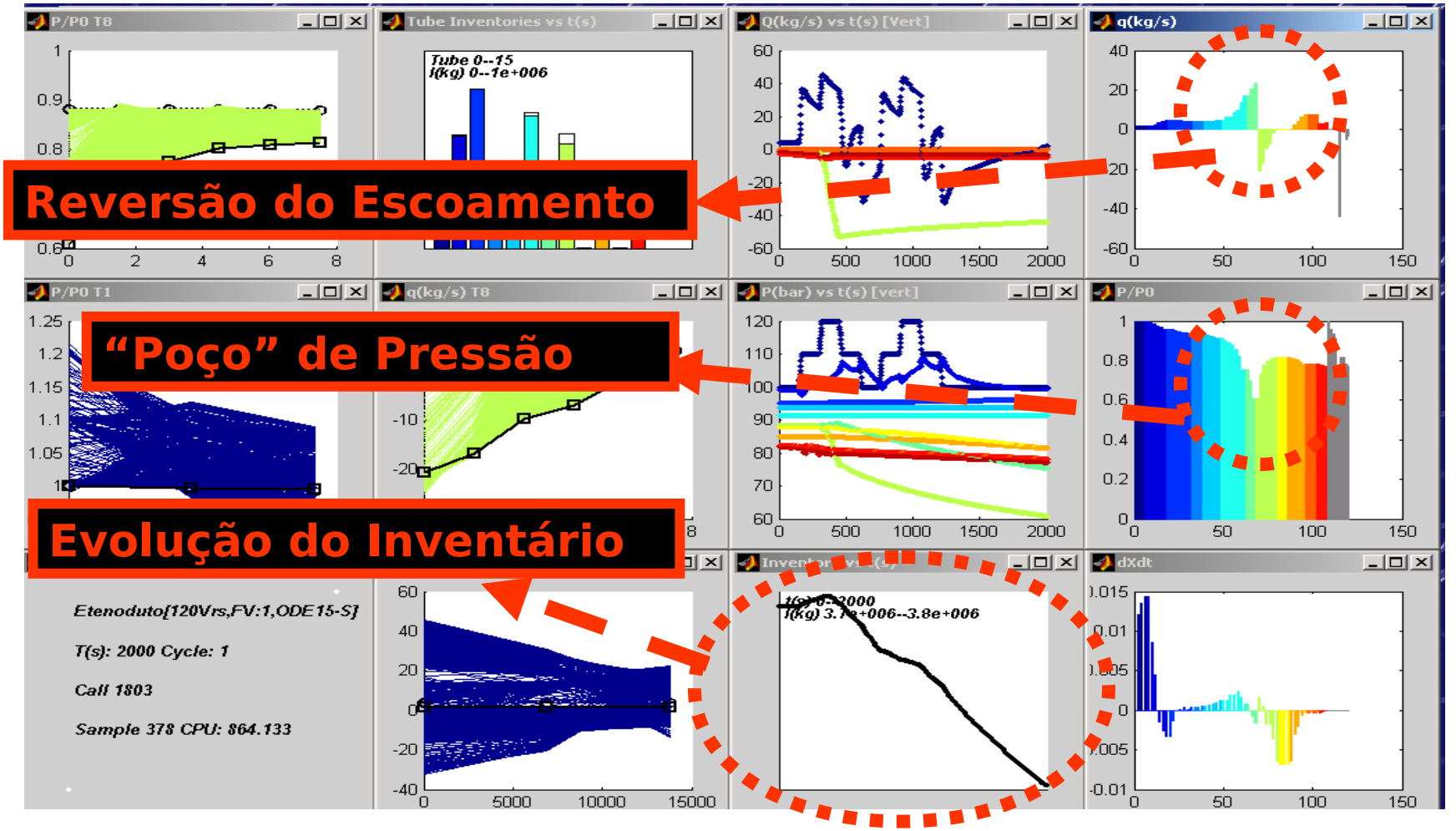


SIMULAÇÃO DINÂMICA DE ETENODUTO

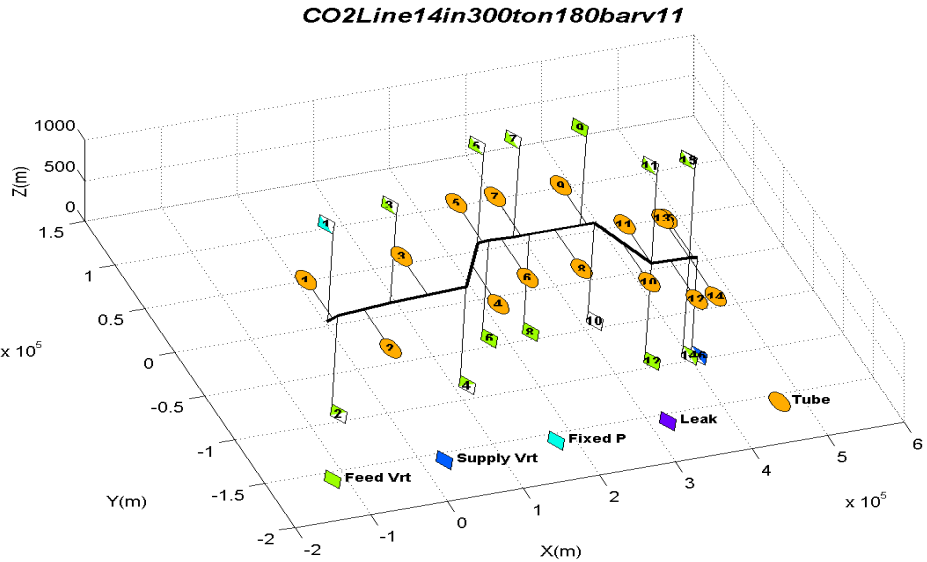
Distâncias : ~ 500km
Faixa de pressão : 110 bar a 40 bar
Vazões: ~ 50 t/h
Faixa de densidade : 100kg/m³ a 300kg/m³
#Altos gradientes de densidade (próximo ao ponto crítico)
Inventário da linha : 3000 a 6000 t

