SAT-LCR-P-2-CT(R)-07

SELECTION OF A STABLE THERMAL REGIME IN DIFFERENT TYPES OF CHEMICAL REACTORS DURING AN EXOTHERMIC REACTION

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Abstract: *The present work aims to consider the peculiarities of the compilation of the heat balances, ensuring a stable mode of operation of two types of chemical reactors during the course of an exothermic reaction. After computational procedures and applied specific methodologies, the heat balances of continuously mixed flow and plug flow reactors, with an irreversible exothermic reaction of the first ordert aking place with set operating parameters, provided that the inlet temperature in the reactors does not exceed 55°C, have been compiled. The temperatures of the reaction mixture at the entrance to the two reactors in polythermal and adiabatic regimes, the degree of conversion reached and the heat consumption for conducting the reaction were found. An analysis and comparison of the heat balances in polythermal and adiabatic regimes for the two reactors was made. In accordance with the specifics of the reaction, a reactor was selected, ensuring low heat consumption and high efficiency of the process.*

Keywords: *Heat balances, exothermic reaction, continuous stirred-tank reactor, continuous plug-flow reactor.*

INTRODUCTION

In most cases, the chemical reactions are accompanied by changes of temperature that affect the kinetics, thermodynamics and the selectivity. Usually, the heat regime is selected to ensure the highest possible efficiency of the process. Heat is supplied to or removed from the chemical reactor or the temperature regime depends on the heat effect of the reaction. For real reactors, it is necessary to know what is the amount of heat the reactor exchanges or does not exchange with the environment in order to ensure steady chemical process. (Froment, G. F., Bischoff, K. B., & Wilde J. De., 2011; Luyben, W. L., 2007; Smith, R., 2005).

When drawing up the heat balances, it is necessary to take ino account the heat amounts associated with the course of the chemical reaction, bearing in mind that each chemical reaction has smaller or bigger heat effect (Harriott, P., 2003; Levenspiel, O., 1999). To calculate the heat balance of a chemical reactor means to find the values of the variable parameters by which the incoming and outgoing heats will be equal under conditions ensuring stable performance of the reactor and achievement of high degree of conversion (Kolmetz, K., 2020; Sari, R. M., & Kolmetz, K., 2020; Jakobsen, H. A., 2008).

Due to the specifics of each reactor related to its construction and flow hydrodynamics, the chemical processes take place with certain differences with respect to the different heat regimes. This means that some special considerations should be made by the drawing up of the heat balances where the economic efficiency and capital investment should be taken into account results in specifics (Wojciechowski, B. W., 1997).

The aim of the present paper is to make up heat balances ensuring steady performance of two reactors (CPFR – continuous plug-flow reactor and CSTR – continuous stirred-tank reactor) where irreversible exothermic reaction of first order is to take place under given operating parameters. The objectives include achieving a high degree of conversion, determining the inlet temperatures of the two reactors, and selecting the reactor operating under a heat regime that minimizes heat consumption.

EXPOSITION

When compiling the heat balances of chemical reactors. One should take into account the type of the reactor, its performance with time and the hydrodynamic regime within the reactor, as well as the heat effect of the chemical reaction that takes place in it. After selecting a reactor and a heat

regime, the final forms of the heat balance equations are obtained after jointly solving the general heat balance equation and the characteristic equation of the material balance that describes the particular reactor.

