Analysis of the Multitubular Reactor for Formaldehyde Production by One-Dimensional Models

Juliana Schotborgh, Gustavo Orozco, Iván D.Gil
Departamento de Ingeniería Química, Universidad de los Andes, Bogotá, Colombia.

In the present work the composition and temperature profiles were determined for the oxidation of methanol to formaldehyde in an industrial packed bed reactor by means of one-dimensional models. In order to obtain the numerical solution corresponding to the system of differential equations that describe the system, the 4th order Runge Kutta numerical method was implemented. A detailed analysis is made about the mechanisms of reaction postulated in the literature for the oxidation of methanol, the formation of sub-products and intermediaries in parallel and consecutive reactions, as well as an analysis of the factibility of the mechanisms proposed by Cozzolino et al (2007) with a generated algorithm that details the Gibbs free energy for the temperature interval of operation. The kinetics studied correspond to Cozzolino et al (2007) and Windes et al (1989) resulting on an identified hot spot in the range of 540-560 K and 25-40 cm from the entrance of the reactor for the latter, and a difference of 10 K and 8 cm for the first author. The same procedure was developed for the kinetic model of Tesser et al (2003) finding no satisfactory results that describe the system. The shooting numerical method was also developed, in order to accomplish a parametric sensibility analysis by solving a boundary value problem; with this, the three possible disposition of the coolant (cocurrent, countercurrent, constant temperature) were studied to analyze its effect on the hot spot dimension and position along the reactor as well as its changes with the entrance conditions of the reactant mixture finding that the parallel disposition of the coolant is the best alternative in terms of hot spot control.

Formaldehyde Production

The catalytic oxidation of methanol represents the best route for formaldehyde industrial production; in particular, the industrial processes used at present involve the use of silver catalysts; this route is based on the partial oxidation of methanol and the later dehydrogenation with air at atmospheric pressure and temperatures between 680-720°C. On the other hand the Formox process use metallic oxide catalysts (Fe-Mo) for the conversion of methanol into formaldehyde by means of oxidation with excess air at atmospheric pressures and temperatures between 250-400°C[1].

When silver catalyst is used, the operation is carried out adiabatically obtaining a selectivity of 90% (minor than the obtained with the Fe-Mo catalyst). The catalyst has a short life depending on the level of impurities of the methanol and the gases of exit that contain considerable quantities of hydrogen and water. Silver as a metal has a low catalytic ativity for the decomposition of methanol even at high temperatures; its activation depends on the chemisorption of the monoatomic oxygen in the metal.

Kinetics for the oxidation of Methanol to Formaldehyde

Besides the mechanisms proposed for the production of formaldehyde, the specific role of the support used with regard to the catalyst and its activity and selectivity, as well as the method of preparation is vital; it defines the interaction of the system with the catalyser and therefore the behavior of the latter. The grafting technique is recognized as the one with the greater degree of dispersion obtained in the catalyst and that supplies the greater stability.

Cozzolino et al [1] recognizes the selective oxidation of the methanol to formaldehyde with metalic oxides catalysts that obeys a redox mechanism. It proposes a complete kinetic analysis of the oxidation of methanol with the use of Vanadium oxide as a catalyst. The reaction scheme studied by Cozzolino takes into account all the products and intermediates formed as shown below[1]:

$$3CH_3OH + \frac{1}{2}O_2 \longrightarrow CH_2(OCH_3)_2 + H_2O$$
$$CH_2(OCH_3)_2 + H_2O \leftrightarrow 2CH_3OH + HCHO$$
$$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$
$$CH_3OH + H_2CO + \frac{1}{2}O_2 \longrightarrow HCOOCH_3 + H_2O$$

Cozzolino assumes a MVK-LH Mars-van Krevelen & Langmuir Hinshelwood model and assumes the equality of the velocity of re-oxidation of the catalytic places; the kinetic parameters were correlated with the temperature through the Arrhenius equation.

