Wall-Cooled Fixed-Bed Reactors: Parametric Sensitivity as a Design Criterion

Multitubular reactors of the heat exchanger type are commonly used to carry out highly exothermic reactions. Two of the main goals, when designing this type of reactor, are to guarantee a safe operation and to minimize the reactor length. Therefore, these concepts are used here as criteria for comparing the performance of the three most common cooling-medium flow arrangements. The analysis of the parametric sensitivity behavior, as well as that of some related measures, indicates that, at least from the steady-state standpoint, the cocurrent arrangement should be considered the most attractive alternative.

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Introduction

Tubular reactors of the heat exchanger type are commonly selected to carry out highly exothermic reactions. Most of the units currently used consist of a group of tubes installed in a heat exchanger body. Each tube is packed with the catalyst, and it frequently includes an inlet section, with inert packing, to preheat the reactants. Part of the heat released during the course of the reaction is transferred to a cooling medium, from which it is eliminated by means of an external boiler.

During the last two decades, great improvements have been made in the design and operation of catalytic reactors. However, in industrial conditions, due to the high exothermicity of the chemical reaction, the temperature tends to rise sharply in the catalytic bed towards a maximum or hot spot, which is usually located near the reactor inlet. These sharp axial temperature gradients can cause poor reaction selectivity, and extreme temperatures can be responsible for a rapid deactivation or even a deterioration of the catalyst. Therefore, in practice, the hot spot must be kept within permissible limits. Also frequently, for safety reasons, the attainable conversion has an upper limit at levels where the temperature profile becomes extremely sensitive to changes in the operational and/or physico-chemical parameters involved. Bilous and Amundson (1956) called such reactor conditions "parametric sensitivity." Many studies have analyzed this phenomenon, which in turn can lead the reactor to runaway operation. They have been reviewed by Hlavacek (1970) and more recently by Froment (1984). The inherent danger in running such systems is widely recognized, and the final reactor design must guarantee safe operation modes.

Most studies on parametric sensitivity (Bilous and Amundson, 1956; Barkelew, 1959; van Welsenaere and Froment, 1970; McGreavy and Adderley, 1974; Rajadhyaksha et al., 1975; Oroskar and Stern, 1979; Morbidelli and Varma, 1982) have assumed constant temperature in the cooling medium. This is a suitable approach for a perfectly mixed coolant or for reactors employing as cooling medium a boiling liquid or a fluid of abnormally large heat capacity. However, in the more common case of molten salts circulation, the thermal gradients in the shell side cannot be neglected in the reactor model. Only few papers have studied the nonisothermal coolant situation. In their analysis of the cocurrent configuration, Soria López et al. (1981) reported qualitatively different operating regimes. They also developed basic equations for a parametric sensitivity criterion, which was completed and generalized recently by Hosten and Froment (1986). Degnan and Wei (1979) also dealth with such a scheme, but considered the possibility that the temperatures of reactants and cooling fluid could be fixed independently. On the other hand, the countercurrent situation was treated by Akella and Lee (1983) who proposed catalyst dilution to improve reactor performance. Finally, McGreavy and Dunbobbin (1978) have analyzed both the cocurrent and countercurrent configurations taking into account the influence of the baffles in the shell side that led to a more detailed description of the coolant flow pattern.

In what follows, three different coolant-flow schemes are compared in light of parametric sensitivity. The results obtained show the advantages of the cocurrent arrangement.

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Mathematical Model

The following pseudohomogeneous (one-phase), one-dimensional model will be adopted in the present work:

$$-\frac{dp_A}{dz} = Ap_A \exp(b - a/T) \quad (1)$$

$$\frac{dT}{dz} = Bp_A \exp(b - a/T) - C(T - Tc) \quad (2)$$

$$\frac{dT_c}{dz} = D(T - T_c) \quad (3)$$

A vectorial character was assigned to the flow rates for the following reasons. As the coolant flow rate (W_c) only directly affects the heat loss parameter for the cooling medium (D), the use of a proper sign for W_c will automatically adapt Eqs. 1 to 3 to cocurrent ($W_c > 0$) or countercurrent ($W_c < 0$) conditions. Furthermore, large (positive or negative) values of W_c will cancel D, allowing the same model to handle the constant coolant temperature operation as well.

