PACKED BED REACTOR SIMULATION FOR ACETALDEHYDE PRODUCTION BY ORTHOGONAL COLLOCATION

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Introduction. Acetaldehyde can be produced in the industry through petrochemical process or alcohol-chemical process. Petrochemical process has relatively low conversions (less than 72%) and yields (less than 95%) and silver is usually employed as catalyst besides being a very expensive metal, is hard to recover it downstream **(1)**. The alcohol-chemical way is a low price process and is viable in agricultural countries, now that they dispose of raw materials like sugar cane and rice for fermentative process in ethanol production, that is forward used in vapor phase partial oxidative process to produce acetaldehyde **(1)**.

Studies reveal the best operating conditions for acetaldehyde production from partial ethanol oxidation as being in the temperature range of 350-420 K at atmospheric pressure, an air/ethanol ratio between 3 and 22 and over a conventional Fe/Mo catalyst, under these conditions only acetaldehyde is detected by gas chromatography **(1, 2)**. Out of these process conditions (specially temperature) undesired products are gotten like acetic acid or carbon dioxide, for this reason the process viability depends on the reactor temperature control. The reaction rate for the ethanol transformation to acetaldehyde has been studied under the Dante and Temkin mechanisms, being the Temkin's one which gives the best correlation when high conversions are considered **(1)**.

Filho and Domingues proposed a baffled multitubular reactor but windowless to avoid parallel flow regions between the coolant flow and the reaction tubes, it guaranties the temperature control **(1)**. These reactor disposals increase its design and operation, now that each baffled region should be fed with different coolant conditions to ensure the reactor temperature control.

The reactor simulation allows you to evaluate the axial changes of concentration and temperature when the process conditions change. The reactor model numerical solution is a critical aspect due to mistakes propagation and the inherent instability of the numerical methods used in the solution of these kinds of problems **(3, 4)**. The most used methods in the solution of diffusion-reaction problems are perturbation method and methods that used weighted residuals like orthogonal collocation (OC) and orthogonal collocation on finite elements (OCFE) that used orthogonal polynomials like Legendre or Hermite polynomials **(3, 4)**.

The aim of this work is to get the concentration and temperature profiles for the gas phase reaction between ethanol and air in a packed bed reactor with Fe/Mo catalysts with sphere shape and the coolant temperature profile by one-dimensional simulation under pseudo-homogeneous and heterogeneous non-isothermal models using the OC and OCFE methods to solve the model. A parametric sensitivity was made with the main process variables.

Methods. The pseudo-homogeneous and heterogeneous non-isothermic models differ each other in the consideration of the concentration and temperature interface gradients between the bulk and catalyst pellet surface **(4, 5)**.

The axial dispersion in the model is evidenced by the second order of the differential equations for the mass and energy balance, the problem is reduced to solve differential equations with boundary value that can be of Newman, Dirichlet or Robin type.

Besides the differential balances over the bulk is necessary the coolant energy balance to evaluate its axial temperature changes due to the heat transfer between the reaction bulk and coolant flow. The coolant physic-chemical properties belong to the Dow Therm Teresso 77.

The differential mass and energy balance over the catalyst pellet complete the reactor description, they involve the effective transport properties. This is a boundary condition problem too, where available information is in the middle and the surface of the pellet. The last one is given by the reactor model.

The Temkin's reaction rate mechanism for the global reaction of the ethanol partial oxidation is:

$$CH_3CH_2OH + 1/2O_2 \Rightarrow CH_3CHO + H_2O$$

$$1.\ CH_3CH_2OH + ZO_2 \xrightarrow{K_1} CH_3CHO + H_2O + ZO$$

$$2.\ O_2 + Z \xrightarrow{K_2} ZO_2$$

$$3.\ CH_3CHO + Z \overset{K_3}{\longleftrightarrow} ZCH_3CHO$$

$$4.\ ZCH_3CHO + H_2O \xrightarrow{K_4} CH_3CH_2OH + ZO$$

Which analyzed under the hypothesis that 1, 2 and 4 are slow and irreversible and step 3 is in equilibrium and oxygen is molecularly absorbed without dissociation in only one active site, the reaction rate equation is **(1)**:

$$(\gamma) = \frac{2K_1K_2P_{O2}P_{Et}}{K_1P_{Et} + 2K_2P_{O2} + K_3K_4P_{Ac}P_{H2O} + K_3K_1P_{Et}P_{Ac}} \quad (1)$$