Table 1. Kinetic parameters reported by Cozzolino et al[1]

$Constant$	$Ln(A)$	$E_A \Delta H(kcal/mol)$
k_1	23.09 ± 2.6	20.4 ± 2.3
k_2	20.6 ± 1.1	11.1 ± 1.0
k_3	15.6 ± 4.8	14.8 ± 4.2
k_4	39.0 ± 3.2	27.8 ± 2.8

In Tesser et al[2]the catalyst utilized was of Fe-Mo (Iron-Molybdenum) and the two reactions studied as a system are cited subsequently and have a redox mechanism behaviour that follow the model suggested by MVK:

$$CH_3OH + \frac{1}{2}O_2 \longrightarrow CH_2O + H_2O$$
$$CH_2O + \frac{1}{2}O_2 \longrightarrow CO + H_2O$$

The inhibition induced by the presence of water in both reactions is considered with the introduction of a Langmuir-Hinshelwood term in the rate expression[2].

$$v_1 = \frac{k_1 k_2 P_m^a P_{O_2}^b}{k_1 P_m^a + P_{O_2}^b} * (\frac{1}{1 + b_w P_w}) \tag{1}$$

Table 2. Kinetic Parameters reported by Tesser et al[2].

$k_1 = exp(-18.4586 + 64790/RT$
$k_2 = exp(-15.2686 + 57266/RT$
$b_w = exp(21.2814 - 111600/RT)$
$\Delta H_1 = -158.8 kJ/mol$
$\Delta H_2 = -238.3 kJ/mol$

Windes et al[8] carried out the study of the oxidation of methanol to formaldehyde in a multitubular reactor with $Fe_2O_3 - MoO_3$ catalyst; the temperature of feed is 250°C and the methanol molar fraction is 0,05.

$$CH_3OH + \frac{1}{2}O_2 \longrightarrow H_2CO + H_2O$$
$$H_2CO + O_2 \leftrightarrow CO_2 + H_2O$$

with a formation enthalpy of -37.9 Kcal/mol and -55.7 Kcal/mol respectivelly.

Table 3. Kinetic parameters reported by Windes et al[8].

$Reaction$	$A_i(s^{-1})$	$H_i^+(cal/mol)$
1	6250	19000
2	5.6	16000

Mathematical and Numerical Models

The modelling of reactors by means of pseudohomogeneous models consider the particle of the catalyst and the mixture as an anisotropic form where the profiles of concentration and temperature in the bed are considered as functions of the radial and axial coordinates[4]. The solution of a model in general,involves the simultaneous solution of ordinary differential equations such as the energy and mass balance for each one of the components and for the fluid of control.

In the pseudohomogeneous model the following equations describe the system:

$$\frac{-d(u_s C_a)}{dt} = \gamma_a \rho_b \tag{2}$$

$$u_s \rho_g C_p \frac{dT}{dZ} = (-\Delta H)\gamma_a \rho_b - \frac{4u}{dt}(T - T_r) \tag{3}$$

under initial conditions, $z = 0$; $C_a = C_{ao}$; $T = T_o$

This model assumes that there are no radial gradients of temperature and concentration, that the profile of velocity has flat form and does not consider the effect that the intraparticle space, wall and center of reactor causes; likewise, no axial dispersion of mass and temperature is considered. The concentration and temperature in the fluid as a whole is equal and constant in the surface of the catalytic pellet, the density of the bed is considered constant as well as the global transference coefficient and void fraction. The heat transfer by radiation is despicable[4].

With the programming language C++ under Linux numerical algorithms were implemented that permit the modelling of the oxidation reaction in a multitubular fixed bed reactor with the kinetic studies proposed by Windes et al[8], Cozzolino et al [1], and Tesser et al [2].
The set of highly non linear ordinary differential equations that represent the system are solved through the programming of the method of Runge-Kutta of fourth order; the previous method permits the analysis of the constant wall temperature reactor and the co-current disposition of the coolant. On the other hand, the shooting method allows the analysis of the reactor with the coolant in a counter-current arrangement in a non linear set of ordinary differential equations with a boundary value.

For the counter-current configuration of the coolant, which originates a problem of boundary value, the method of Newton for its conversion to a problem of initial values was implemented and, through an iterative process and a system of variational equations allows its solution. This algorithm is called method of Shooting in which the boundary conditions correspond to final and initial values.