The objects of the study are two reactors CSTR and CPFR where the initial concentration of reagent A is $C_{A_0} = 3{,}8\ \text{kmol/m}^3$, and the rate of feeding the reaction mixture in the reactor is $\vartheta = 0{,}8.10^{-3}\ \text{m}^3/\text{s}$. In both reactors, first order exothermic reaction occurs with heat effect of $\Delta H_r = -35\,600\ kJ/kmol$. The rate constant of the irreversible exothermic reaction $2A \xrightarrow{k} B + D + \Delta H_r$ is $k = 1{,}62.10^5.e^{\left(\frac{-44\,400}{RT}\right)}\ s^{-1}$. The initial concentrations of the inert component R and the products are: $C_{R_0} = 10{,}1\ \text{kmol/m}^3$; $C_{B_0} = C_{D_0} = 0\ \text{kmol/m}^3$. The molar specific heat capacities of the reagents and the products do not depend on temperature and are as follows: $c_{p_A} = 66\ kJ/kmol.K$; $c_{p_R} = 52\ kJ/kmol.K$; $c_{p_B} = 58\ kJ/kmol.K$; $c_{p_D} = 54\ kJ/kmol.K$. The reaction volume of the reactors is $V_r = 0{,}147\ m^3$, their heat-exchange area is $F = 12{,}8\ m^2$, and reactors lengths are equal $L = 2{,}9\ m$. Water is fed in direction counter to the flow in the reactors jackets with initial temperature 12°C and final temperature 22°C. The heat transfer coefficient is $K = 290\ W/m^2.K$. The temperature of the reaction mixture within the reactors should not be higher than 55°C.

For the aims of the study, specific methodologies for carrying out polythermal and adiabatic regimes in both reactors were elaborated, aiming to determine the degree of conversion and find the initial temperature of the reaction mixture under the condition that the temperature of the reaction mixture within the reactors is not higher than 55°C (Jakobsen, H. A., 2008; Smirnov, N. N., & Volzhinsky, A. I., 1977: Domansky, I.V., Isakov, V.P., et al., 1982; Pavlov, K. F., Romankov, P. G., Noskov, A. A., 1990; Koleva, D., 2023; Dobrev, S., & Koleva, D., 2024).

Since CPFR is a gradient reactor, the reactor parameters vary along reactor length wich means that the temperature and the degree of conversion also vary along reactor length. Therefore, to compile the heat balance, the reactor is divided into sections. For this purpose, the CPFR is assumed to be composed of n sections and calculations were carried out for each section. For convenience, the length of the reactor of 2.9 m is divided into 29 sections, 0.1 m each. For the calculation of the polythermal regime in CPFR, the system of equations (1) to (7) was used for the material and heat balances, while for the adiabatic regime the equations used were (2), (3), (6), (7) and (8).

$Q_{\text{chem.reac.}} = Q_{\text{heating(cooling)}} + Q_{\text{environment}}$ (1) $Q_{\text{chemreac.}} = 108{,}22.\left(X_{A_n} - X_{A_{n-1}}\right)$, kW (2)

$Q_{\text{heating(cooling)}} = 0{,}621.(T_n - T_{n-1}) + 0{,}0304.(X_{A_{n-1}}.T_{n-1} - X_{A_n}.T_n)$, kW (3)

$Q_{\text{environment}} = 0{,}064.\left(T_n + T_{n-1} - (2T'_{ncp})\right)$, kW (4) $T'_{n,avr} = \frac{T'_{n+1} + T'_n}{2}$ (5)

$-ln\left(1 - X_{A_n}\right) = 6{,}34\ \sum_{i=0}^{i=n-1} k_i$ (6) $k_n = 1{,}62.10^5.e^{\left(\frac{-44\,400}{RT_n}\right)}, s^{-1}$ (7)

$Q_{\text{chem.reac.}} = Q_{\text{heating(cooling)}}$ (8)

T'_{n+1}, T'_n - temperature of the cooling water at the inlet and outlet of the n[th] section, K; T_{n-1}, T_n - temperature of the reaction mixture at the inlet and outlet of the n[th] section; K

For the polythermal regime, the temperature of the reaction mixture at the outlet of each section T_n is determined by equation (9), and for adiabatic regime by equation (10).