The application of the conservative laws over the reactor generates the mass (2), energy (3) and momentum (4) bulk balances and the energy balance for the coolant (5). For the momentum balance was used the Ergun´s equation **(4)**.

$$(D_x)\frac{d^2C_A}{dx} - (\upsilon_x)\frac{dC_A}{dx} = \rho_B\eta(-\gamma_{AW}) \quad (2)$$

$$K_x\frac{d^2T}{dx^2} - (\rho\upsilon_xC_p)\frac{dT}{dz} = -\rho_B\eta(-\gamma_{AW})(-\Delta H_{RA}) + \frac{4}{d_T}U(T - T') \quad (3)$$

$$\frac{dP}{dx} = -f\frac{\rho\upsilon_x^2}{d_p} \quad (4)$$

$$(\pm)\frac{dT'}{dx} = \frac{U\pi d_TN_T(T - T')}{\dot{m}_mC_{pm}}$$

$$\text{Co - current } (+) \text{ , } \vee \text{ , Counter – current } (-)$$

(5)

The mass and energy boundary conditions for the bulk are:

$$x = 0 \rightarrow C_A = C_{AR} + \left(\frac{D_x}{\upsilon_x}\right)\left.\frac{dC_A}{dx}\right|_{x=0}$$

$$T = T_{AR} + \left(\frac{K_x}{\rho\upsilon_xC_p}\right)\left.\frac{dT}{dx}\right|_{x=0}$$

$$x = L \rightarrow \frac{dC_A}{dz} = 0$$

$$\frac{dT}{dx} = 0$$

While the coolant energy balance and the bulk momentum balance have initial conditions, the coolant condition can vary according to its flow course.

$$x = 0 \rightarrow T' = T_m \text{ (co - current)}$$

$$P = P_{AR}$$

$$x = L \rightarrow T' = T_m \text{ (counte- current)}$$

The mass and energy transfer from the bulk to the catalytic pellet balances over the catalytic pellet can or not consider interface gradients between them. This consideration modifies the boundary conditions of the mass (6) and energy (7) balances for the catalytic pellet.

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dC_A}{dr}\right] = \frac{(-\gamma_{AW})\rho_B}{D_{eff}} \quad (6)$$

$$\frac{d}{dr}\left[r^2\frac{dT}{dr}\right] = -\frac{(-\Delta H_{RA})(-\gamma_{AW})\rho_Br^2}{K_{eff}} \quad (7)$$

The mass and energy boundary conditions for the pseudo-homogeneous model are:

$$r = 0 \rightarrow \frac{dC_A}{dr} = 0$$

$$\frac{dT}{dr} = 0$$

$$r = R \rightarrow C_A = C_{Ao}$$

$$T = T_o$$

while the mass and energy boundary conditions for the heterogeneous model are:

$$r = 0 \rightarrow \frac{dC_A}{dr} = 0$$

$$\frac{dT}{dr} = 0$$

$$r = R \rightarrow -D_{eff}\frac{dC_A}{dr} = K_ga_m(C_{As} - C_{Ao})$$

$$-K_{eff}\frac{dT}{dr} = ha_m(T_s - T_o)$$

The simultaneous solution of the mass (6) and energy (7) balances over the catalytic pellet under the conditions of each model and for every axial bulk concentration and temperature point through the reactor allows you to calculate the effectiveness factor (η) that is defined as:

$$\eta = \frac{\phi^2\int_0^1 R_1(c(r), T(r))r^{a-1}dr}{\phi^2\int_0^1 R_1(c(1), T(1))r^{a-1}dr}$$

The OC method was employed to solve the pellet differential balances for the pseudo-homogeneous model and the OCFE method was employed to solve the pellet differential balances for the heterogeneous model and reactor balance equations. These methods reduce the problem to a system of non-lineal algebraic equations (that was solved by the Newton-Raphson method); each algebraic equation is function of the concentrations and temperatures at the collocation points that are unknown variables of the system.
Both methods OC and OCFE require normalization of the differential equations system due to the definition range of the Legendre orthogonal polynomials (OP) between 0 and 1.

These OP were employed in the expansion of the assay function. For this reason, it is settled down dimensionless variables to normalize the balance equations of the reactor and catalytic pellet.