The variational equations are the assembly of differential equations partially derived by the initialized variables for a solution that requires de resolution of n differential equations[9] with r equations with initial conditions specified and n-r equations with final conditions.

With the accomplishment of the partially derivations of the differential equations with respect to each one of the variables initialized; the variational equations are obtained.

$$\frac{d(\frac{\delta y_i}{\delta \sigma_j})}{dx} = \sum_{k=i}^{n} \frac{\delta f_i}{\delta y_k} (\frac{\delta y_k}{\delta \sigma_j}) \qquad (4)$$

$$S_{ij} = \frac{\delta y_i}{\delta \sigma_i} = Sensibility \qquad (5)$$

at this point the variational differential equations are denoted as:

$$\frac{dS_{ij}}{dx} = \sum_{k=1}^{n} \frac{\delta f_i}{\delta y_k} S_{kj} \qquad (6)$$

and the consequential ordinary differential equations n(n-r) with initial conditions;

$$S_{ij}(xo) = 1; \qquad i = j \qquad (7)$$

$$S_{ij}(xo) = 0; \qquad i \neq j \qquad (8)$$

From the sensibility at x_f the Jacobian matrix is obtained and corresponds to:

$$J(x_f, \sigma) = \begin{pmatrix} \frac{\delta y_{r+1}}{\delta \sigma r+1} & \frac{\delta y r+1}{\delta \sigma r+2} & \frac{\delta y r+1}{\delta \sigma n} \\ \vdots & \vdots & \vdots \\ \frac{\delta y_n}{\delta \sigma r+1} & \frac{\delta y_n}{\delta \sigma r+2} & \frac{\delta y_n}{\delta \sigma n} \end{pmatrix} \qquad (9)$$

obtaining new values by the inversion of the matrix where σy is a vector formed by the differences between the boundary value and the calculated one with the initialized conditions. The iterations culminate when an specified tolerance is reached.

$$\sigma_{new} = \sigma_{old} + [J(x_f, \sigma)]^{-1} \sigma y \qquad (10)$$

Results

From the algorithm generated for the study of the feasibility of the process and following the mechanism of reaction proposed by Cozzolino et al [1] the following results were obtained:

There can be observed that for the first reaction that corresponds to the oxidation of methanol to dimetoxymethane, the energy has a small range of temperature in which its value is negative; it corresponds to temperatures between (250K and 700 K) that fit the range chosen by Cozzolino (250C and 400C). Above 700 K the Gibbs free energy turns positive indicating the unfeasibility of the formation of the intermediary dimetoxymethane and therefore the impossibility of formation of formaldehyde as the product of interest.

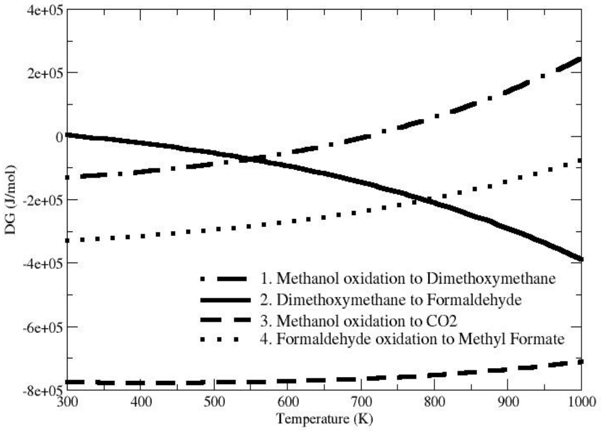

Figure 1. Gibbs free Energy vs T (K) for the mechanism of reaction proposed Cozzolino et al[1].