The above model must be solved using the following boundary conditions:

Cocurrent case:

$$p_A = p_{Ao} \quad \text{at } z = 0$$
$$T_c = T_{co} \quad \text{at } z = 0$$

Countercurrent case:

$$p_A = p_{Ao} \quad \text{at } z = 0$$
$$T_c = T_{cL} \quad \text{at } z = L$$

As the efficiency of the preheating section is assumed to be one ($\epsilon = 1$), the remaining boundary conditions becomes:

$$T = T_c \quad \text{at } z = 0$$

The values of the parameters used in the calculations, as well as the chosen reaction rate expression, correspond to an industrial packed-bed reactor, where air oxidation of O-xylene to phthalic anhydride is carried out (van Welsenaere and Froment, 1970; Soria López et al., 1981). The global heat transfer coefficient was calculated from the correlation reported by Crider and Foss (1965). The effective radial thermal conductivity and the internal wall heat transfer coefficient have been computed using correlations derived by Yagi and Kunii (1957, 1960). The shell-side heat transfer coefficient was estimated from equations reported by Kern (1950).

Parametric Sensitivity Computation

In the present work, parametric sensitivity is calculated similar to that proposed by Hlavacek and Votruba (1977). Thus, the parametric sensitivity (S_{ij}) of the variable χ_i with respect to the parameter or inlet variable π_j, is defined as:

$$S_{ij} = \frac{\partial \chi_i}{\partial \pi_j}$$

In the present paper, the inlet coolant temperature T_{ci} will be taken as the inlet variable. Consequently, π_j will correspond either to T_{co} or T_{cL} for co- or countercurrent, respectively. This is because, in industrial practice, the inlet coolant temperature is commonly selected as the manipulative variable for control purposes. The next step is to differentiate the governing equations (Eqs. 1 to 3) to obtain numerical values for the parametric sensitivity of the variables $\chi_1 = p_A$, $\chi_2 = T$, and $\chi_3 = T_c$.

$$\frac{dS_1}{dz} = -A \exp(b - a/T)\left[S_1 + \frac{ap_A}{T^2} S_2\right] \quad (4)$$

$$\frac{dS_2}{dz} = B \exp(b - a/T)\left[S_1 + \frac{ap_A}{T^2} S_2\right] - C(S_2 - S_3) \quad (5)$$

$$\frac{dS_3}{dz} = D(S_2 - S_3) \quad (6)$$

where

$$S_1 = \partial p_A / \partial T_{ci}$$
$$S_2 = \partial T / \partial T_{ci}$$
$$S_3 = \partial T_c / \partial T_{ci}$$

However, it is clear that from the three sensitivity profiles, only $S_2(z)$ is critical and must be kept within bounds to guarantee a safe operation.

To integrate the new problem defined by Eqs. 1 to 6, three additional boundary conditions are needed, i.e.:

$$S_1 = 0 \quad \text{at } z = 0$$
$$S_2 = S_3 \quad \text{at } z = 0$$
$$S_3 = 1 \quad \text{at } z = \begin{cases} 0 & \text{(cocurrent operation)} \\ L & \text{(countercurrent operation)} \end{cases}$$

As before, the preheating section is assumed to have 100% efficiency (which is implicit in the condition $S_2 = S_3$ at $z = 0$).

Operation Zones

From numerical integration of the reactor model, T_{co} vs. T_{cL} curves for different values of the coolant flow rate W_c are displayed in Figure 1, covering the three configurations mentioned previously. The straight line of unitary slope corresponding to $|W_c| \rightarrow \infty$ (constant coolant temperature arrangement) divides this plane into two regions. The lower one corresponds to $W_c > 0$, i.e., cocurrent operation where always $T_{co} < T_{cL}$, whereas the upper one, where always $T_{co} > T_{cL}$, corresponds to countercurrent operation.