For the pellet

$$z=\frac{r}{R}\ ;\ \theta=\frac{T}{T_o}\ ;\ u=\frac{C_A}{C_{Ao}}\ ;\ f(u,\theta)=\frac{(-\gamma_{AW})}{(-\gamma_{AW})_o}$$

For the reactor

$$y=\frac{x}{L}\ ;\ \tau=\frac{T}{T_{AR}}\ ;\ \zeta=\frac{C_A}{C_{AR}}$$

$$\psi=\frac{T_m}{T_{AR}}\ ;\ \varphi=\frac{P}{P_{AR}};\ f(\zeta,\tau)=\frac{(-\gamma_{AW})}{(-\gamma_{AW})_{AR}}$$

The normalized mass (8) and energy (9) balance equations of the catalytic pellet generate the dimensionless groups of Thiele (ϕ) and Prater (β).

$$\frac{1}{z^2}\frac{d}{dz}\left[z^2\frac{du}{dz}\right]=\phi^2 f(u,\theta) \qquad (8)$$

$$\frac{1}{z^2}\frac{d}{dz}\left[z^2\frac{d\theta}{dz}\right]=-\phi^2\beta f(u,\theta) \qquad (9)$$

The normalized mass and energy boundary conditions for the pseudo-homogeneous model are:

$$z=0\ \rightarrow \frac{du}{dz}=0$$

$$\frac{d\theta}{dz}=0$$

$$z=1\rightarrow\ u=1$$

$$\theta=1$$

while the normalized mass and energy boundary conditions for the heterogeneous model are:

$$z=0\ \rightarrow \frac{du}{dz}=0$$

$$\frac{d\theta}{dz}=0$$

$$z=1\rightarrow -\frac{d\theta}{dz}=Bi_h(\theta_{(1)}-1)$$

$$-\frac{du}{dz}=Bi_m(u_{(1)}-1)$$

The normalized mass (10), energy (11) and momentum (12) bulk balance equations and the coolant energy balance equation (13) in the reactor generate additionally the dimensionless groups of Peclet for mass and energy and Nusselt and involve the effectiveness factor.

$$\frac{d^2\zeta}{dy^2}-Pe_m\frac{d\zeta}{dy}=\Phi^2\eta f(\zeta,\tau) \qquad (10)$$

$$\frac{d^2\tau}{dy^2}-Pe_h\frac{d\tau}{dy}=-\Phi^2\beta_R\eta f(\zeta,\tau)+Nu(\tau-\psi) \qquad (11)$$

$$\frac{d\varphi}{dy}=-\frac{Lf}{P_{AR}}\frac{\rho\upsilon_x^2}{d_p} \qquad (12)$$

$$\frac{d\psi}{dy}=Bi_w(\tau-\psi) \qquad (13)$$

The normalized boundary conditions for the reactor balance equations are:

$$y=0 \qquad \zeta=1+\frac{1}{Pe_m}\frac{d\zeta}{dy}$$

$$\tau=1+\frac{1}{Pe_h}\frac{d\tau}{dy}$$

$$\varphi=1$$

$$\psi=\frac{T_m}{T_{AR}} \quad \text{(co - current coolant flow)}$$

$$y=1 \qquad \frac{d\zeta}{dy}=0$$

$$\frac{d\tau}{dy}=0$$

$$\psi=\frac{T_m}{T_{AR}} \quad \text{(counter - current coolant flow)}$$

The simultaneous solution of the mass and energy balance equations of the catalytic pellet for every of the studied models allow you to have the temperature in function of the concentration.

$$\theta_j=1+\beta(1-u_j)\ \text{(pseudo - homogeneous)}$$

$$\theta_j=1+\beta(u_{N+2}-u_j)+\beta\frac{Bi_m}{Bi_h}(1-u_{N+2})\ \text{(heterogeneous)}$$

Then the simultaneous solution of this and the pellet mass balance equation under the respectively boundary conditions let calculate the u_j for each collocation point.

