



3rd Latin American CFD Meeting
Applied to Oil & Gas Industry

August 18 - 19, 2008

Mirador Rio Hotel - Rio de Janeiro, Brazil

OXYCHLORINATION FLUID BED REACTOR MODELLING AND SIMULATION

Jeã Carlos Santos Moreira (RLAM/OT)

<jea.carlos@petrobras.com.br>



www.cfdoil.com.br

PVC Trade

The PVC world demand for the next 5 years is estimated in 10 million ton but only 6,5 million tons will be added in new plant capacities. In Brazil 560 thousand ton until 2010.

Experts forecast an yearly growth rate of 4,5% for the PVC world consumption, mainly because in the emerging countries such as China, India and Brazil. Projections for South America and Brazil indicate yearly growth of 5% and 7%, respectively.

The South America PVC production capacity is only 1,4 million tons a year and the per capita consumption is of 4 kg for inhabitant a year in Brazil and 3 kg in Argentina. On the other hand, in Europe and in the United States, 15 kg of PVC are used by inhabitant a year. In China, where the market PVC expansion is one of the largest of the world, the consumption is of 7 kg.

Problem characterization



The goal was develop a model for the simulation a fluidized bed oxychlorination reactor in order to investigated through the sensitivity analysis the effect of different parameters which influence the reactor performance and then apply optimization using a commercial software.

Oxyreactor Parameters



ϵ_{mf}	u_o/u_{mf}	H_{mf} (m)	H (m)	Fr_{mf}	d_p (μm)	d_{eq} (m)
0,48	436	8,1	11,1	0,00151	45	0,27

Fr_{mf} is the Froude number at minimum fluidization conditions. **characterizes the quality of the fluidização (<0,13 indicative of particle fluidization)**

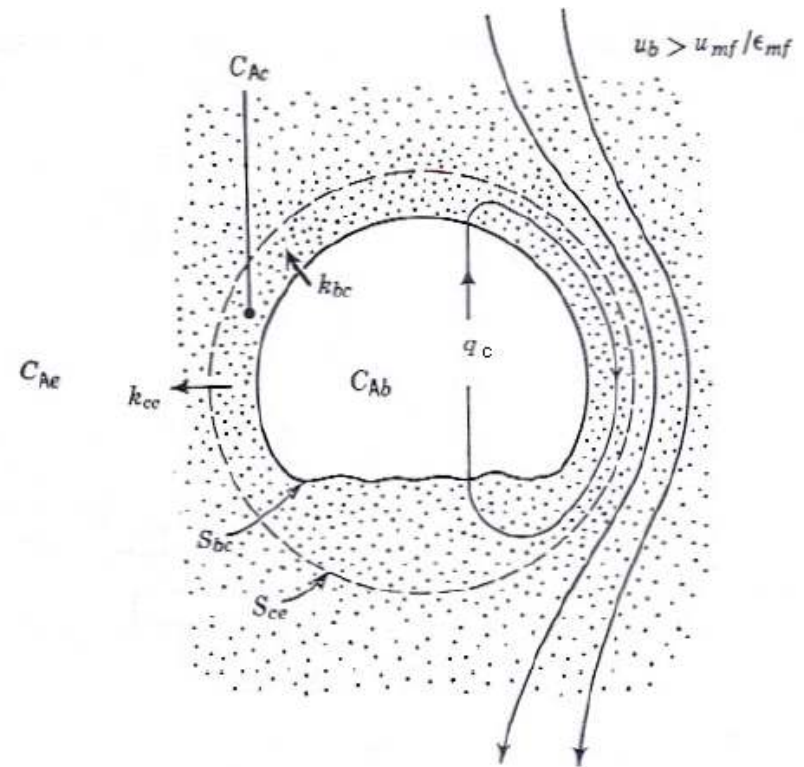
u_o/u_{mf} is the ratio between the feeding speed and the fluid surface velocity in the minimum fluidization conditions. **Indicates the potential of particle drag or the bed channeling**

Particle Fluidynamic

The two-phase fluidized bed model (bubble – emulsion)