The S-shaped curves found in the countercurrent zone denote three possible solutions, which exist for a range of inlet coolant temperatures. However, a stability analysis shows that the intermediate solutions are unstable (Luss and Medellin, 1972) and cannot be realized in practice. The range of T_{cL} over which multiplicity exists, decreases as the coolant flow rate increases and tends to disappear at high values of W_c. This behavior is not found in the limiting case of a constant coolant temperature arrangement. Similarly, in the cocurrent zone, only one steady

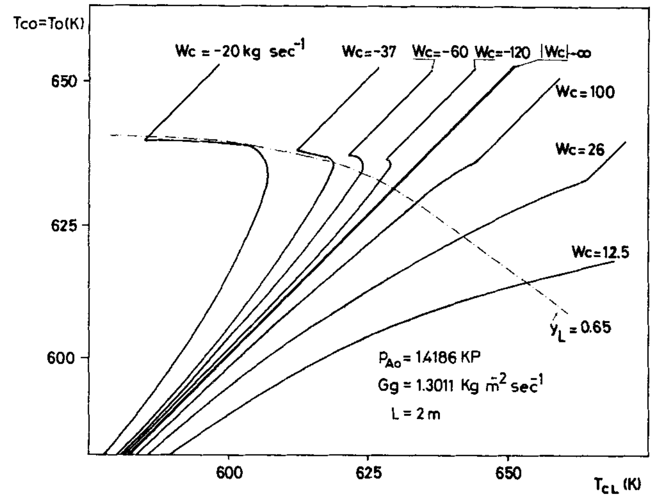

Figure 1. Temperature profiles of cocurrent, countercurrent and perfectly-mixed cooling configurations.

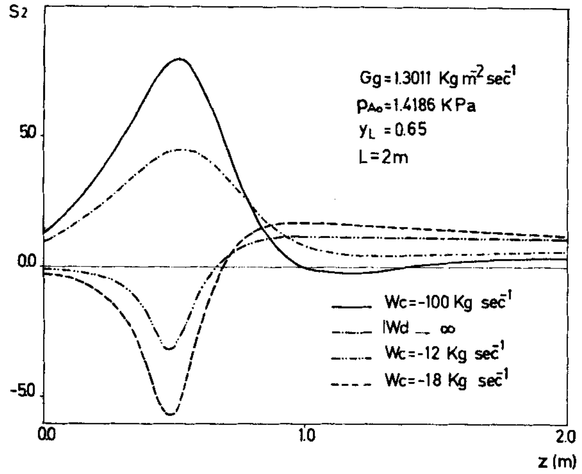

Figure 2b. Parametric sensitivity axial profiles for countercurrent and perfectly-mixed cooling schemes.

state occurs. Figure 1 also shows a curve joining all the operation points with conversion $y_L = 0.65$. It will be discussed in the next section.

Finally, in both zones, the straight portions of the T_{co} vs. T_{cL} curves correspond to steady states with almost complete conversion. In those conditions, both the maximum temperature and the parametric sensitivity of the reactor reach extremely high values (usually referred to as "runaway conditions").

Cooling Arrangements

The performance of the cooling arrangements—cocurrent, countercurrent, and constant temperature—can be compared by defining common operational conditions in the reactor as a basis for the analysis. A reasonable choice is to keep the reactor production rate constant. (All operation points to be compared correspond to the same G_g and p_{Ao}, and yield the same outlet conversion y_L.)

Figures 2a and 2b show the axial sensitivity profiles of operation points on the curve $y_L = 0.65$ (cf. Figure 1) for different cooling conditions. To characterize the sensitivity of each operation condition by a single value (and due to its critical importance), the absolute extreme of $S_2(z)$, which can be a maximum or a minimum, has been selected and will be referred to as S^*. In Figure 2a, corresponding to cocurrent operation, all curves begin at $S_2 = 1$ at the reactor inlet (as $T_o = T_{co} = T_{ci}$) and all the values of S^* are positive. On the other hand, the occurrence of negative values of S^* for a range of values of W_c can be seen in Figure 2b as a distinctive characteristic of the countercurrent scheme. The $S_2(z)$ curves corresponding to very high coolant flow rates are obviously coincident in both figures, as they, in practice, correspond to the same limiting case of constant coolant temperature.

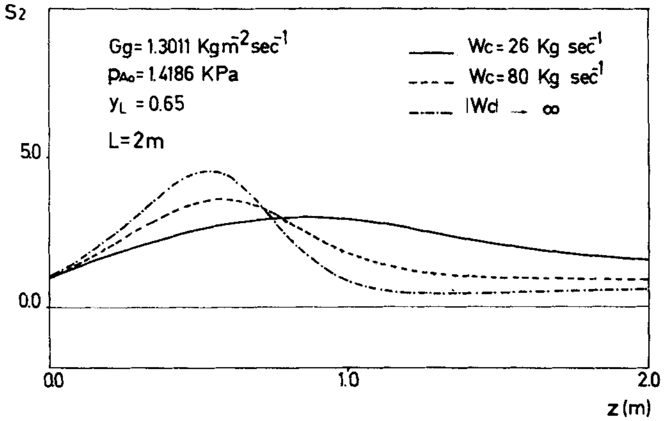

Figure 2a. Parametric sensitivity axial profiles for cocurrent and perfectly-mixed cooling schemes.