The OC method was used to evaluate the mass balance residuals for the pseudo-homogeneous model (16), that is settled from 2 to N+1 (now that 1 and N+2 are boundary points that are held to their own conditions), in this case was used a fifth order Legendre orthogonal polynomial. The OCFE was used to evaluate the mass balance residuals for the heterogeneous model (17), in this case was used a fifth order Legendre orthogonal polynomial and the domain was divided into two elements (h_k = 0.5).

$$\sum_{i=1}^{N+2}\aleph_{ji}u_i-\phi^2 f(u_j,\theta_j)=0 \quad \text{where } j=2,3,\ldots,N+1 \qquad (16)$$

Boundary conditions

$$z = 0 \rightarrow \sum_{i=1}^{N+2} \mathfrak{R}_{1,i} u_i = 0$$

$$z = 1 \rightarrow u_{N+2} = 1$$

$$\frac{1}{h_k^2} \sum_{i=1}^{NP} \mathfrak{I}_{ji} u_i + \frac{2}{z_i h_k} \sum_{i=1}^{NP} \mathfrak{I}_{ji} u_i - \phi^2 f(u_j, \theta_j) = 0 \qquad (17)$$

where $j = 2, 3, \ldots, NP - 1$

Boundary conditions

$$z = 0 \rightarrow \frac{1}{h_k} \sum_{i=1}^{NP} \mathfrak{I}_{1,i} u_i = 0$$

$$z = 1 \rightarrow \frac{1}{h_k} \sum_{i=1}^{NP} \mathfrak{I}_{NP,i} u_i + Bi_m (u_{NP} - 1) = 0$$

The simultaneous solution of the non-lineal algebraic equations gotten from the pseudo-homogeneous or heterogeneous model gives the effectiveness factor.

$$\eta = \frac{3}{\phi^2} \sum_{i=1}^{N+2} \mathfrak{R}_{N+2,i} u_i \quad \text{(pseudo−homogeneous)}$$

$$\eta = \frac{3}{\phi^2} \sum_{i=1}^{NP} A_{NP,i} u_i \quad \text{(heterogeneous)}$$

The OCFE was used to solve the mass (18), energy (19), momentum (20) reactor balance equations and the coolant energy balance (21), for this case was used a tenth order Legendre polynomial and the domain was divided in four elements ($h_k = 0.25$)

$$\frac{1}{h_k^2} \sum_{J=1}^{NP} B_{IJ} \zeta_J - \frac{Pe_m}{h_k} \sum_{J=1}^{NP} A_{IJ} \zeta_J = \Phi^2 \eta f(\zeta_I, \tau_I) \qquad (18)$$

$$\frac{1}{h_k^2} \sum_{J=1}^{NP} B_{IJ} \tau_J - \frac{Pe_h}{h_k} \sum_{J=1}^{NP} A_{IJ} \tau_J = -\Phi^2 \beta_R \eta f(\zeta_I, \tau_I) + \chi$$

$$\chi = Nu \left[\tau_I - \frac{T_m}{T_{AR}} \right] \qquad (19)$$

$$\frac{1}{h_k} \sum_{J=1}^{NP} d_J (J-1) u^{J-2} = -\frac{Lf}{P_{AR}} \frac{\rho \upsilon_x}{d_p} \qquad (20)$$

$$\frac{1}{h_k} \sum_{J=1}^{NP} A_{IJ} \psi_J = Bi_W (\tau_I - \psi_I) \qquad (21)$$

con $i = 2, 3,.., NP - 1$

Boundary values

$$\zeta_1 = 1 + \frac{1}{h_k} \frac{1}{Pe_m} \sum_{J=1}^{NP} A_{1,J} \zeta_J \quad , \quad \frac{1}{h_k} \sum_{J=1}^{NP} A_{NP,J} \zeta_J = 0$$

$$\tau_1 = 1 + \frac{1}{h_k} \frac{1}{Pe_h} \sum_{J=1}^{NP} A_{1,J} \tau_J \quad , \quad \frac{1}{h_k} \sum_{J=1}^{NP} A_{NP,J} \tau_J = 0$$

$$\varphi \big|_{u=0} = 1 \quad , \quad \psi = \frac{T_m}{T_{AR}}$$

All the physic-chemical properties and transport properties were correlated to temperature and composition, and were calculated at each collocation point (data not shown).

Results and Discussion. The concentration and temperature profiles of each model (pseudo-homogeneous and heterogeneous) for the catalytic pellet showed mean statistics differences lower than 1% between them (data not shown). In the Fig. 1 are shown the dimensionless concentration profiles and can be noticed that the difference between the models are at higher temperatures, this is due to the fact that near the 420 K is the higher yield and the transport properties (mainly diffusion) are sensible to little changes of composition at higher temperatures.