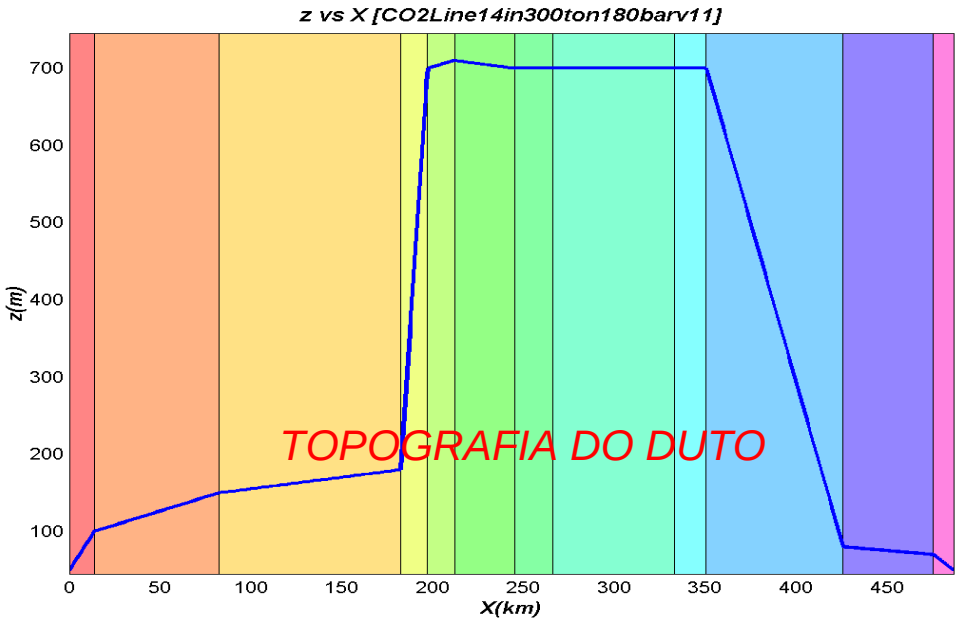


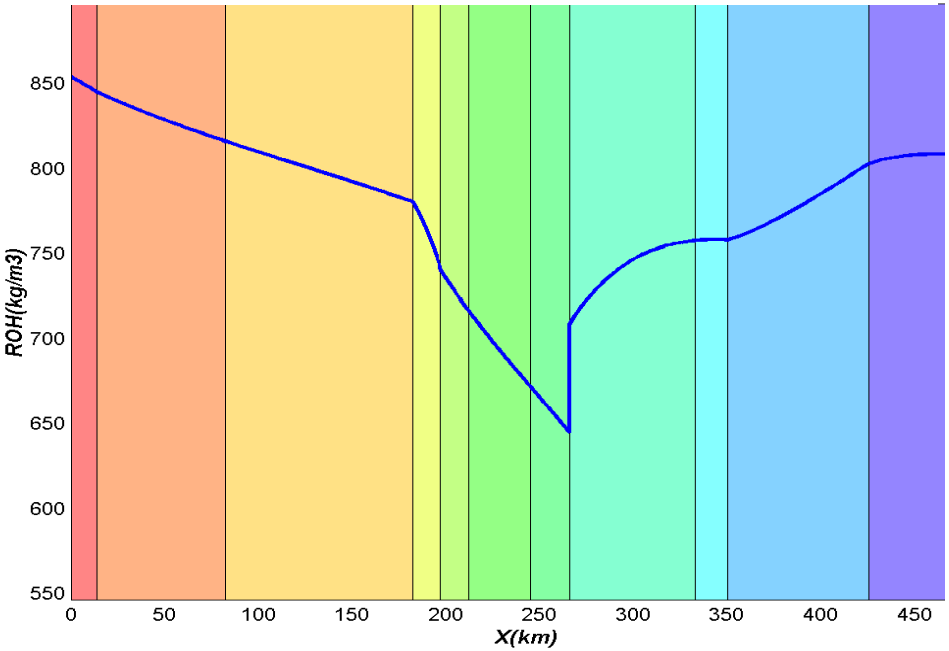
SIMULAÇÃO DINÂMICA DO ETENODUTO

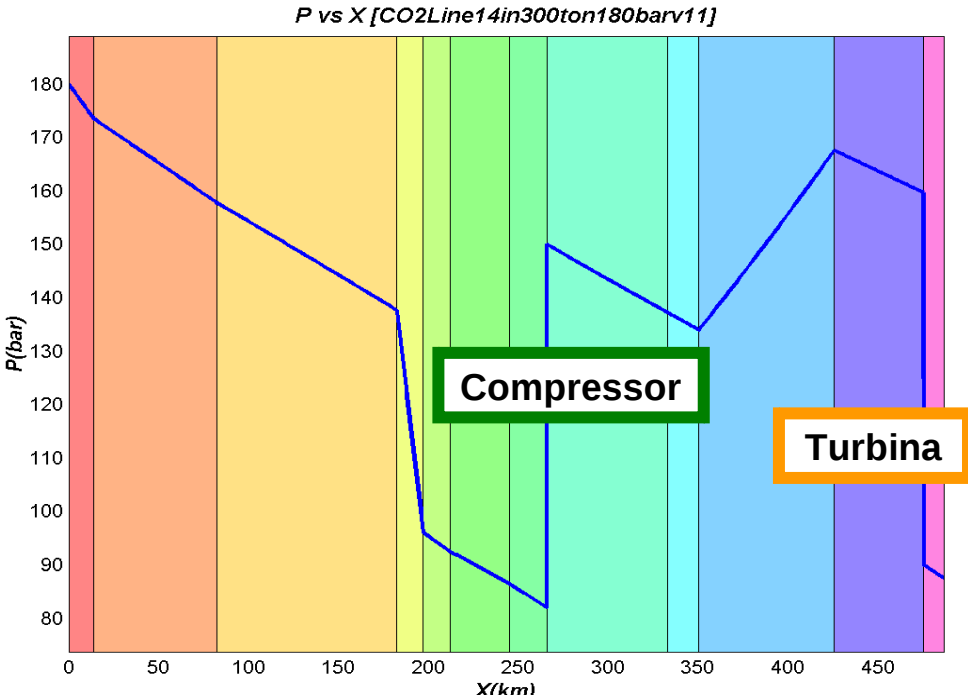


CARBODUTO


CO2Line14in300ton180barv11
Z(m)
Y(m)
X(m)
x 10^5
Tube
Leak
Fixed P
Supply Vrt
Feed Vrt

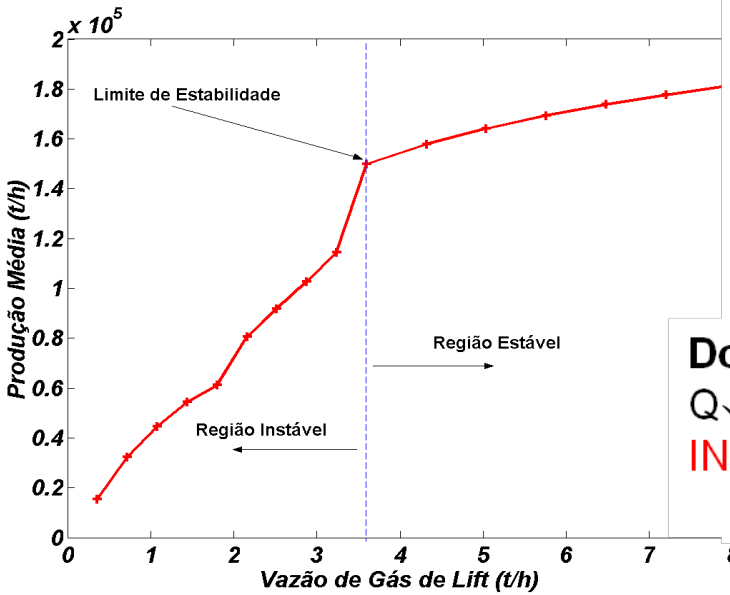

z vs X [CO2Line14in300ton180barv11]
z(m)
X(km)
TOPOGRAFIA DO DUTO

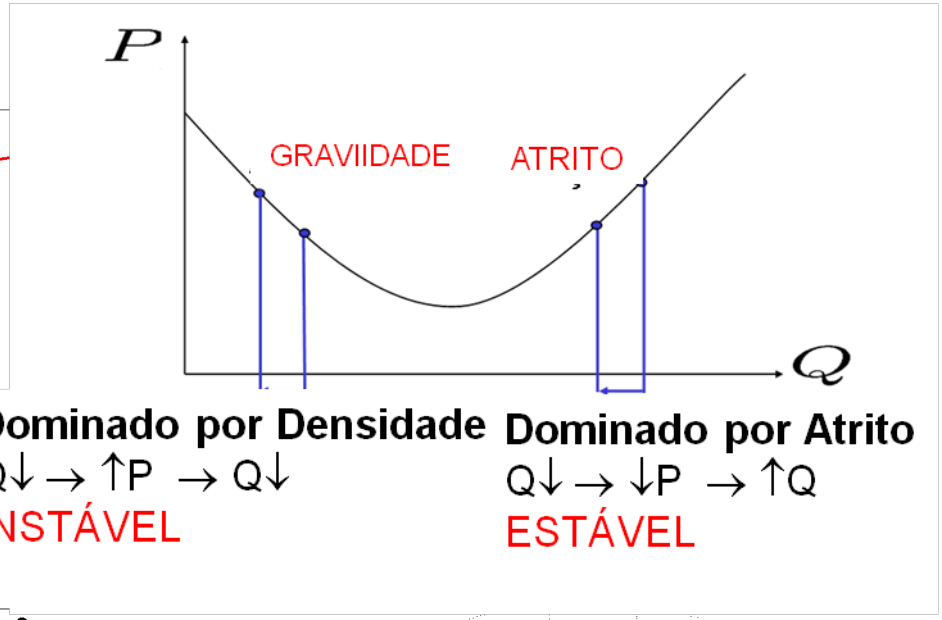

ROH(kg/m3)
X(km)