The reactor performance can, in principle, be assessed only by observation of all the different variables. However, a selected set is generally enough to draw a complete picture of the reactor condition. Remembering that for a prespecified production rate a safe mode of operation is the goal, the maximum temperature (T_m), maximum parametric sensitivity (S^*), and inlet reactant temperature (T_o) have been chosen as measures of the reactor's performance. A clear illustration of the influence of the cooling configuration on the reactor operation can be obtained by plotting the above mentioned variables at different coolant flow rates. To do this, the inverse of the coolant flow rate in the abscissa axis is a convenient choice for various reasons, among which the following three deserve to be noted:

a. The resulting left and right half planes correspond to countercurrent and cocurrent configurations, respectively.

b. The effect of those arrangements increase for decreasing $|W_c|$, which means moving away from the ordinate axis.

c. Both cocurrent and countercurrent flow tend to coincide as $|W_c| \rightarrow \infty$. Therefore, a continuous behavior can be expected at the origin $W_c^{-1} = 0$, which in turn corresponds to the constant coolant temperature arrangement.

Now, it can be easily shown that, to achieve a given production rate in a prespecified reactor length L, countercurrent schemes require higher inlet reactant temperatures. This can be seen in Figure 3, where T_o has been plotted against W_c^{-1}. It can also be seen that the hot-spots curve (T_m) shows a minimum for a given value of the coolant flow rate (W_{c1}). It can be demonstrated that, for all production rates, this minimum always lies in the cocurrent zone. Moreover, except for impractically low

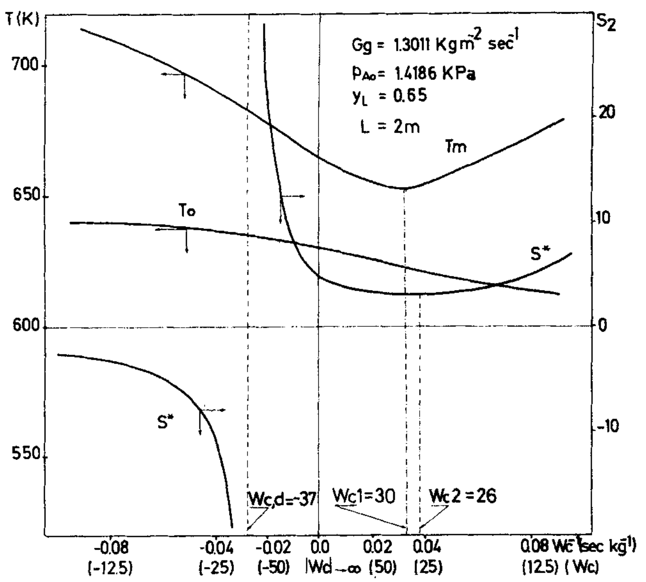

Figure 3. T_o, T_m and S^* vs. W_c^{-1} curves at conditions of constant production rate for a fixed reactor length.

values of W_c, the maximum temperatures exhibited by the cocurrent operations are significantly lower than those reached in any countercurrent conditions.

However, hot spots in themselves are not the whole story. To guarantee a safe mode of operation, it is absolutely necessary to operate the reactor in zones of low parametric sensitivity, but the behavior of this property is more complex than the already discussed T_o and T_m. In fact, in Figure 3 where S^* is plotted against W_c^{-1}, two branches are found and a discontinuity is observed for a specific value of the coolant flow rate (for the conditions of Figure 3, around $W_c = -37$ kg · s^{-1}). Such a discontinuity can be explained through the analysis of Figure 1, where the intersection of the curve of $y_L = 0.65$ with the one corresponding to $W_c = -37$ kg · s^{-1}, occurs at a point where $|dT_o/dT_{cL}| \rightarrow \infty$. It is, therefore, reasonable that $S^* = (dT/dT_{ci})_{\max/\min}$ exhibits an analogous behavior.