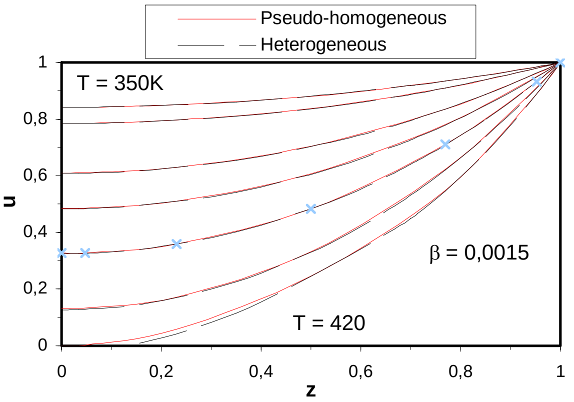


Fig. 1 Dimensionless concentration profiles in the catalytic pellet for the pseudo-homogeneous and heterogeneous models at different bulk temperatures and a Prater number of 0.0015.

The effectiveness factor was gotten for different catalytic shapes (slab, cylinder and sphere), Fig 2. shows a normal behavior at different Thiele module values, the spherical shape has the higher effectiveness factor. The comparison of the effectiveness factor for the spherical shape under the pseudo-homogeneous and heterogeneous models evidence that the effectiveness factor is greater for the heterogeneous model in the way the Thiele module increases, but this difference is less at low Prater numbers Fig. 3.

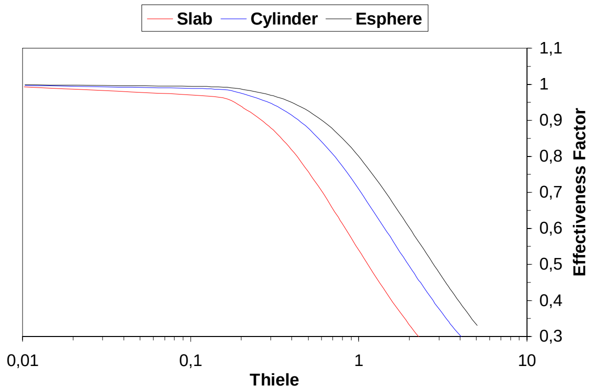


Fig. 2 Effectiveness factor for different pellet geometry shapes.

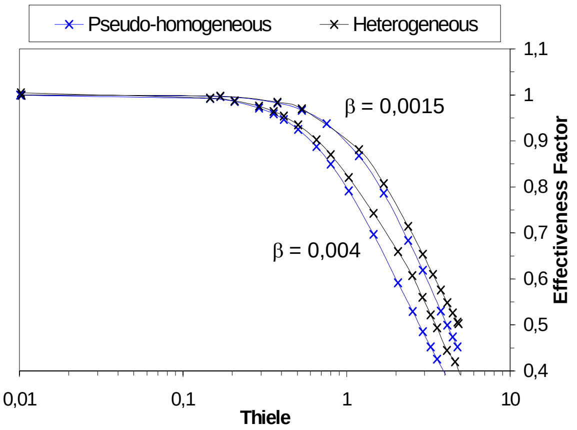
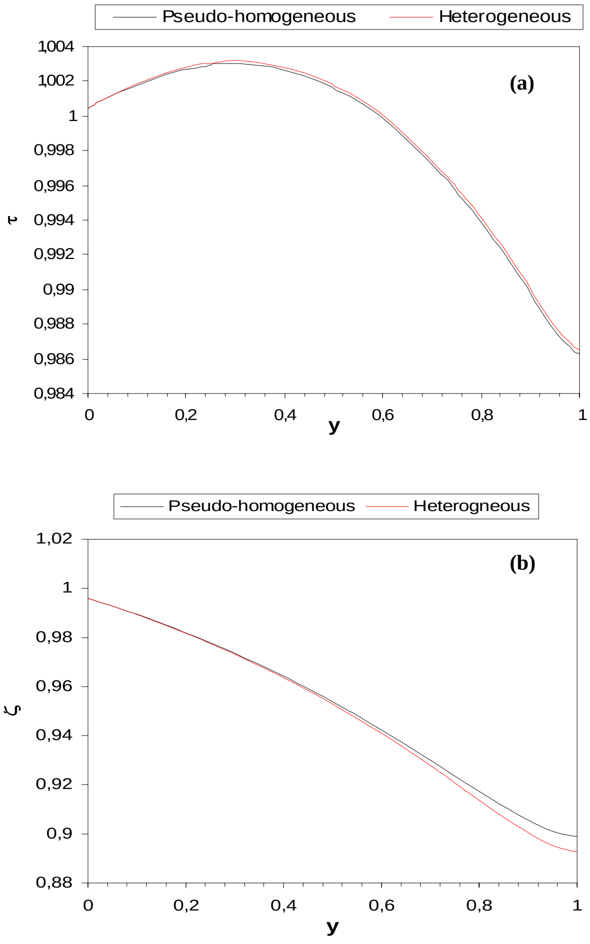