The reaction that corresponds to the formation of formaldehyde from dimetoxymethane shows negative values of the energy from 450K; nevertheless, keeping in mind that the formation of the intermediary dimetoxymethane is given at temperatures between 250K and 700K and that at greater temperatures its formation is not favored, the range of temperature that is taken into account is the one that shows greater viability of formation of the dimetoxymethane (250K to 700K) slanted from 250K to 450K. This slant is carried out because it corresponds to the temperature range in which the formation of the product of interest is favored; therefore, these two reactions will define the limits of temperature in which the operation should be carried out(450K-700K).The mechanism of reaction inferes the oxidation of methanol into carbon dioxide reducing the selectivity of the process to formaldehyde; this last one can be oxidized to methylformate. None of the two oxidation behaviours is desired in the process since they interfere with the selectivity of the process. The oxidation of methanol to carbon dioxide exhibits the smaller values of Gibbs free energy in the system of the 4 reactions throughout all the range of temperature chosen; this behavior shows that its formation is not easy to control; the same observations are shown for the oxidation of formaldehyde to methylformate.

If temperatures close to the upper limit of the range of temperature indicated (450K-700K) are taken, the formation of the dimetoxymethane, vital intermediary in the formation of the formaldehyde is unfavorable. If on the contrary temperatures close to the lower limit of the range of temperature are taken, although the formation of dimetoxymethane is favored, the Gibbs free energy for the formation of the formaldehyde is risen. With this, and, analyzing the cross point of the curve representing the formation of dimetoxymethane and that of formaldehyde, conclusions can be made about the operation temperature range. The process should be adapted to be above the temperature that exhibits the cross point in 550K. Likewise, analyzing the cross point of the representative curve for the formation of formaldehyde with that of the oxidation of the same one; the process should be adapted to be below the temperature that exhibits this cross in 750K so that the oxidation of the product of intereset can be avoided at its most.

Constant Temperature wall Reactor model.

With the parameters reported by Windes et al for wall and reactant entrance temperature of 523 K, changes in the partial pressure of methanol at the entrance in the range of 0,07 to 0,2 atm are carried out. Differences in magnitude of 5 K for the hot spot are observed when the reactant mixture is fed at partial pressures from 0,07 to 0,09; in the same way when the change in the entrance of partial pressure of Methanol is of 0.2 atm runaway occurs in the reactor, which changes the temperature of the mixture drastically. Additionally a displacement of 5 cm to the right in the hot spot position along the reactor is observed as the concentration enlarges. Simulations respond to the partial pressure of methanol actually managed at industry level (0.07atm) as a result of the flammability limits of the mixture. This limits are located at 6.7-36.5

% in volume of methanol in dry air at 100C. This concentrations defines the range in which combustion or explotion can be produced at an ignition source and its limits expand as temperature increases and contracts with increasing vapor concentration. With the parameters reported by Cozzolino et al a difference in magnitude of 10 K for the hot point is observed if compared with the results thrown by Windes et al; likewise a displacement of 8 cm to the right of the reactor is also inferred. This behaviour is attributed to the differences in the parameters reported by the authors; the activation energy reported by Windes el al are smaller in magnitude than the ones reported by Cozzolino et al throwing a displacement to the right of the reactor and higher in magnitude hot points for the latter.

In the response of the partial pressure of methanol along the reactor, the decline observed assumes its consumption along the reactor and therefore formaldehyde's formation; this behavior is observed for partial pressures of methanol at the entrance between 0,07 and 0,1 atm, in the same way; for partial pressures at the feed over 0.1 atm a pronounced fall in partial pressure values is observed which coincides with the results of the temperature profile. The behavior of the composition of methanol for feeds over 0,1 atm matches the drastic change in the mixture temperature in the reactor.

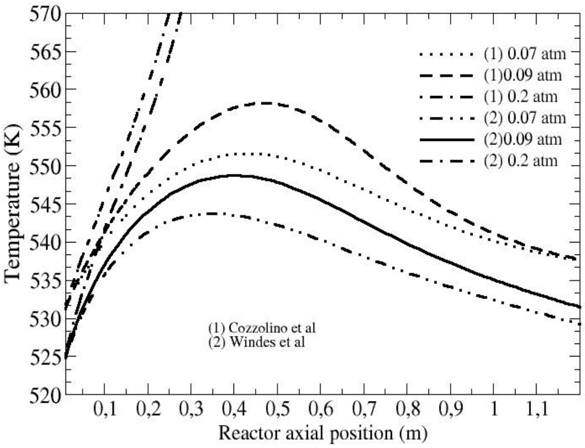

Figure 2. Hot spot response to methanol concentration changes for parameteres reported by Windes et al and Cozzolino et al To=Twall=523K.