Fluid Surface velocity in minimal fluidization condition:

$$u_{mf} = \frac{d_p^2 (\rho_s - \rho_g) g}{1650 \mu}$$



Particle Fluidynamic

Bubble diameter:

$$d_{eq,m} = 0,374 \left\{ \pi D^2 (u_o - u_{mf}) \right\}^{0,4}$$

$$d_{eq,o} = 0,374 \left\{ A_o (u_o - u_{mf}) \right\}^{0,4}$$

$$d_{eq} = d_{eq,m} - (d_{eq,m} - d_{eq,o}) e^{-\frac{0,3Z}{D}}$$

Relative velocity:

$$u_{br} = 0,711 (gd_b)^{1/2}$$

Absolute Velocity:

$$u_b = u_o - u_{mf} + u_{br}$$

Particle Fluidynamic

Void fraction at minimal fluidization:

$$\varepsilon_{mf} = 0,586 \left(\frac{1}{Ar} \right)^{0,029} \left(\frac{\rho_f}{\rho_p} \right)^{0,021} \quad Ar = (\rho_p - \rho_f) g \left(\frac{\rho_f d_p^3}{\mu^2} \right)$$

Catalytic bed Porosity:

$$\varepsilon = 1 - (1 - \delta)(1 - \varepsilon_{mf})$$

Bed height:

$$\frac{L_f}{L_{mf}} = \frac{1 - \varepsilon_{mf}}{1 - \varepsilon_f} = \frac{\rho_{mf}}{\rho_f}$$

Hypotheses



The two-phase fluidized bed is a valid model

The one-dimension model with heat and mass axial scattering is valid

The chemical reaction occurs only during the emulsion phase

The catalyst particle elutriation outward the bed is not being considered

The chosen reaction network is represented by five chemical reactions: oxychlorination, dehydrochlorination of the 1,2-dichloroethene, oxidation of ethene for CO and CO₂, formation of chloride

Diffusivity and the coefficient of convection remain constant in the axial direction

The reactor is adiabatic

Mass Balance



Bubble Phase:
$$\frac{dN_{ib}}{dz} = A_b (k_{be}) \left(\frac{N_{ie}}{Q_e} - \frac{N_{ib}}{Q_b} \right)$$

$$\left(\frac{N_{ib}}{Q_b} - \frac{N_{ie}}{Q_e} \right) = \left(\frac{N_{iF}}{Q_F} - \frac{N_{ie}}{Q_e} \right) e^{-\sigma_i z} \quad \sigma_i = \frac{(K_{be})_{ib}}{u_b}$$

Emulsion Phase:

$$N_{ie} = N_{ieF} + \int_0^H (k_{be})_{ib} A_b \left(\frac{N_{iF}}{Q_F} - \frac{N_{ie}}{Q_e} \right) e^{-\sigma_i z} dz + V(1-\delta)(1-\varepsilon).r_i$$

$$N_{ie} = \frac{Q_e}{Q_F} N_{iF} + \overline{u_b} A_b \left(\frac{N_{iF}}{Q_F} - \frac{N_{ie}}{Q_e} \right) (1 - e^{-\sigma_i z}) + V(1-\delta)(1-\varepsilon).r_i$$

Energy Balance



Bubble Phase:

$$u_b \rho_f C_{pf} \frac{dT_b}{dz} = -(H_{be})_b (T_b - T_e)$$

$$z = 0 \Rightarrow T_b = T_F; T_e = T_F$$

$$u_b \rho_f C_{pf} \int_{T_F}^{T_b} \frac{dT_b}{(T_e - T_b)} = (H_{be})_b \int_0^z dz$$

$$u_b \rho_f C_{pf} \cdot \ln \frac{T_e - T_b}{T_e - T_F} = -(H_{be})_b z$$

$$T_b = T_e - (T_e - T_F) e^{-\beta z}$$

$$\beta = \frac{(H_{be})_b}{u_b \rho_f C_{pf}}$$

Energy Balance



Emulsion Phase:

$$Q_{e,F} \rho_{f,F} C_{p,f,F} (T_F - T_{ref}) - Q_{e,o} \rho_{f,o} C_{p,f,o} (T_e - T_{ref}) + \int_{z=0}^H (H_{be})_b (T_b - T_e) A_b dz +$$

$$+ V(1 - \delta)(1 - \varepsilon) \sum_{j=1}^n (-\Delta H_{rj}) r_j + UA_w (T_w - T_e) = 0$$

$$UA = \frac{1}{\frac{1}{h_i A_i} + \frac{\ln(D_o / D_i)}{2\pi k L} + \frac{1}{h_w A_w}}$$

$$Nu_D = 0,023 Re_D^{4/5} Pr^{0,4} \quad h_i = Nu_D \frac{k}{D_i}$$

$$h_w = 0,01844 \cdot C_R \cdot \frac{K_g}{d_p} (1 - \varepsilon) \left(\frac{\rho_g C_{pg}}{K_g} \right)^{0,43} \left(\frac{d_p \rho_g u_o}{\mu} \right)^{0,23} \left(\frac{C_{ps}}{C_{pg}} \right)^{0,8} \left(\frac{\rho_p}{\rho_g} \right)^{0,66}$$

Mathematic Model- Molecular Diffusion



The “i” component mass flow is given by the Fick’s Law for molecular diffusion:

$$N_i = -cD_{mi} \nabla x_i$$

Diffusion coefficient for no polar gases (Equation of Chapman-Enskog):

$$D_{AB} = b \times 10^{-3} \frac{T^{3/2}}{P \sigma_{AB}^2 \Omega_D} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}$$

To polar componentes:

$$\Omega_D = \Omega_D^* + \left(0,196 \frac{\partial_{AB}^2}{T^*} \right) \quad (\text{Brokaw})$$

Mathematic Model- Molecular Diffusion Coefficient



Stefan-Maxwell:

$$D_{i,m} = \frac{N_i(1 - y_i) - y_i \sum_{j \neq i}^n N_j}{\sum_{j \neq i}^n \frac{1}{D_{i,j}} (y_i N_j - y_j N_i)}$$

The effective diffusivity is obtained by considering $\alpha_i = 0$ (diffusion controlled by chemical reaction over the surface of the catalyst):

$$N_i = \alpha_i y_i \sum N_i - c D_{ief} \nabla y_i$$

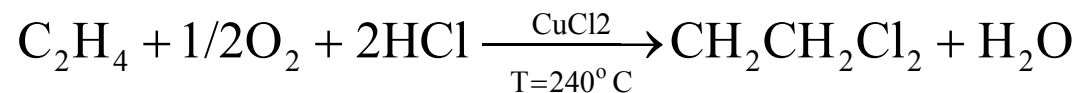
Then,

$$D_{ief} = \frac{1}{\sum_{\substack{j=1 \\ i \neq j}}^n \frac{y_i}{D_{i,j}} \left[1 - \frac{y_i}{y_j} \frac{N_j}{N_i} \right]}$$

Kinetic Model



For the main reaction a kinetics model following the Langmuir-Hinshelwood theory was used. For the remaining 4 reactions, empirical kinetics models proposed by Gel'Perin *et al.* (1979a) were used.