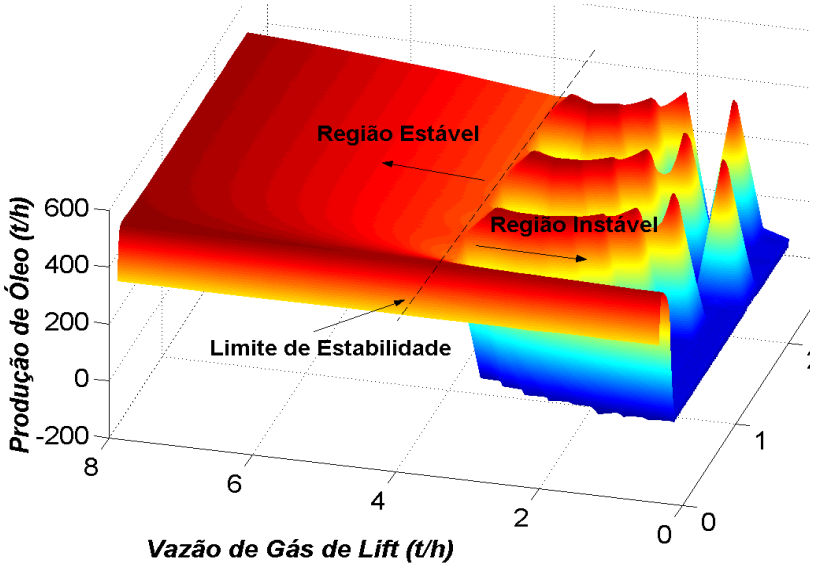

P vs X [CO2Line14in300ton180barv11]
P(bar)
X(km)
Compressor
Turbina

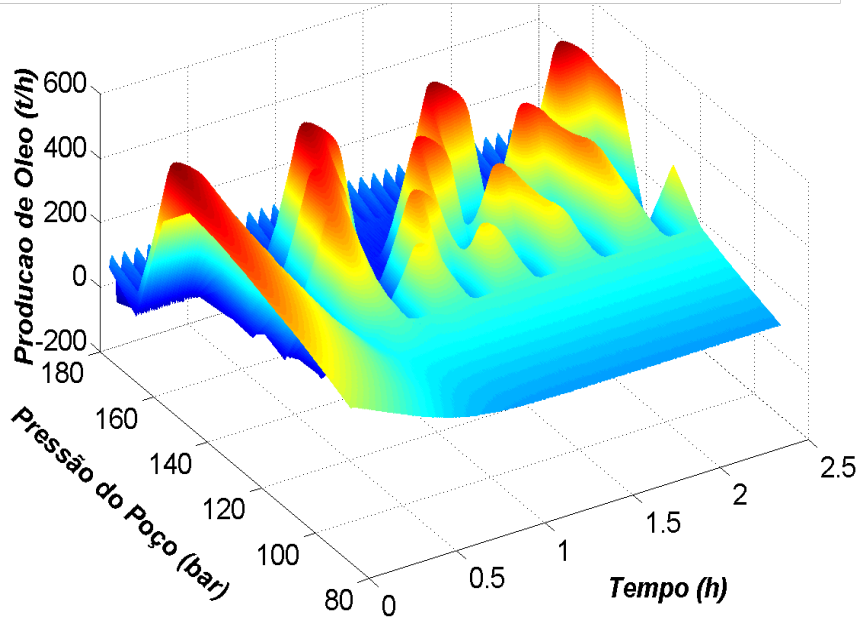
PROCESSAMENTO DE ÓLEO E GÁS

RISERS & GAS LIFT

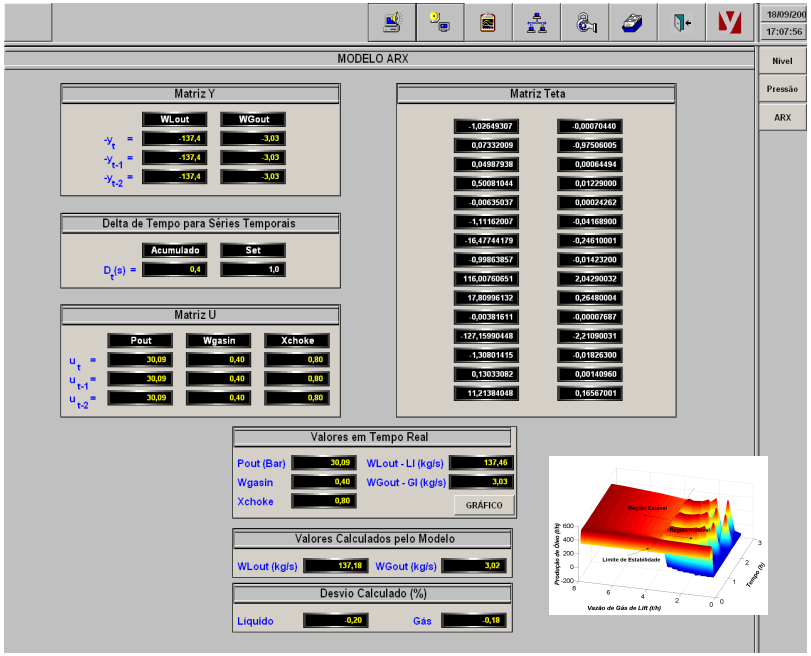


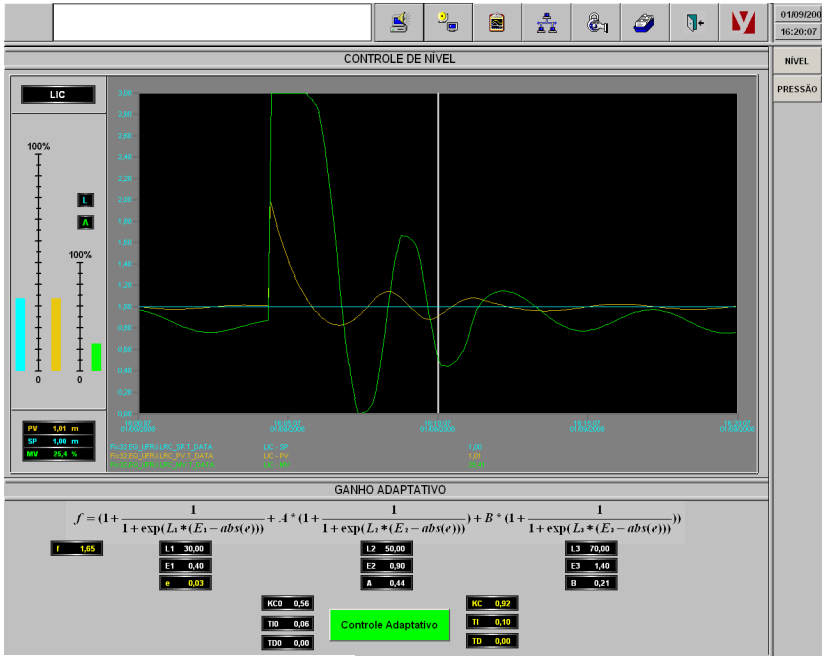






SIMULAÇÃO , OTIMIZAÇÃO E CONTROLE DE PROCESSAMENTO OFFSHORE





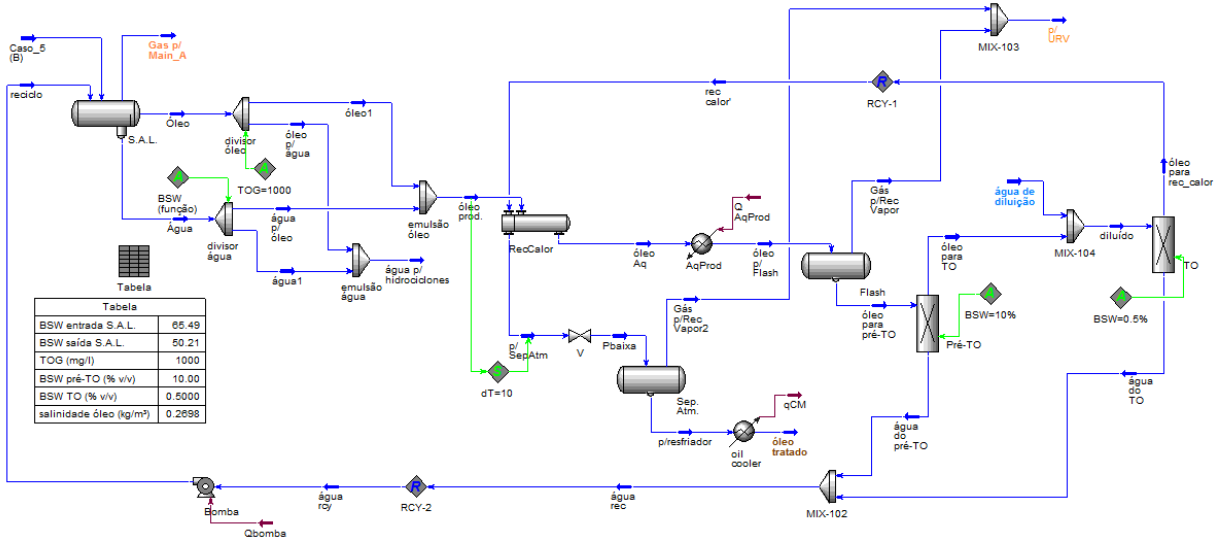
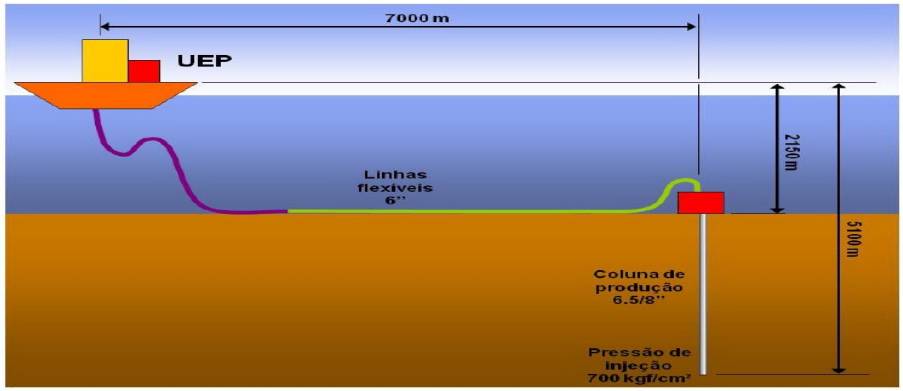