With reference to the left (negative) branch of the S^* curve, it can be seen that all its points are located in the countercurrent zone, Figure 3, and that they correspond to intermediate unstable steady states. Again, this characteristic is more clearly seen from inspection of Figure 1. If we adopt a conversion of 0.65 and, for example, a coolant flow rate $W_c = -20$ kg · s^{-1}, the inlet sensitivity will be negative, i.e., $S_{2,o} = (dT/dT_{cL})_{z=0} < 0$. And from figure 2b, the same mathematical sign is to be expected for $S_{2,o}$ and its corresponding extreme S^* at any operation condition.

Unfortunately, this characteristic ($S_{2,o} < 0$) does not permit the derivation of an analytical tool to predict the existence of unstable steady states. However, this prediction can be done by means of steady-state simulations based on the proposed model of Eqs. 1–6, without the need to resort to the more complex and time-consuming dynamic models.

On the other hand, the right branch of the S^* plot corresponds to stable steady states. This is the zone of feasible operational conditions and covers the high coolant flow rate range in the countercurrent scheme, and the constant coolant temperature, and cocurrent arrangements.

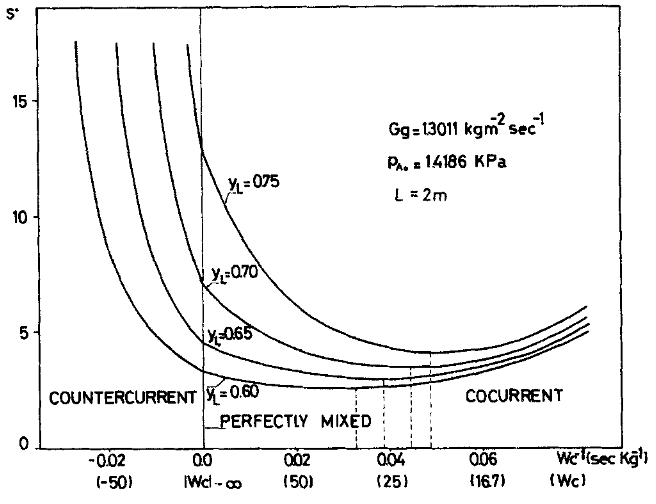

Figure 4. S^* vs. W_c^{-1} curves (right branches) at different production rates for a fixed reactor length.

With regard to the countercurrent scheme, the above range can be defined as $|W_{c,d}| < |W_c| < \infty$, Figure 3. Therefore, Figure 4, where only right branches of S^* are plotted for different values of y_L, shows that the higher the conversion, the smaller is the range of W_c that can be tolerated in stable countercurrent steady-state operation. It must also be pointed out that the curves of Figure 4 exhibit a minimum at a given value of the coolant flow rate (W_{c2}). This value depends on the conversion, but it always lies in the cocurrent zone. Therefore, for a prescribed production rate, it is always possible to find a coolant flow rate range in cocurrent operation conditions yielding values of S^* lower than those encountered either at constant coolant temperature configuration or at any stable countercurrent operation condition. Furthermore, it is noted from Figure 4 that the minima are more pronounced as the production rate increases, which means that for these conditions a particularly careful selection of the coolant flow rate is needed. From direct inspection of the shapes of T_m and S^* curves, Figure 3, a reasonable choice of the operation flow rate range seems to be $W_{c1} \geq W_c \geq W_{c2}$.

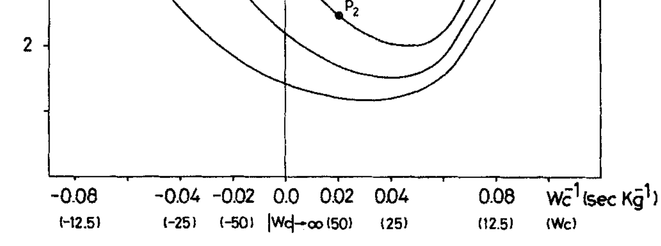

Figure 5. L vs. W_c^{-1} curves at different production rates for a given maximum temperature.