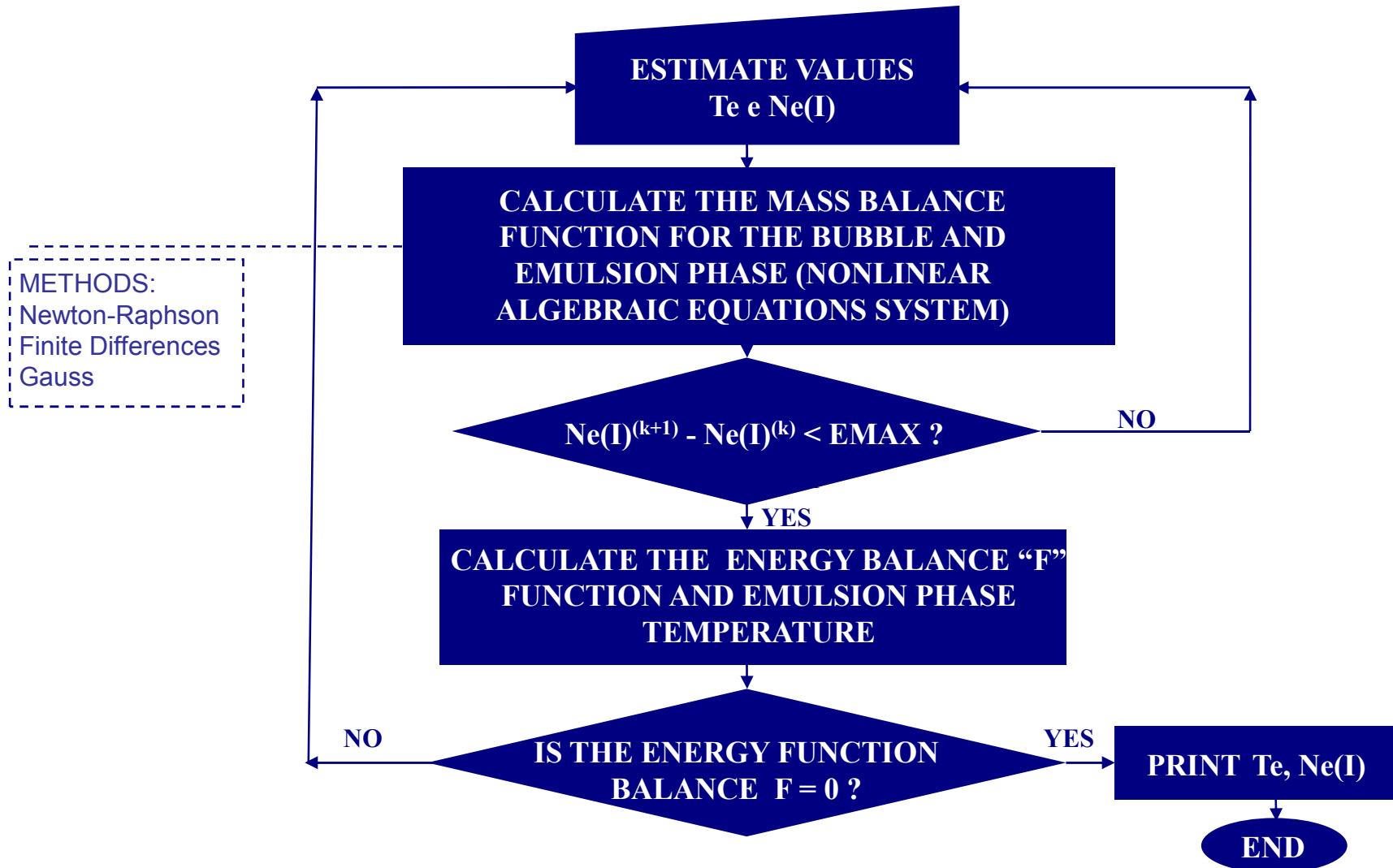


Langmuir-Hinshelwood

$$r = \frac{k_r K_a C_E C_c}{1 + K_a C_E}$$

$$k_r = 269 \exp(-37,8/RT) ; K_a = 0,63$$

Algorithm



Results – Conditions for Model



Reactor pressure: 3,8 kgf/cm²g

Temperature of the emulsion phase: 240 °C