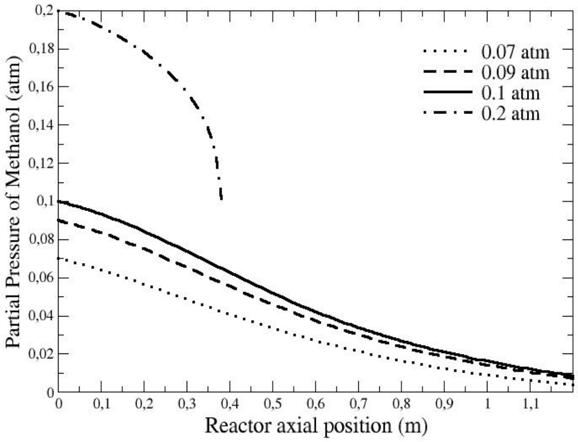

Figure 3. Methanol partial pressure response along the reactor. To=Twall=523K

Simulations that respond to the change of concentration of methanol in the reactor with respect to the mixture temperature at the entrance were carried out alos. The entrance concentration condition were maintained constant and an increase in the velocity of consumption of the methanol at high temperatures was observed like was expected. For the same studied parameter in regard to the wall temperature of the reactor results were obtained. A rapid consumption of methanol was observed as the temperature increased to 560 K and a consumption of considerable slowness when the entrance of the mixture is below 523 K. It is important to pay attention to the high exothermicity of the reaction, and, along with this, the ambiguity of the suposition of higher wall temperatures than the one at which the mixture enters the reactor.The analysis carried out also included the variation of the composition of formaldehyde as the product of interest along the reactor in response to the change on partial pressure of the methanol in the reactant mixture, the reactants entrance temperature and wall temperature of the reactor; the results obtained showed an increase of formaldehyde with the increase of methanol in the reactant mixture but, it is important to clarify that the increase in the partial pressure of methanol causes runaway behaviour as shown in the temperature profile; for operating conditions, one should keep in mind the extreme conditions modelled and to distinguish therefore the reactants entrance limit temperature, partial pressure and wall temperature. The behaviour of the partial pressure of formaldehyde as the product of interest shown in figure 4 inferes that a wall temperature of 523 K is the best choice for the operation conditions since at values below or above this corroborates the drastic change in the temperature profile or likewise a poor production of the product.

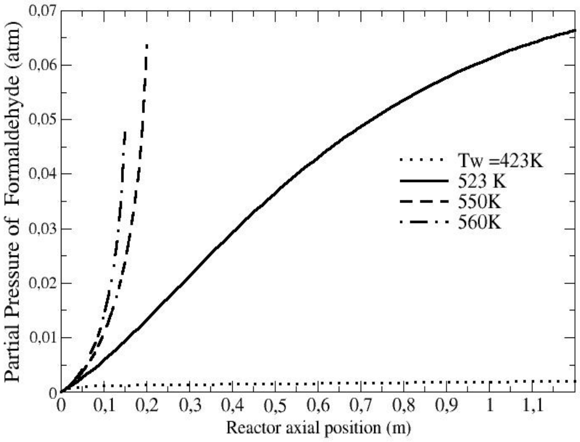

Figure 4. Formaldehyde's partial pressure response along the reactor by changing the reactor's wall temperature To=523K Pmethanol=0.07 atm

Co-current and Counter-Current configuration for the coolant.

The temperature profile was obtained for this configuration obeying the parameters reported by Windes et al[8].Variations in the entrance partial pressure of methanol were made to obtain a difference of 5 K in hot spot magnitude with a co-current arrangement of the coolant; this agrees with the response for the constant temperature wall model. Nevertheless a difference of minus 10 K in the hot spot magnitude for the co-current arrengement was found between configurations. In the same way when the change in the entrance of partial pressure of methanol is greater to 0,1 atm runaway occurs in the reactor.In the behavior of the partial pressure of methanol along the reactor a decline is observed that assumes its consumption along the reactor; as in the constant temperature wall reactor, when the configuration of the refrigerant is co-current, a pronounced fall in the partial pressure coincides with the reactor runaway.