Tabela	
BSW entrada S.A.L.	65.49
BSW saída S.A.L.	50.21
TOG (mg/l)	1000
BSW pré-TO (% v/v)	10.00
BSW TO (% v/v)	0.5000
salinidade óleo (kg/m³)	0.2698

COMPRESSÃO DE CO_2 - EOR & CCS



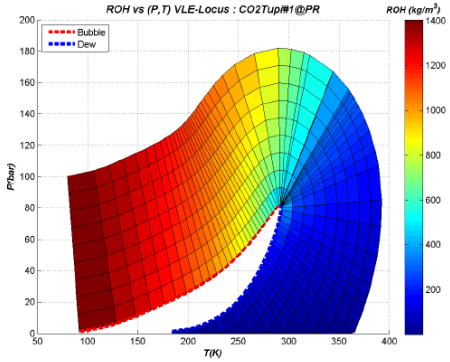


Figura A1.15 : *ROH* vs (*P,T*) p/ Envelopes VLE+LSR+VSA [Carga 1]

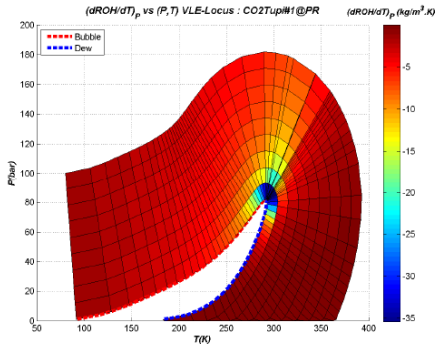


Figura A1.16 : *dROH/dT* vs (*P,T*) p/ Envelopes VLE+LSR+VSA [Carga 1]

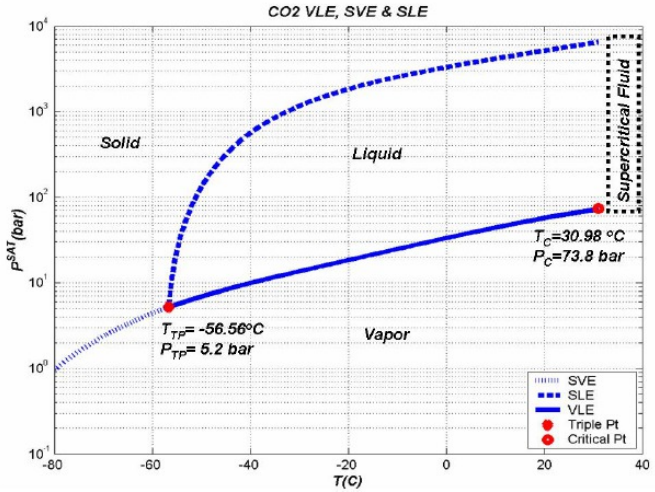


Figura 1.4 : Diagrama de Equilíbrio de Fases para CO_2 Puro (de Medeiros et al., 2008)

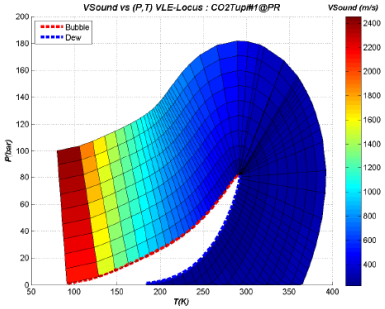


Figura A1.19 : *Velocidade do Som* vs (*P,T*) p/ Envelopes VLE+LSR+VSA [Carga 1]

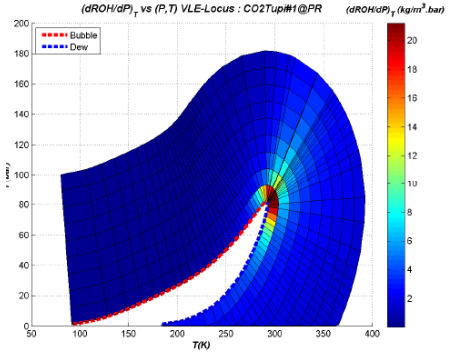
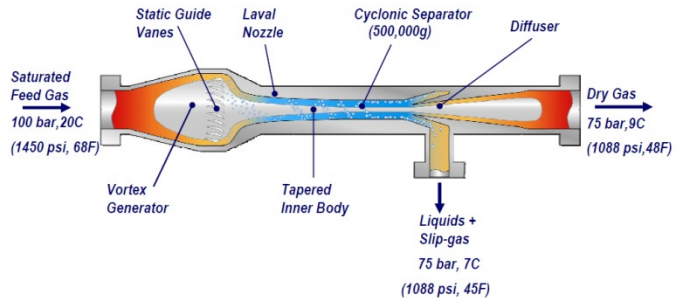
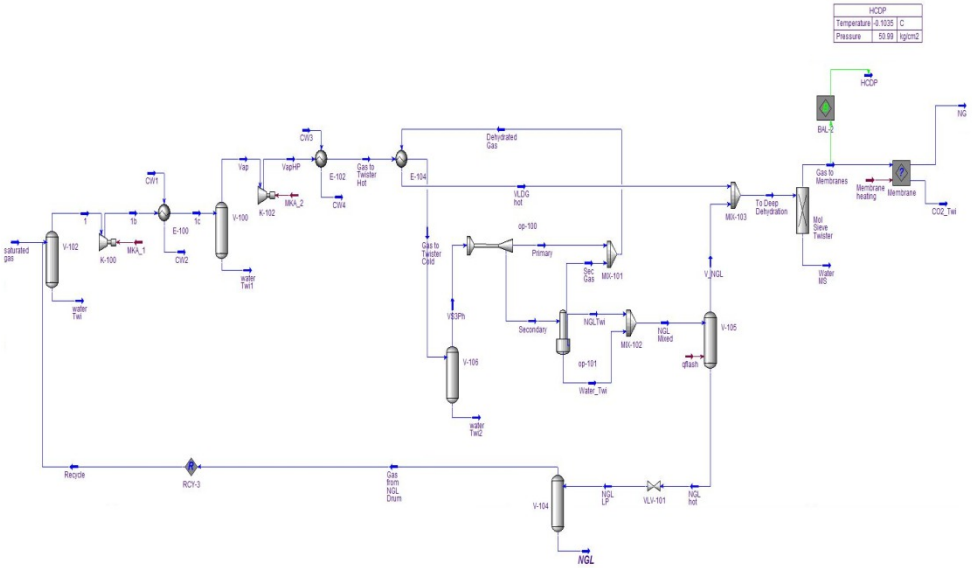
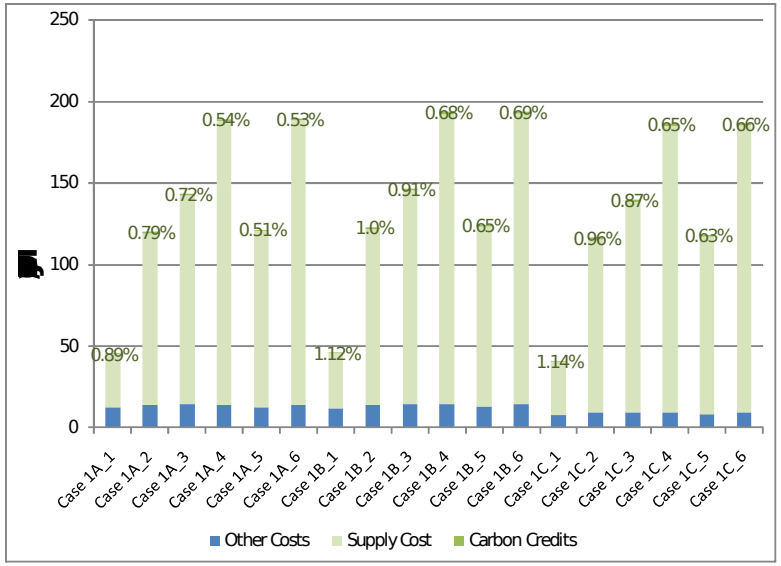