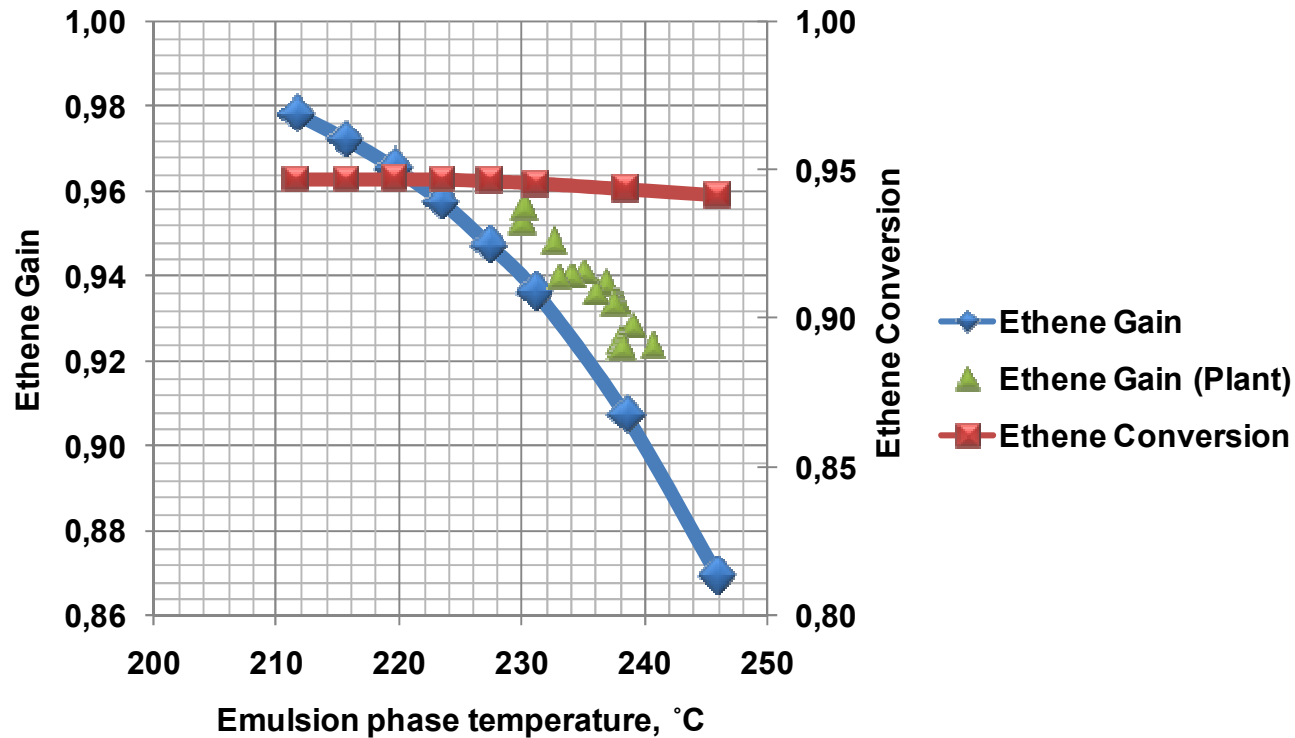
Feed temperature: 154 °C

Temperature of the cooling water: 200 °C

Parameters	Plant	Model	Relative Deviation %
Residence time, s	35,35	35,27	-
Ethene conversion, %	96,39	94,39	2,08%
Ethene gain, %	97,61	95,99	1,65%