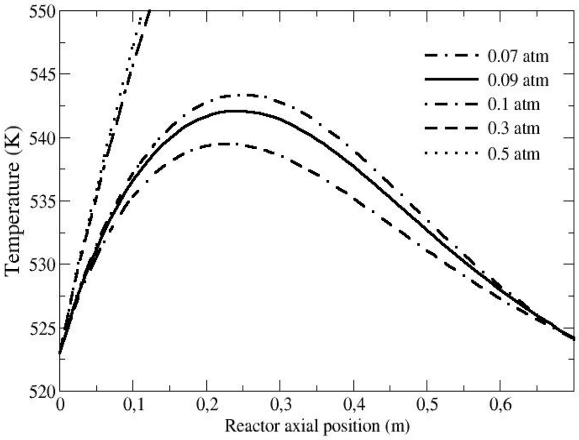

Figure 5.Temperature profile for co-current configuration of the coolant. Hot spot response varying partial pressure of methanol To=Tcoolant=523K.

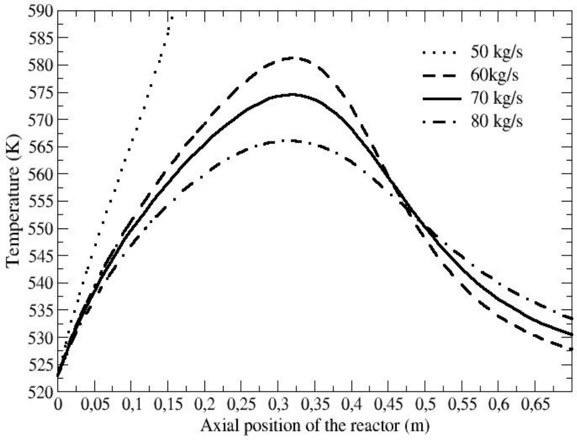

Figure 6.Counter-current configuration for the cooland. Response for the hot spot to coolant flow variations. To=Tcoolant=523K.

Changes at the entrance of the partial pressure of methanol and the coolant flow conditions in counter-current were carried out finding the hot spot 30 K above the magnitude than in co-current configuration. Likewise, runaway is presented with coolant flows below 60 kg/s and the hot spot magnitude is lowered and seriously diminished as the flow is enlarged.The behavior of the partial pressure of methanol along the reactor with regard to changes of the other varaibles coincide with the behavior of the profiles that describe the behavior of the reactor and the other configurations described.

Sensibility analysis.

From the sensibility profiles of the paths of the reactant mixture temperature, it can be inferred that the maximum of this behaviour is located near to the position of the reactor in which the hot spot is presented and because of it is an indicative of the parametric sensibility of the system. In the same way, if the coolant flow is studied and the counter-current is taken as negative flows and co-current as positive ones, a smaller parametric sensibility is obtained when the coolant flows with the same direction as the mixture; that is when the configuration is co-current.The simulations carried out permit to infer that the disposition or configuration of the coolant in co-current is the best alternative for the system of the oxidation of methanol to formaldehyde; this based on favorable results of decrease of the hot spot in the reactor and, according to the profiles of sensibility for the different coolant flows. The system analyzed responds for the lowest sensibility values when flow of the coolant is 60 ks/s. The parametric sensibility of greater magnitude in the operation is found when the configuration of the coolant fluid is arranged in counter-current. The simulations carried out validate the co-current disposition of the coolant as an excellent alternative for the oxidation system of methanol into formaldehyde; this conclusion is based on favorable results obtained by the simulations that show a decrease in the hot spot magnitude thorugh the reactor and, supporting the sensiblity profiles which show bigger values when the operation is carried out at counter-current configuration.