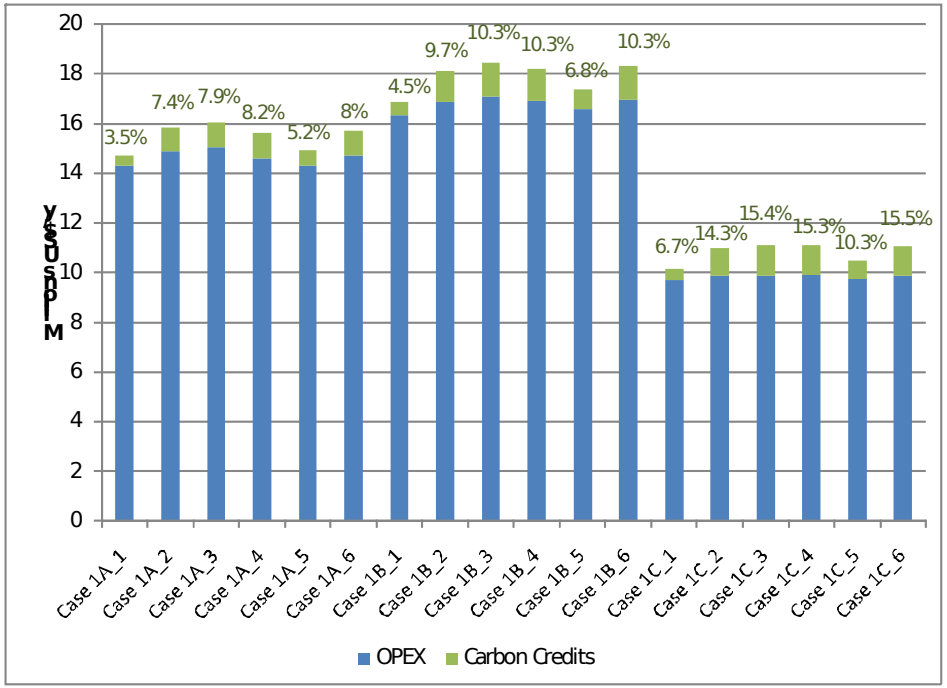
Figura A1.17 : *dROH/dP* vs (*P,T*) p/ Envelopes VLE+LSR+VSA [Carga 1]

TWISTER


Static Guide Vanes
Laval Nozzle
Cyclonic Separator (500,000g)
Diffuser
Saturated Feed Gas
100 bar,20C
(1450 psi, 68F)
Dry Gas
75 bar,9C
(1088 psi,48F)
Vortex Generator
Tapered Inner Body
Liquids + Slip-gas
75 bar, 7C
(1088 psi, 45F)

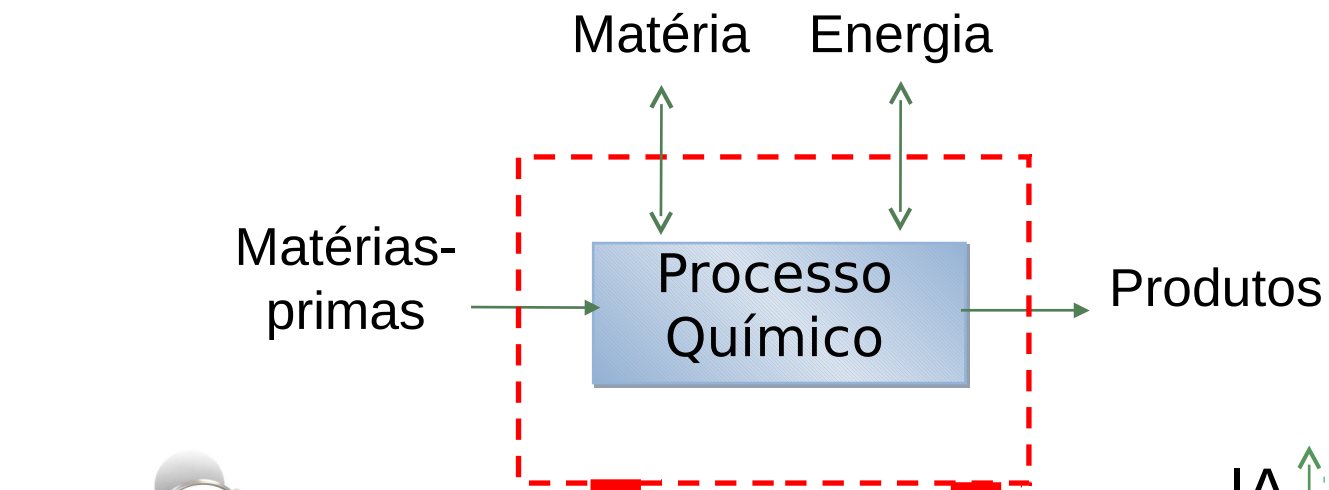



250
200
150
100
50
0
0.89%
0.79%
0.72%
0.54%
0.51%
0.53%
1.12%
1.0%
0.91%
0.68%
0.65%
0.69%
1.14%
0.96%
0.87%
0.65%
0.63%
0.66%
Case 1A_1
Case 1A_2
Case 1A_3
Case 1A_4
Case 1A_5
Case 1A_6
Case 1B_1
Case 1B_2
Case 1B_3
Case 1B_4
Case 1B_5
Case 1B_6
Case 1C_1
Case 1C_2
Case 1C_3
Case 1C_4
Case 1C_5
Case 1C_6
Other Costs
Supply Cost
Carbon Credits


20
18
16
14
12
10
8
6
4
2
0
3.5%
7.4%
7.9%
8.2%
5.2%
8%
4.5%
9.7%
10.3%
10.3%
6.8%
10.3%
6.7%
14.3%
15.4%
15.3%
10.3%
15.5%
Case 1A_1
Case 1A_2
Case 1A_3
Case 1A_4
Case 1A_5
Case 1A_6
Case 1B_1
Case 1B_2
Case 1B_3
Case 1B_4
Case 1B_5
Case 1B_6
Case 1C_1
Case 1C_2
Case 1C_3
Case 1C_4
Case 1C_5
Case 1C_6
OPEX
Carbon Credits

ENGENHARIA VERDE

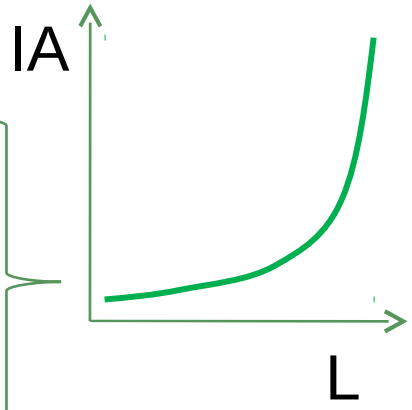
ENGENHARIA VERDE



$S = w_{IA}.IA + w_L.L$

Lucro

Impacto Ambiental



Função Sustentabilidade

Fronteira de Pareto

ENGENHARIA VERDE

Índices Abióticos

- Aquecimento global
- Esgotamento da camada de ozônio
- Despejos ácidos
- Formação de névoa

Índices Relacionados à Saúde Humana

- Toxicidade por inalação
- Toxicidade por ingestão
- Carcinogenicidade por inalação
- Carcinogenicidade por ingestão

Índices de Ecotoxicidade

- Toxicidade aquática a peixes

ENGENHARIA VERDE

Ambiental

- Índices Abióticos
- Acidentes (Frequencia, Severidade, Worst-case Scenario)
- Resíduos
- Dispersões tóxicas

Intensidade Material

- Rendimento Percentual
- Consumo de Água
- Eficiência de Massa
- Eficiência Atômica