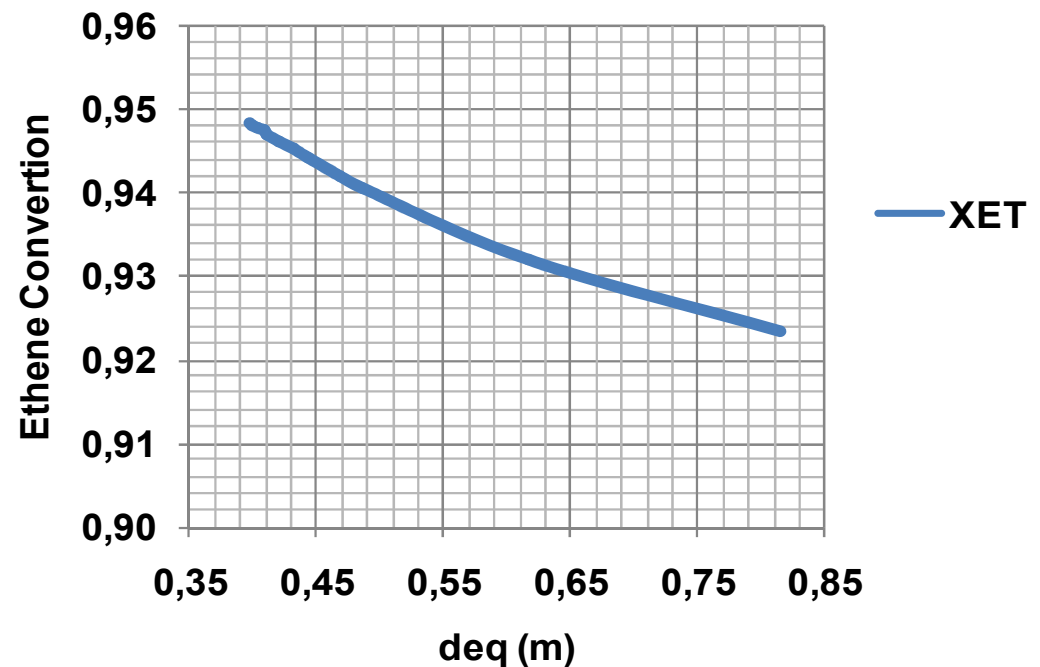
Results – Emulsion Phase Temperature

The temperature rise reduces the selectivity of the reaction. Such reduction in the selectivity as well the temperature rise can be observed by the higher formation of CO and CO₂.



Results – Bubble Diameter

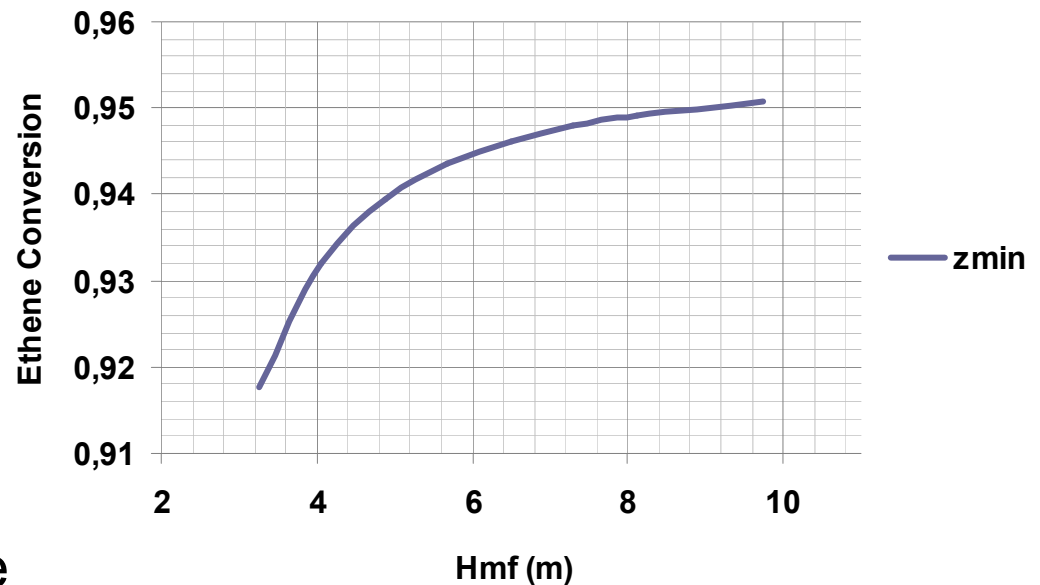
When the bubble diameter increases mass transfer between the bubble phase and the emulsion decreases. Besides, an increase in the bubble diameter favors a higher transportation of non-reacted gas through the bed, once reagents will not meet the catalyst particles.