Fig. 3 Effectiveness factor for a spherical pellet under the pseudo-homogeneous and heterogeneous models.

The bulk concentration, temperature and momentum dimensionless profiles like the coolant temperature profile show a mean statistic difference lower than 1.5% between the pseudo-homogeneous and heterogeneous model. In Fig. 4. can be noticed that the higher difference can be found in the concentration and pressure profiles, this difference increase at higher difference, as is expected due to the behavior of the effectiveness factor with the temperature.



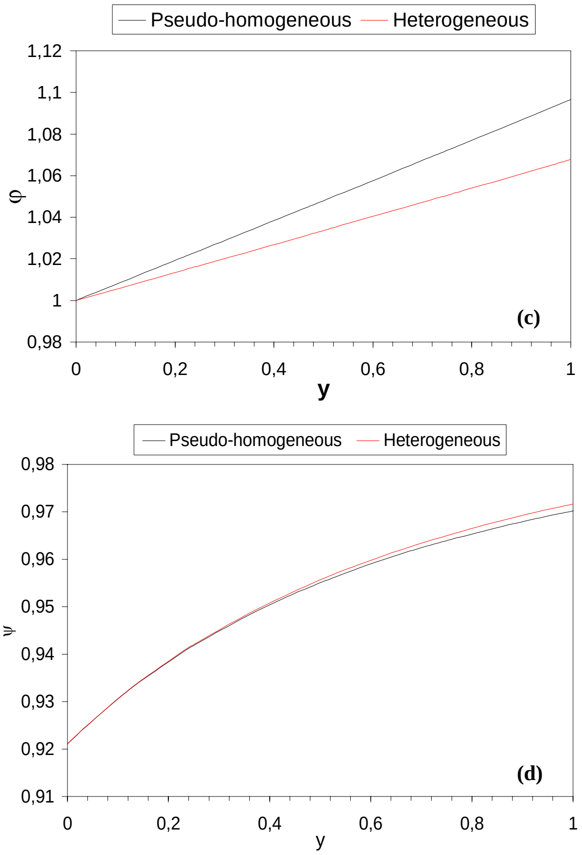


Fig. 4 Bulk dimensionless profiles, temperature (a), concentration (b), momentum (c) and coolant temperature dimensionless profile (d). The operation conditions were: coolant at 350 K and 0.1 Kg s^{-1} at co-current flow and a feed air: ethanol relation of 20 and 380K.

The reaction temperature was control in a better way by the counter-current disposal, changes in the coolant mass flow and inlet temperature have a strong effect over the bulk temperature and yield. In Fig. 5 is shown the effect of the fluid flow disposal over the bulk and coolant temperature profile, can be noticed that the counter-current arrangement is the most effective for the heat removal, in Fig. 6 is shown the effect of the coolant inlet temperature over the bulk temperature and concentration profiles, as is noted a coolant inlet temperature under or near the lower optimal process temperature (350K) turn down the reaction, the best coolant inlet temperature is in the range of 370 and 390K (data not shown) and in Fig. 7 is shown the effect of coolant mass flow over the temperature and concentration bulk profiles and the coolant temperature profile, is noticed that at higher mass flow the bulk temperature and yield are lower at a coolant inlet temperature 350K, the optimal coolant mass flow is in the range of 0.05 and 0.1 kg s^{-1}(data not shown) this results can vary according to the physic-chemistry properties of the Dow Therm or according to the coolant system.