Social

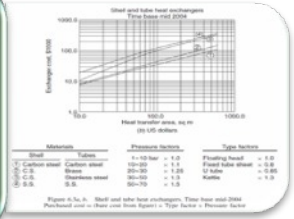
- Desflores-tamento
- Footprint Ecológico (ha/unidade de produto)
- Relação de Salário Max/Min
- Employee Turnover, age of death of employees, etc

Energy Intensity

- "Emergia" (embodied energy ratio)
- Kcal/kg
- Consumo mínimo de energia
- Uso total de energia

ENGENHARIA VERDE

CAPEX



OPEX

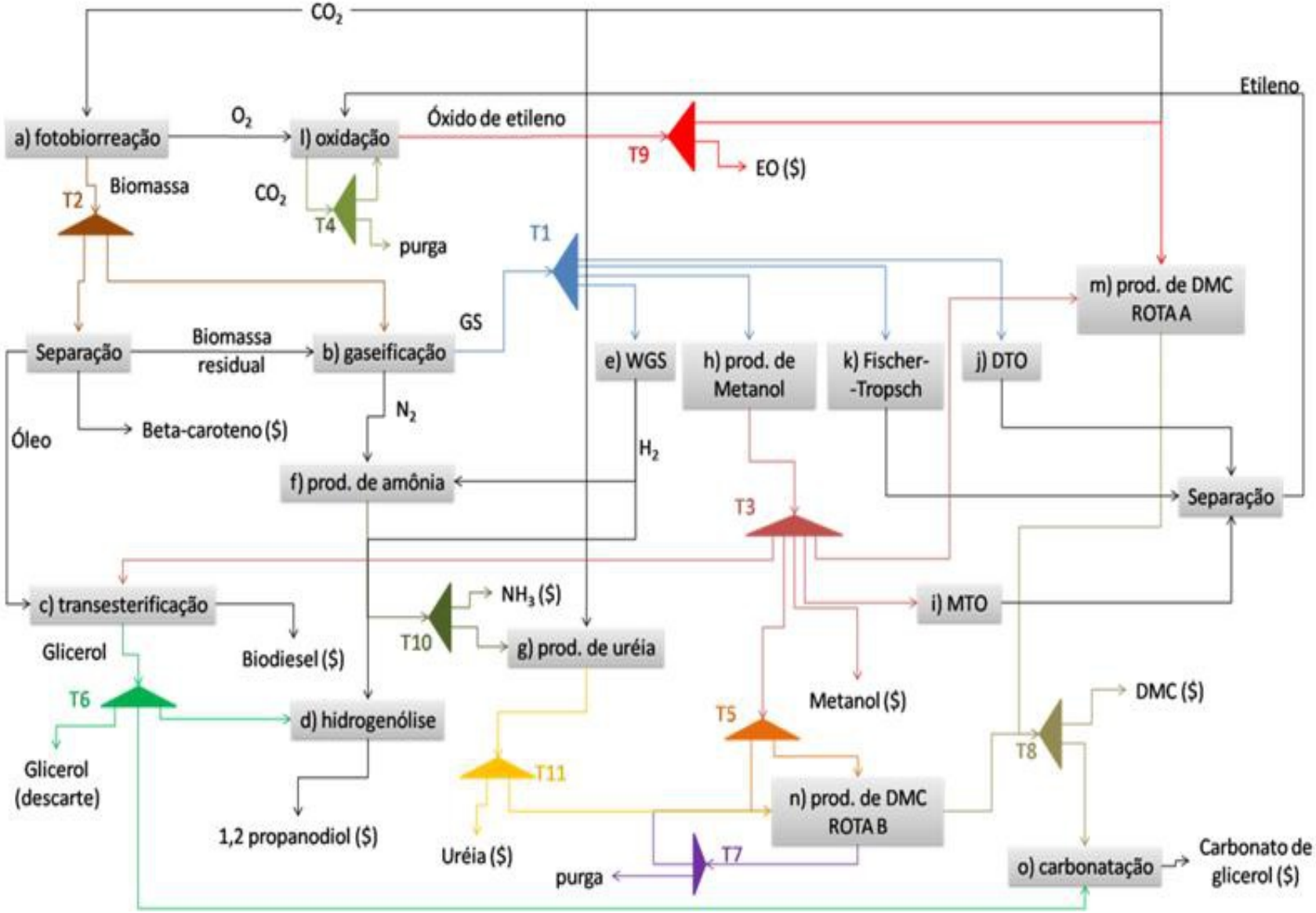
- CUSTOS OPERACIONAIS
- CRÉDITOS DE CARBONO

SEGURANÇA