$$T_n = \frac{\left(Q_{\text{chem.reac.n}} + 0{,}557.T_{n-1} - 0{,}0304.X_{A_{n-1}}.T_{n-1} + 0{,}064.(2T'_{n,avr})\right)}{\left(0{,}685 - 0{,}0304.X_{A_n}\right)} \quad (9)$$

$$T_n = \frac{\left(Q_{\text{chem.reac.n}} + 0{,}621.T_{n-1} - 0{,}0304.X_{A_{n-1}}.T_{n-1}\right)}{\left(0{,}621 - 0{,}0304.X_{A_n}\right)} \quad (10)$$

For the polythermal regime in CSTR, the calculations were carried out using the system of equations for the material and heat balances from (11) to (17) while for the adiabatic regime – equations (11), (13), (14), (16) and (18).

$Q_{heating(cooling)} = 0{,}6208.(T - T_0) - 0{,}0304.X_A.T, kW$ (11)

$Q_{\text{environment}} = 3{,}712.(T - 290)$,kW (12)

$$X_A = \frac{k.\tau}{1+k.\tau} \quad (13)$$

$$k_n = 1{,}62.10^5.e^{\left(\frac{-44\,400}{R.T}\right)}, s^{-1} \quad (14)$$

$$Q' = 0{,}6208.(T - T_0) - 0{,}0304.X_A.T + 3{,}712.(T - 290), \text{kW} \quad (15)$$

$$\mathrm{Q_{chem.reac.}} = 108{,}22.\mathrm{X_A} \quad (16)$$

$$Q_{chem.reac.} = Q' \quad (17)$$

$$\mathrm{Q_{chem.reac.}} = \mathrm{Q_{heating(cooling)}} \quad (18)$$

$\tau = \frac{V_r}{\vartheta}$ – time of stay of the reagents within the reactor, s

Considering the condition that the temperature of the reaction mixture in the reactor should not exceed 55°C (328 K), we assume a range of inlet temperatures for the reaction mixture $T_{n-1} = T_0$, K and perform calculations for both polythermal and adiabatic regimes (as shown in Table 1). If he condition is not obeyed, the calculation procedure is repeated with new choice for the reaction mixture temperature at reactor inlet$T_{n-1} = T_0$, until the condition is met.

Table 1. Results obtained from the calculations for the degree of conversion and reaction mixture temperature $T_{n-1} = T_0$ at the inlet of CPFR under polythermal and adiabatic regimes

№	Reaction mixture temperature at reactor inlet, $T_{n-1} = \mathrm{T_0}$, K	Reactor length, L, m	Section number, n	Reaction mixture temperature at reactor outlet, T_n, K	Degree of conversion, X_A
Polythermal regime - CPFR					
1.	301,55	1,6	16	327,42	0,5761
		2,9	29	296,17	0,7649
Adiabatic regime - CPFR					
2.	272,15	1,0	10	279,22	0,0376
		2,0	20	291,93	0,1049
		2,9	29	327,42	0,2905

The calculations for CPFR in polythermal regime were carried out with the following set of reaction mixture temperatures at reactor inlet $T_{n-1} = T_0$, K: 318 K; 312 K; 306 K; 305 K; 304 K; 303 K, 302 K and 301,9 K provided that the equivalence of the heats in equation (1) is obeyed.

It can be seen from the results shown in Table 1 that for CPFR in polythermal regime and for the different sections corresponding to different reactor lengths, the condition for the reaction mixture temperature within the reactor to be not higher than 55°C (328 K) was obeyed at reaction mixture temperature at reactor inlet $T_{n-1} = T_0 = 301{,}55$ K.

Under these conditions, the degree of conversion at reactor outlet was 76,49 %.

The calculations for adiabatic regime of operation of CPFR were carried out with the following set of reaction mixture temperatures at reactor inlet $T_{n-1} = T_0$, K: 301,55 K; 301 K; 287 K; 272 K and 250 K provided that the equivalence of the heats in equation (8) is obeyed.

Under these conditions, the degree of conversion observed at reactor outlet was 29,05 % (Table 1).