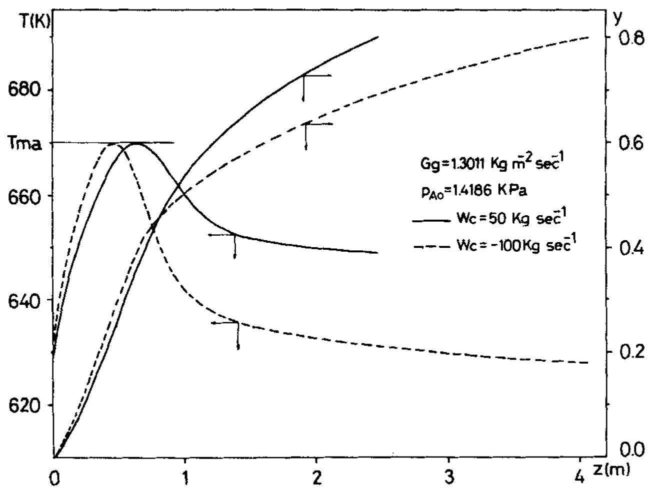

Figure 6. Axial temperature and conversion profiles corresponding to points P_1 and P_2 of Figure 5. (counter- and cocurrent operation, respectively).

However, as not only safety but also economic aspects are relevant at the design stage, the total reactor length needed to achieve a given conversion is important. The cocurrent scheme will also yield the shortest reactor for a given production rate, provided the operation is subject to an upper constraint, e.g., $T_m \leq T_{ma}$. Figure 5 shows the total reactor length that is plotted against W_c^{-1} for different conversion levels. Each point on these curves corresponds to operational conditions verifying T_m = 670 K as a common constraint. All the curves present a minimum, which always lies in the cocurrent zone.

This feature can be explained through a better use of the reactor outlet zone, which for cocurrent design operates at a significantly higher temperature level. This still permits the reaction to proceed at a reasonable rate in this zone, despite the low concentration levels. Figure 6 verifies this point, where axial temperature and conversion profiles corresponding to operation points P_1 and P_2 of Figure 5 are displayed. The desired value $y_L = 0.8$ can be reached with a total length $L = 2.46$ m for the cocurrent operation (maximum sensitivity $S^* = 4.05$). Conversely, 4.06 m (with $S^* = 6.34$) is needed in the countercurrent operation to achieve the same production rate.

Conclusions

A unified treatment was used to compare three different cooling designs for multitubular fixed-bed reactors. The designs studied are cocurrent, countercurrent and constant coolant temperature. The co-current scheme yields the lowest values for the maximum temperature and the parametric sensitivity. Therefore, as low T_m guarantees longer catalyst life (and improved selectivity in case of multiple reactions), and low S^* ensures safe operational conditions, the cocurrent configuration, which also yields shorter reactors, should be seriously considered when designing this type of unit.

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Notation

$a = E/R$
$A = (\rho_b P M p_{Bo})/(u\rho_g)$
$b = \ln(k_\infty)$
$B = (\rho_b(-\Delta H)p_{Bo})/(u\rho_g c_{p_g})$
$C = (4U)/(ud_t\rho_g c_{p_g})$
c_p = specific heat, kJ · kg^{-1} · K^{-1}
d = diameter, m
$D = (\pi d_t t_n U)/(W_c c_{p_c})$
E = activation energy, kJ · kmol^{-1}
G = specific mass flow rate, kg · m^{-2} · s^{-1}
k_∞ = preexponential factor
L = reactor length, m
M = molecular weight of the gaseous mixture, kg · kmol^{-1}
p = partial pressure, kPa
P = total pressure, kPa
R = universal gas constant, kJ · kmol^{-1} · K^{-1}
S = parametric sensitivity
S^* = absolute extreme (max. or min.) of $S_2(z)$ curves, K/K
t_n = number of reactor tubes
T = temperature, K
u = gas superficial velocity, m · s^{-1}
U = overall heat transfer coefficient, W · m^{-2} · K^{-1}
W = mass flow rate, kg · s^{-1}
y = conversion
z = axial coordinate, m

Greek letters

ΔH = heat of reaction, kJ · kmol^{-1}
ϵ = efficiency of the preheating section
ρ = density, kg · m^{-3}

Subscripts

a = allowable
A = o-xylene
b = bulk
B = second component
c = cooling medium
g = gas
i = at inlet axial position
L = at axial position, $z = L$
m = at maximum temperature axial position
t = tube
o = at axial position, $z = 0$

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