- SEGURANÇA INTRÍNSECA

Minimize	Moderate
Substitute	Simplify

CO2TL
CCIS - SEQUESTRO BIO&QUIMICO DE CO_2



CCIS – SEQUESTRO BIO&QUIMICO DE CO_2

$$PEI(x,y) = \sum y \; P(i(x))$$

St

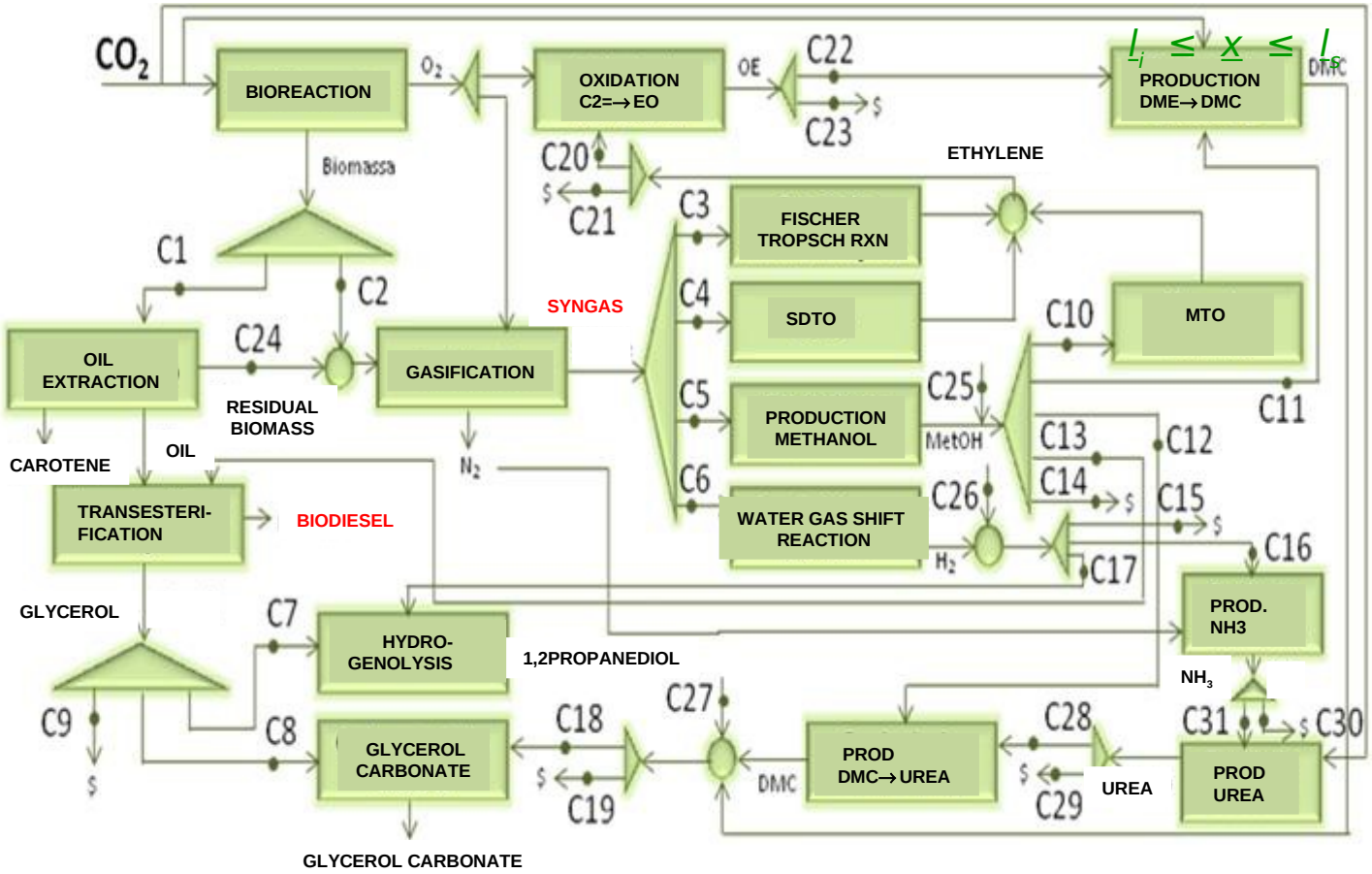
$$\underline{c}_i(\underline{x}) = 0$$

$$\underline{c}(\underline{x}) > 0$$

$$\underline{A}_i \, \underline{x} = \underline{b}_i$$

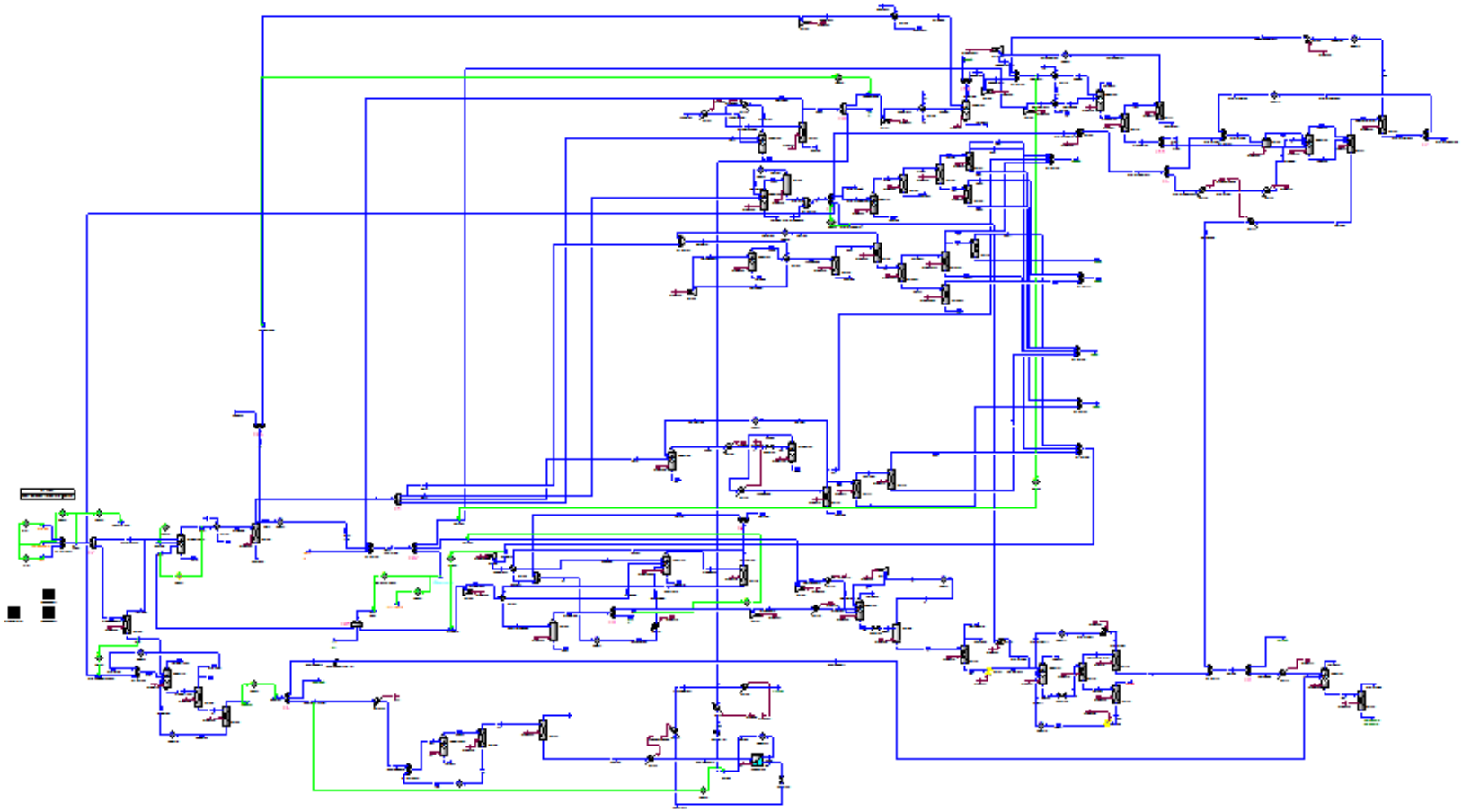
$$\underline{A} \, \underline{x} \leq \underline{b}$$