Table 2. Results obtained from the calculations for the degree of conversion and reaction mixture temperature T_n at the outlet of CSTR under polythermal and adiabatic regimes.

№	Reaction mixture temperature at reactor inlet,	Reaction mixture temperature at reactor outlet,	Heat generated as a result from the chemical reaction,	Heat consumption, $\boldsymbol{Q} = Q_{heating(cooling)} + Q_{environment}, \boldsymbol{kW}$	Degree of conversion, X_A

	$T_{n-1} = \mathrm{T}_0$, К	T_n, К	$Q_{chem.reac.}$, kW		
Polythermal regime - CSTR					
1.	301,55	301,87	41,3138	40,7568	0,3818
Adiabatic regime - CSTR					
2.	287,85	327,23	22,3899	22,3899	0,2069

Table 3. Comparison of the heat balances of CPFR and CSTR under polythermal and adiabatic regimes.

№	Heat generated as a result from the chemical reaction, $Q_{chem.reac.}$, kW	Heat necessary to heat or cool the reaction mixture, $\mathrm{Q}_{\mathrm{heating(cooling)}}$, kW	Heat released to the environment, $\mathrm{Q}_{\mathrm{environment}}$, kW	Reaction mixture temperature at reactor inlet, $T_{n-1} = \mathrm{T}_0$, К	Reaction mixture temperature at reactor outlet, T_n, К	Degree of conversion, X_A
Polythermal regime - CPFR						
1.	2,2393	1,2324	1,0069	301,55	303,84	0,0207
Incoming: 2,2393		Consumption: 2,2393				
2.	4,1693	-0,6993	4,8686	301,55	327,42	0,5761
Incoming: 4,1693		Consumption: 4,1693				
3.	0,4326	-1,0879	1,5205	**301,55**	**296,17**	**0,7649**
Incoming: 0,4326		Consumption: 0,4326				
Polythermal regime - CSTR						
1.	41,3138	-3,3047	44,0614	**301,55**	**301,87**	**0.3818**
Incoming: 41,3138		Consumption: 40,7568				
Adiabatic regime - CPFR						
4.	0,3335	0,3335	-	272,15	272,73	0,0031
Incoming: 0,3335		Consumption: 0,3335				
5.	4,4625	4,4625	-	**272,15**	**327,42**	**0,2905**
Incoming: 4,4625		Consumption: 4,4625				
Adiabatic regime - CSTR						
2.	22,3899	22,3899	-	**287,85**	**327,23**	**0,2069**
Incoming: 22,3899		Consumption: 22,3899				

Table 2 shows the results obtained from the calculations for the degree of conversion if the reaction is carried out in CSTR at reaction mixture temperature at reactor inlet $T_{n-1} = \mathrm{T}_0 = 301{,}55$, К. It was found that if the reaction is carried out in CSTR under polythermal regime, the degree of conversion achieved 38,18 % will be lower than that achieved with CPFR (76,49 %) and the reaction mixture temperature at reactor outlet will be $T_n = 301{,}87$ К. The small difference between the reaction mixture temperatures at CPFR inlet and outlet under polythermal regime is due to the hydrodynamic of ideal mixing present in this reactor type, which leads to levelling of the temperature within the reaction volume.

Under adiabatic regime in CSTR, the conversion degree obtained is lower (20,69 %) than that observed under polythermal regime while the reaction mixture temperature at reactor outlet is higher $T_n = 327{,}23$ К (Таблица 2). The reaction mixture temperature at CSTR outlet under adiabatic regime is higher because the amount of heat generated as a result, of the chemical reaction is used to heat up the reaction mixture since, under this regime, there is no heat-exchange with the environment.