The calculated data showed a mean deviation in the range from 10 to 13% to the experimental data for the different profiles (data not shown), the higher deviation was in the ethanol yield. These could be due to the lack of adjust of the physic-chemical and transport correlations to the real reactor behavior and the numerical error gotten by elements of very low order (10^{-4} and 10^{-6}) in the matrixes of the OC and OCFE numerical methods.

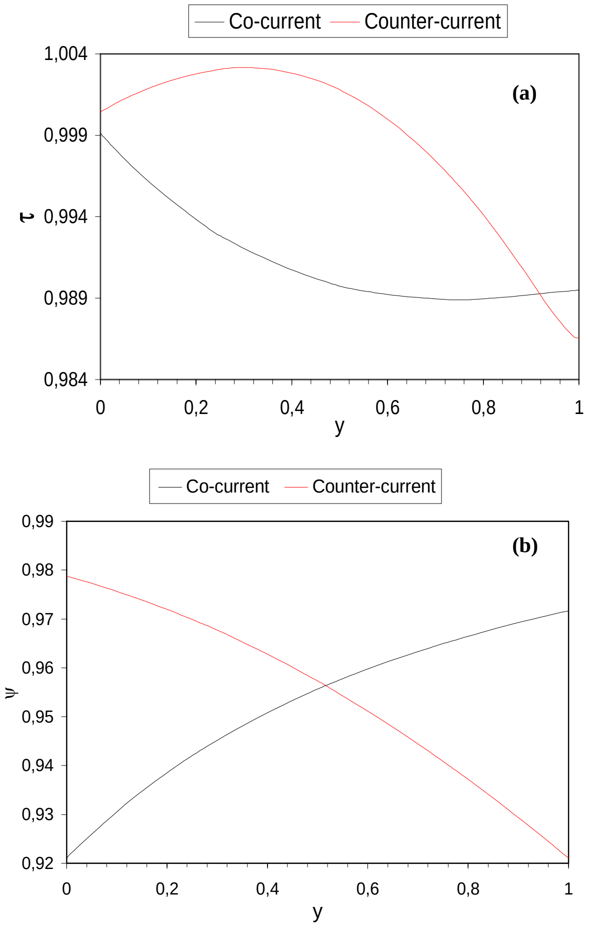
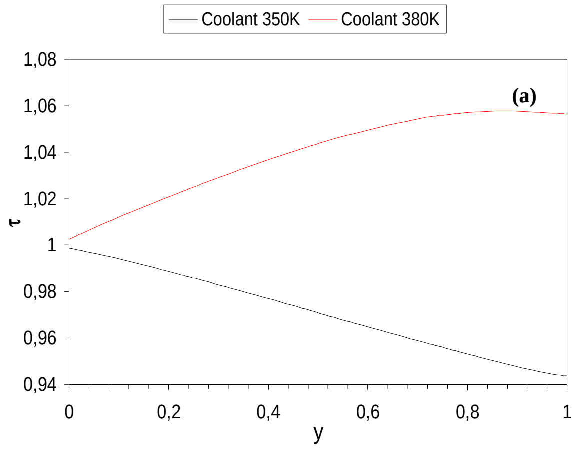


Fig. 5 Dimensionless temperature profiles for the bulk (a) and for the coolant (b) at co-current and counter-current. The operation conditions were: coolant at 350 K and 0.3 Kg s^{-1} and a feed air: ethanol relation of 20 and 380 K.



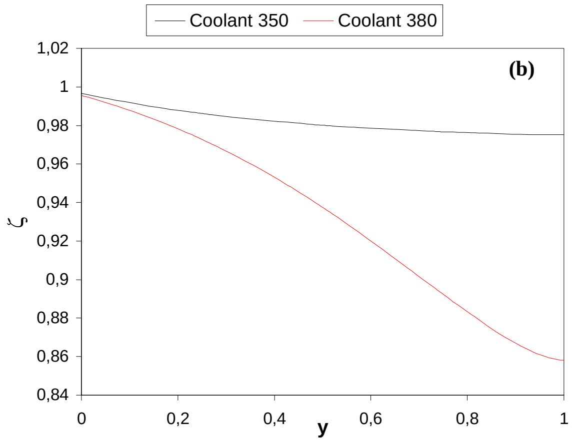


Fig. 6 Coolant inlet temperature effect over the bulk temperature (a) and concentration (b) profiles. The operation conditions were: coolant at 350 K and 0.08 (—), 0.1 (– –) or 0.25 (– — –) Kg s^{-1} and a feed air: ethanol relation of 20 and 380K.