Results – Bed Height



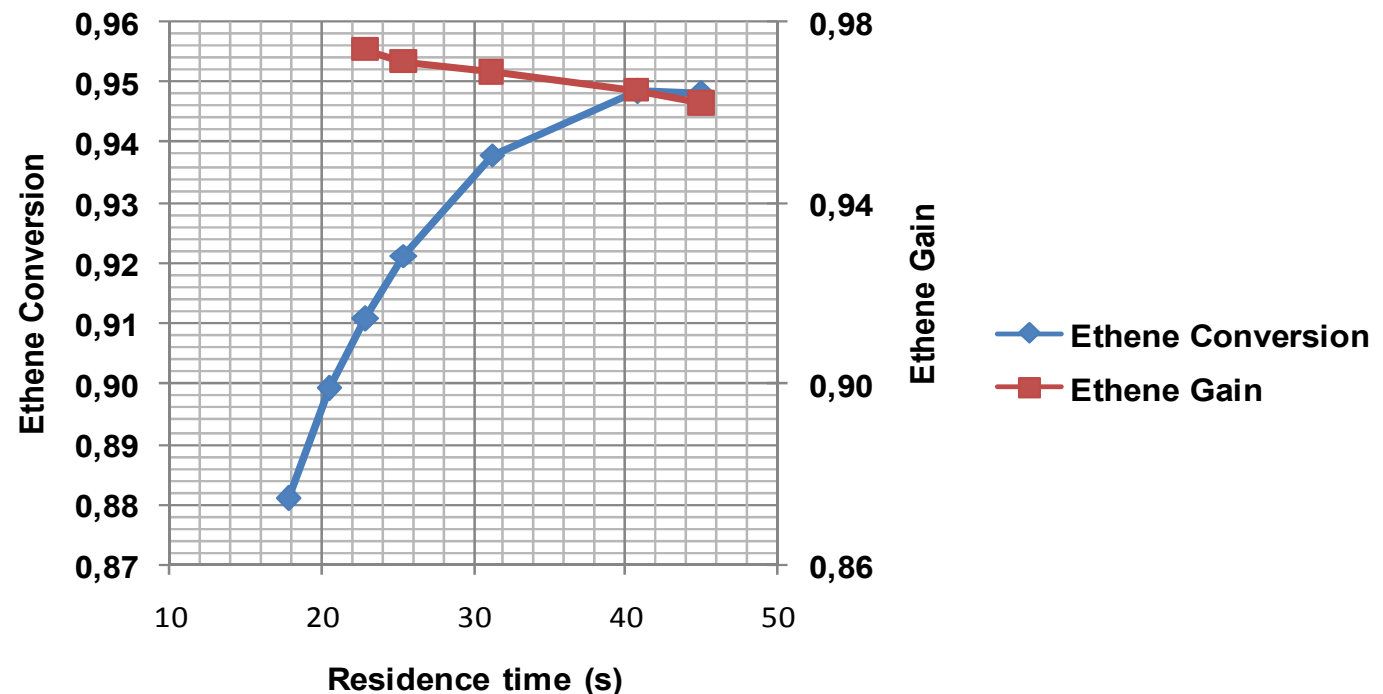
Only about 5% of the catalyst is used for the reaction. Light variations in bed height at minimum fluidization have outstanding effects over the conversion up to 8 m. Beyond this value, any trials to increase the catalyst concentration in the bed to promote increases in the ethene conversion, become economically not feasible. For the expanded bed, this point corresponds to 9 m height.



Results – Residence Time



Decreasing in the gas surface velocity, the residence time increases and the average bubble size decreases as the interface mass and energy transfer increases. An increase in residence time will produce a reduction in selectivity what can be explained by the parallel reactions.



Final Comments



The pseudo-homogeneous model hypothesis is valid and it was possible to conclude that the diffusion process does not pose as a limiting phase for this system.

The optimized values for the residence time tend to be closed to 24 s for systems with recycle. Non-converted ethene may be reprocessed.

Variations in bed heights have effect on reaction gains up to 9 m; above this value, investments in catalyst quantity increase become economically impracticable as a way to increase ethene conversion.

Develop a simulation applying multi-dimension model (CFX, Fluent, ...):

Varying the distributor design to control bubbles diameters by limiting their size and thus, enlarging the feasible area for mass and energy transfer between phases. Besides, the larger reagents volume, confined inside the bubbles, favors the passage of gas through the bed without its contact with the catalyst particles. Some accessories such as baffles can be used for reduction of bubbles diameter. Analyzer effect of PSD (multi-phase).