$$\underline{l}_i \leq \underline{x} \leq \underline{l}$$

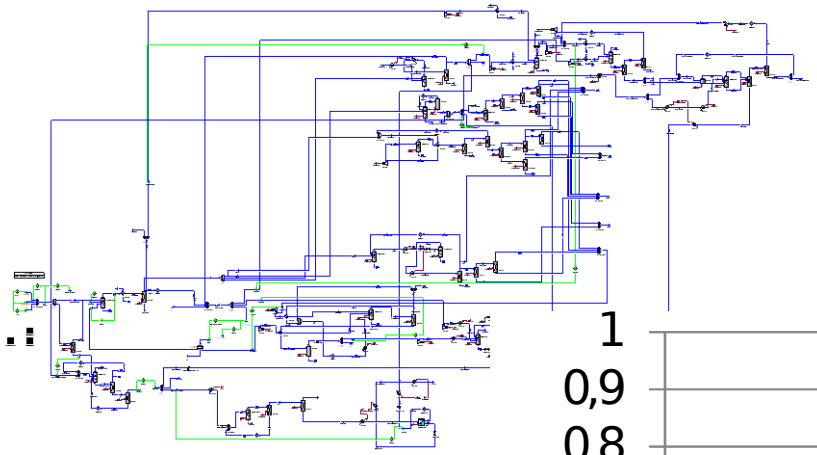


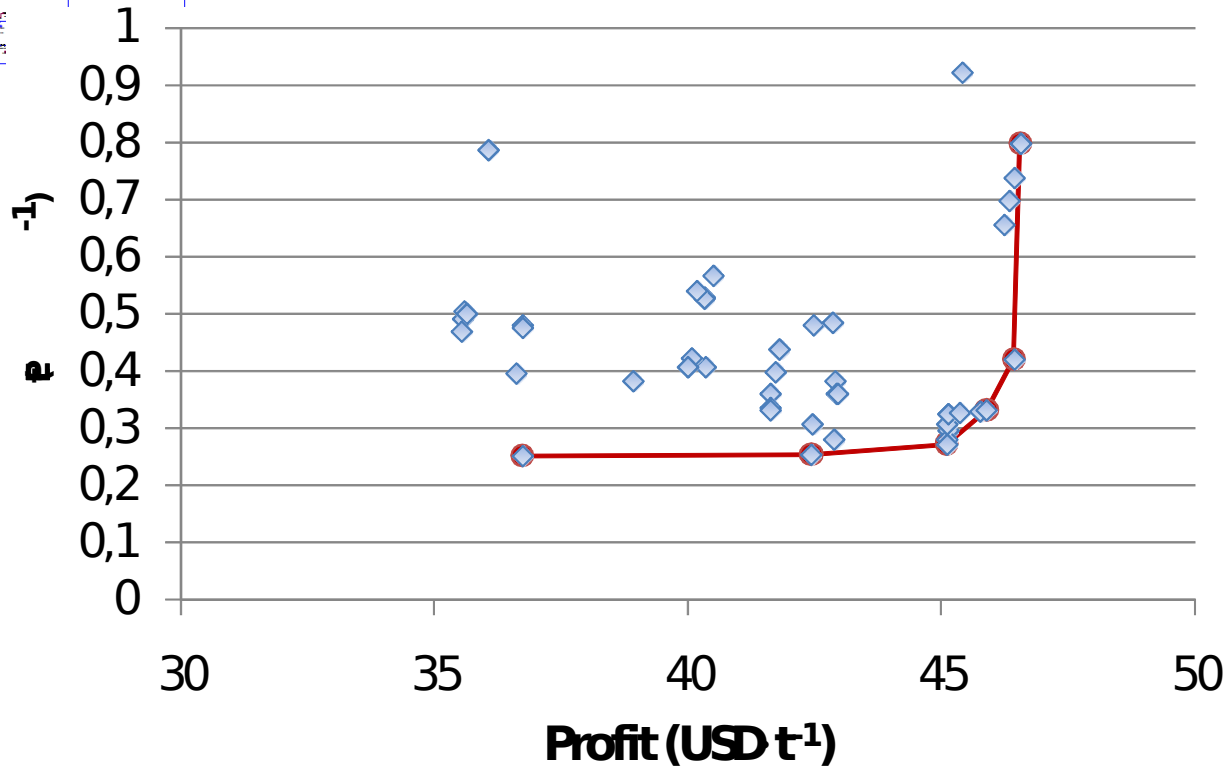
SEQUESTRO QUÍMICO DE CO_2

- ✓ 228 correntes de processo
- ✓ 115 operações unitárias
- ✓ 15 reciclos

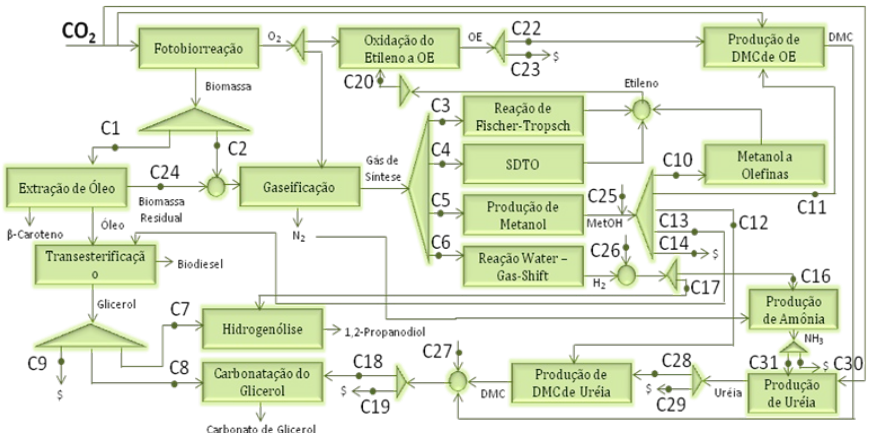


SEQUESTRO QUÍMICO DE CO_2

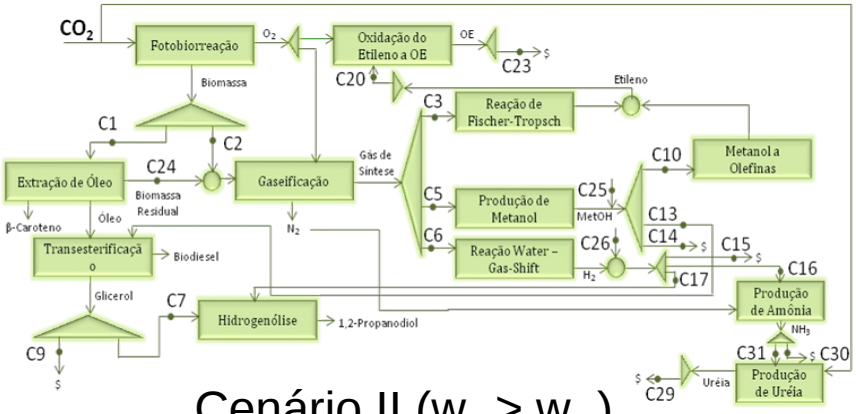




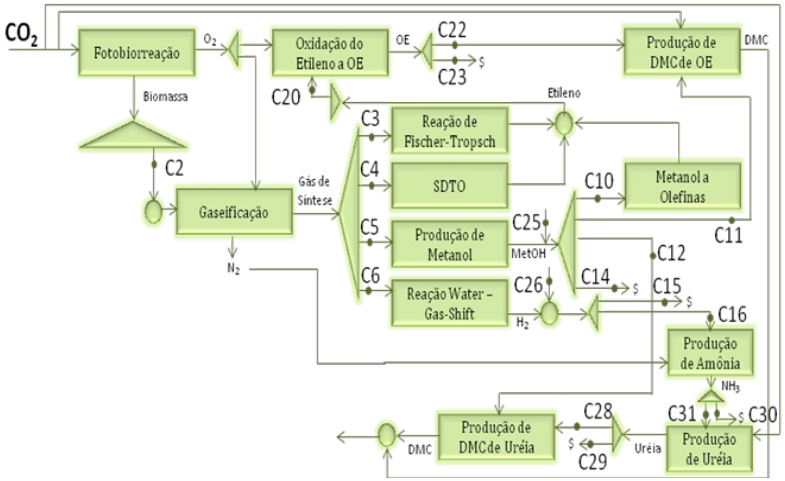
CCIS - SEQUESTRO BIO&QUIMICO DE CO_2



Cenário I ($w_L = w_{IA}$)



Cenário II ($w_L > w_{IA}$)



Cenário III ($w_L < w_{IA}$)

2ª LEI DA TERMODINÂMICA X FOTOSSÍNTESE *INDOORS*

FOTOSSÍNTESE *INDOORS* - SUSPENSÃO DE CÉLULAS VEGETAIS

Produto	Uso	Espécie Vegetal	Custo (US$/kg)
Ajmalicina	Antihipertensivo	*Catharanthus roseus*	37.000
Ajmalina	Antimalarial	*Rauvolfia sepentine*	75.000
Camptotecina	Antitumor	*Camptotheca acuminata*	432.000
Codeina	Sedativo	*Papacer somniferum*	17.000
Colchicina	Antitumor	*Colchium autumnale*	35.000
Elipticina	Antitumor	Orchrosia elliptica	240.000
Morfina	Sedativo	*Papaver somniferum*	340.000
Xiconina	Antibacterial	*Lithospermum erythrorhizon*	4.500
Taxol	Anticâncer	*Taxus brevifolia*	600.000
Vinblastina	Antileucêmico	*Catharanthus roseus*	1.000.000
Vincristina	Antileucêmico	*Catharanthus roseus*	2.000.000

✓**Viabilidade econômica do processo fortemente definida pela produtividade**.

✓Agregação, alta concentração de biomassa (acima de 70g de biomassa seca por litro), resultando em **suspensões de alta viscosidade, com características não-Newtonianas**

FOTOSSÍNTESE *INDOORS* - SUSPENSÃO DE CÉLULAS VEGETAIS

Substância Química	MM (g/gmol)	Índice Técnico (t/tCO_2)	Produção Calculada (t/a)
CO_2	44	1.00	-
H_2O	18	0.41	-
$C_6H_{12}O_6$	180	0.68	28145.45
O_2	32	0.73	30021.82

$$6CO_2(g) + 6H_2O(l) = C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta G_1^2 = +2458\ kJ/mol\ Glicose$$

$$\frac{17}{4} C_6H_{12}O_6(s) = CH_3(CH_2)_{14}(CH)_2COOH(l) + \frac{15}{2} CO_2(g) + \frac{17}{2} H_2O(l) \quad \Delta G_2 = +448\ kJ/mol$$

Espécie	Mol g/mol	Coeficiente Técnico tÓleo/tGlicose	Consumo Estequiométrico (t/a)	Produção (t/a)	Perdas (t/a) com metabolismo secundário
$C_6H_{12}O_6$	180	1.00	25893.8		2251.6
$C_nH_{2(n-w)}O_2$	279.82	0.37		9606.4	
CO_2	44	0.62		10928.1	
H_2O	18	0.02		5359.2	

$$EE^{MIN} = 106.5 * 10^6\ kWh/a$$

R$43,00/kg óleo

Óleo = produto com valor inferior a US$ 3/kg

Economicamente inviável usar-se Luz Elétrica para converter CO_2 em Glicose sem que algum outro produto com preço acima de US$100/kg seja formado simultaneamente

PARCERIAS

PETROBRAS

- ✓ HDT e HCC de Frações de Petróleo
- ✓ Processos Gas Lift
- ✓ Processamento de Gás Natural
- ✓ Separação de CO_2 de Gás Natural por Alcanolaminas
- ✓ Separação de CO_2 de Gás Natural por Membranas
- ✓ Simulação e controle de processos *offshore*

TRANSPETRO

- ✓ Detecção de Vazamentos em Redes de Escoamento

Braskem

- ✓ HDT de Pygas
- ✓ Detecção de Vazamentos – Etenoduto
- ✓ Engenharia de Processos Verdes

Twister
Supersonic Gas Solutions

- ✓ Separador supersônico
- ✓ Processamento de Gás Natural

utc engenharia

- ✓ Análise de Sistemas de Alívio de Pressão

MPX
An EBX Group Company

- ✓ Captura e Sequestro de CO_2
- ✓ Análise de Viabilidade de Processos