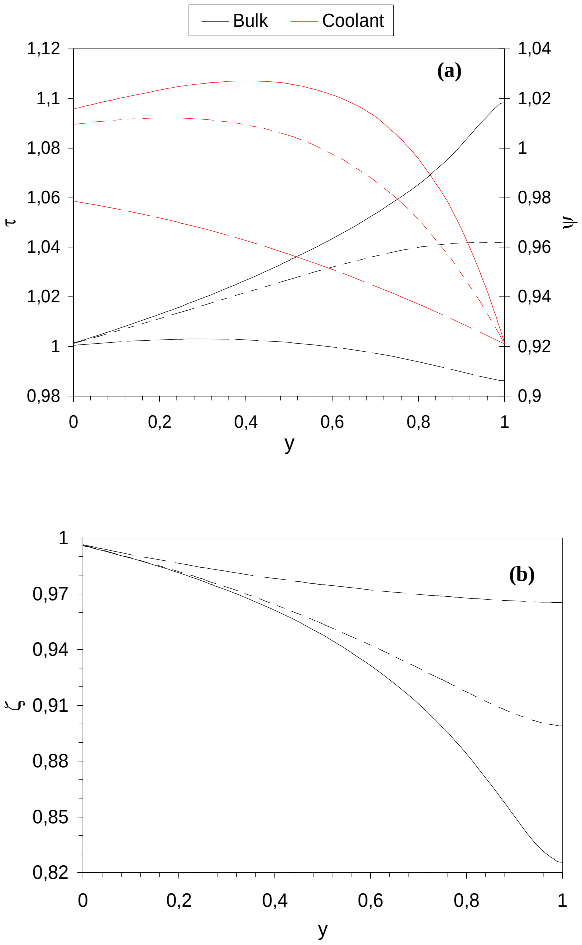


Fig. 7 Coolant mass flow effect over the bulk and coolant temperature profiles (a) and bulk concentration profile (b). The operation conditions were: coolant at 350 K and 0.08 (—), 0.1 ((() or 0.25 ((— () Kg s-1 and a feed air: ethanol relation of 20 and 380K.

Conclusions. The OC and OCFE numerical methods allow a fast and easy convergence to the solution of the catalytic pellet and reactor models. The OCFE has the advantage that the domain division can help to avoid convergence problems when you have to use OC with a high order orthogonal polynomial (tenth order or higher) because the matrixes gotten have elements of very low order (10^{-8} and lower) that cause instability in the program, based in the continuity criteria we used OCFE for the reactor modeling.

The models showed the presence of hot spots in the ethanol catalytic conversion to acetaldehyde and thermal instability like run-away in the reactor. The counter-current operation showed to be the most efficient system for the temperature control.

The critical parameters to be control in the reactor are mainly the inlet temperature and the mass flow of the coolant.

We recommend to make more experimental runs to verify the prediction power of the program and to extend the numerical method to a two-dimensional simulation to verify if there is a higher accuracy. And develop optimization studies to get the better acetaldehyde production conditions.

Notation. (I.S.U)

$\mathbf{Bi_m}$, $\mathbf{Bi_{h\ or\ w}}$	Biot of mass and heat
$\mathbf{Pe_m}$, $\mathbf{Pe_h}$	Peclet of mass and heat
$\mathbf{C_A}$	Ethanol concentration
$\mathbf{D_{eff}}$, $\mathbf{K_{eff}}$	Effective Diffusivity and thermal conductivity
$(-\gamma_{AW})$	Kinetic expression
$\mathbf{K_g}$, **h**	Mass and heat transfer coefficients
ΔH_{RA}	Reaction heat
R, r	Pellet radius and radial position
T	Temperature
u, ζ	Dimensionless concentration
z, y	Dimensionless radial and axial position
θ, τ, ψ	Dimensionless temperature
$f(u, \theta)$	Dimensionless kinetic
ρ_B	Pellet density
ϕ, Φ	Thiele module
β	Prater number
$\mathbf{h_k}$	Domain division
$\mathbf{T_{AR}}$	Coolant inlet temperature
$\mathbf{P_{AR}}$	Initial pressure
$\Im, \Re, \aleph$	Matrix notation for OC
A, B	Matrix notation for OCFE

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