All the results obtained for the heat balances of the two reactors under polythermal and adiabatic regimes are summarized in Table 3. Comparing the heat balances of CPFR for polythermal and adiabatic regimes, it was noted that the conversion degree reached was 76,49 % under polythermal regime, the reaction mixture temperature at reactor inlet was 301,55 К and the

heat consumption was 0,43 kW. Under adiabatic regime and reaction mixture temperature at reactor inlet lower by 29,4 K, the conversion degree achieved was significantly smaller (29,05 %) and the heat consumption was higher - 4,46 kW (Table 3). This can be explained with the specifics of the adiabatic regime at which the all the heat generated as a result of the chemical reaction is spent for heating the reaction mixture, while under polythermal regime, certain amount of heat released into the environment is added to the balance.

Comparing the heat balances of CSTR under polythermal and adiabatic regimes, it was found that higher degree of conversion (38,18 %) at slightly higher temperature of the reaction mixture at reactor inlet (301,55 K) and higher heat consumption 41 kW (Table 3). Under adiabatic regime, however, the lower degree of conversion (20,69 %) results in lower temperature of the reaction mixture at reactor inlet (287,85 K) and lower heat consumption 22 kW (Table 3).

The comparison of the heat balances of CSTR and CPFR indicated that, at the same reaction mixture temperature at reactor inlet (301,55 K) under polythermal regime, the conversion degree achieved in CPFR (76,49 %) is higher than that reached in CSTR (38,18 %), under lower heat consumption in CPFR (0,43 kW), and lower temperature of the reaction mixture at reactor inlet (296,17 K) compared to CSTR (41 kW and 301,87 K) (Table 3). This is because, for the same reaction volume, a higher degree of conversion is achieved in CPFR than in CSTR. Under adiabatic regime and lower reaction mixture temperature at reactor inlet (272,15 K), the degree of conversion reached in CPFR was higher (29,05 %) at lower heat consumption (4,46 kW) compared to that in CSTR (287,85 K; 20,69 %; 22 kW), respectively (Table 3). Therefore, if a choice is to be made for a reactor and heat regime that ensures higher process efficiency and lower heat consumption, then the CPFR under polythermal regime is preferred. Another advantage of CPFR is its tubular design allowing realization of polythermal regime when carrying out exothermic reaction.

CONCLUSION

The choice of stable heat regime for an exothermic reaction carried out in different by design chemical reactors, it is necessary to elaborate a complex estimation of the economic efficiency and capital investments for particular reactor aiming to achieve high efficiency of the process. A stable heat regime is the one in which, after applying external influence, the reactor will restore its normal operation after removing the influence. The present work discusses the specifics in the elaboration of the heat balances of two reactors CPFR and CSTR stipulated by their special design characteristics and the hydrodynamic regimes when exothermic reaction takes place in them.

After carrying out certain calculation procedures and applying special methodologies, the heat balances were made, which ensure the stable thermal regime in both the CPFR and CSTR when irreversible first order exothermic reaction takes place in them under given operating parameters with an initial condition for the temperature at reactor inlet to be not higher than 55°C. After applying the calculation procedures, the temperatures of the reaction mixture at reactors' inlets were calculated under polythermal and adiabatic regimes, as well as the achieved degree of conversion and the heat consumption necessary for the reaction.

It was established that when the reaction is carried out under polythermal regime at the same temperature of the reaction mixture at the inlets of both reactors, the degree of conversion achieved in CPFR is higher than that in CSTR, with lower heat consumption and lower temperature of the reaction mixture at the reactor outlet. However, when the reaction is carried out under adiabatic regime at lower reaction mixture temperature at reactor inlet, the degree of conversion reached in CPFR was higher than that reached in CSTR with lower heat consumption.

After the analysis of the heat balances, it was concluded that higher process efficiency and lower het consumption can be achieved when the reaction is carried out in CPFR under polythermal regime. For the reactors considered, the specific methodologoes applied for polythermal and adiabatic regimes to determine the degree of conversion and the initial temperature of the reaction mixture can also be used for exothermic reactions of order higher than first. The considered theoretical method can be successfully applied in the training of students of Chemical Engineering and Chemical Technologies on reactors.

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