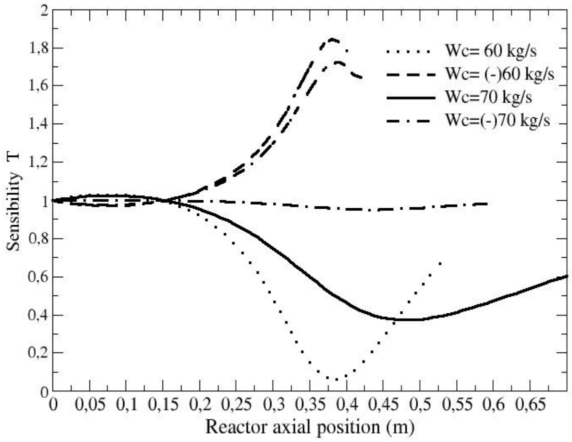

Figure 7.Sensibility profile for different coolant flows for co-current (positive flows) and counter-current (negative flows) configurations of the coolant.

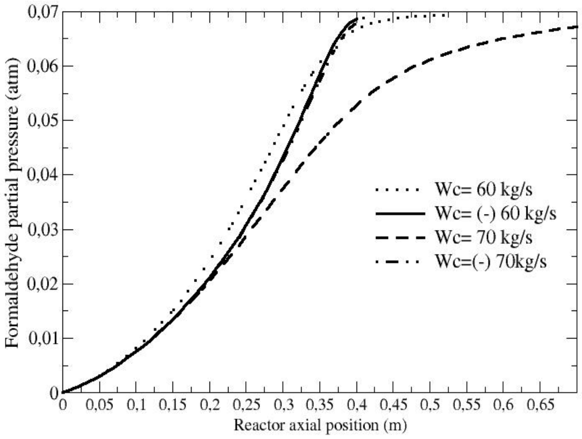

Figure 8.Formaldehyde partial pressure for different coolant flows for co-current(positive flows) and counter-current (negative flows) configurations.

References

[1] COZZOLINO M., TESSER R., DISERIO M., D'ONOFRIO P., SANTACESARIA E. Kinetics of the oxidative dehydrogenation of methanol to formaldehyde by supported vanadium-based nanocatalysts. Catal.Today 2007. Vol 128. pg 191 - 200.

[2] TESSER R, DI SERIO M, SANTACESARIA E. Catalytic oxidation of metane to formaldehyde: an example of kinetics with transport phenomena in a packed-bed reactor. Catal.Today. 2003. Vol 77, pg 325 - 333.

[3] LYNGGAARD H, ANDREASEN A, STEGELMAN C, STOLTZE P. Analysis of simple kinetic models in heterogeneous catalysis. Prog.Surf.Sci. 2004. Vol 77 ,pg 71 - 137.

[4] OROZCO G.A. Análisis del Reactor Multitubular de Lecho fijo para la producción de Anhidrido Ftálico. Tesis de grado para optar al título de Magister en Ingeniería Química. Universidad Nacional de Colombia, 2006.

[5] SATTERFIELD C. Heterogeneous Catalysis in Industrial Practice. Krieger Publishing Company. Malabar,Florida, 2nd ed. 1991

[6] KIRK-OTHMER. Concise Encyclopedia of Chemical Technology. A wiley-interscience publication. John Wiley and sons. USA. 1985

[7] BARTHOLOMEW C.H, FARRAUTO R.J, Fundamentals of Industrial Catalytic Processes. Wiley, 2nd ed.

catalysts. Appl.Catal. 1999. Vol 188. pg 337 - 353.

beds. Chem.Eng.Sci. 2007. Vol 62. pg 4948 - 4953.

[8] WINDES L, SCHWEDOCK M. Steady State and dynamic modelling of a packed bed reactor for the partial oxidation of methanol to formaldehyde. Ceh.Eng.Comm, 1989. vol 68. pg 1-43

[9] RANGEL H.,BOGOYA D., Análisis de la Sensibilidad Paramétrica en reactores de lecho fijo. Ingeniería e Investigación pg 70-79.

[10] FROMENT G., BISCHOFF K. Chemical Reactor Analysis and Design. Wiley, NewYork,1990.