SAFE DESIGN OF COOLED TUBULAR REACTORS FOR EXOTHERMIC, MULTIPLE REACTIONS; PARALLEL REACTIONS—II

THE DESIGN AND OPERATION OF AN ETHYLENE OXIDE REACTOR

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Abstract—In part I a model and criteria have been developed for the safe design and operation of cooled tubular reactors for multiple reactions of the parallel type. In this Part II the model is extended to parallel reactions with an arbitrary stoichiometry. The results are applied to the industrial process of the ethylene oxidation with pure oxygen. It is shown that the criteria derived in part I lead to useful guidelines for the design and operation of an ethylene oxide reactor.

DETERMINATION OF THE TUBE DIAMETER FOR AN ETHYLENE OXIDE REACTOR

In Part I[1] a model has been derived for the design and operation of multiple reactions of the parallel type in a cooled tubular reactor. This model will now be applied to the Ethylene Oxide reactor. In Part I two selectivity criteria were developed for the pseudo-homogeneous model of the cooled tubular reactor in which the reactions were assumed to have stoichiometric coefficients equal to one. In order to apply the derived criteria to the ethylene oxidation, where the stoichiometric coefficients differ from one, we have to reformulate these criteria for a more general stoichiometry. This has been done in the appendix.

The industrial production of ethylene oxide is based on the direct oxidation of ethylene in the gas phase with a silver-based catalyst. In this oxidation process either air or pure oxygen is used. It has been shown[2, 3] that the process using oxygen is more economical than the air-based process. Packed-bed, multitubular cooled reactors are used in the oxygen-based process and an excess of ethylene is applied. Non-converted ethylene is recycled. The main by-products are CO_2 and H_2O formed according to:

Most kinetic studies[4] agree on the predominance of the parallel reactions and the combustion of ethylene oxide can be neglected under industrial reaction conditions, so we simplified the reaction scheme (1) to a

system of two parallel reactions:

which corresponds to the general parallel reaction system. The reaction rate expressions reported in literature[4] range from purely empirical correlations to complicated rate expressions of the Langmuir-Hinshelwood type. At a large excess of ethylene as applied in the oxygen-based oxidation units, literature[5-7] agrees that the rate equations simplify to first order kinetics in the oxygen concentration, so that in this case $R_{wP} = k_p C_{\text{O}_2}$ and $R_{wX} = k_x C_{\text{O}_2}$. From the literature data we selected the rate expressions reported in Table 1, in which also the system parameters and the chosen reactor design data are given. We will now use the criteria derived to determine safe tube diameters for a differential selectivity in the hot spot of $S'_{PB} = 0.70$. The reactor inlet temperature is assumed to be equal to T_c . For the prescribed value of the differential selectivity $S'_{PB} = 0.70$ the value of the differential reciprocal selectivity ratio based on ethylene as the key-component is:

$$(S'_{XP})_B = \frac{1 - S'_{PB}}{S'_{PB}} = \frac{1 - 0.70}{0.70} = 0.429.$$

The kinetics of reactions (2) and (3) are controlled by the oxygen concentration, therefore it is convenient to use oxygen as the key-component and the maximum allowable differential reciprocal selectivity ratio $(S'_{XP})_{\text{ma}}$.

Table 1. Values of system and design parameters for the ethylene oxide reactor

Kinetic rate coefficients	
$k_p = 70.4 \exp(-\frac{7200}{T}) \text{ m}^3/\text{kg s}$	$k_x = 49.4 \cdot 10^3 \exp(-\frac{10800}{T}) \text{ m}^3/\text{kg s}$
System parameters	
$-\Delta H_p = 210 \text{ MJ/kmol O}_2$	$-\Delta H_x = 473 \text{ MJ/kmol O}_2$
$k_R = 1.32 \cdot 10^{-4} \text{ m}^3/\text{kg s}$	$T_R = 546 \text{ K}$
$P = 1.50$	$\gamma_p = 13.2$
$H = 2.25$	$\rho_B = 850 \text{ kg/m}^3 \text{ reactor vol.}$
$c_p = 1.16 \text{ kJ/kg K}$	
Design data	
$p = 1 \text{ MPa}$	$\rho_g = 6.06 \text{ kg/m}^3 \text{ reaction mixture}$
$C_{AO} = 6.0 \text{ mol per cent}$	$d_p = 4 \text{ mm}$
$u_o = 1.3 \text{ m/s}$	

From eqn (A14) we get $(S'_{XP})_{ma}$:

$$(S'_{XP})_{ma} = \left(\frac{\nu_{B1}}{\nu_{B2}}\right) (S'_{XP})_B = \frac{2}{1/3} \cdot 0.429 = 2.571$$

The maximum allowable temperature is calculated from eqn (A9):

$$T_{ma} = \frac{\gamma_p(p-1)}{\gamma_p(p-1) - \ln \left[\frac{\nu_X}{\nu_P} (S'_{XP})_{ma} \right]} = 0.977$$

or $T_{ma} = 533.5 \text{ K}$ (260.5°C).

The minimum cooling temperature is calculated from eqn (A12) resulting in $(T_c)_{\min} = 0.8963$ or $(T_c)_{\min} = 489.4 \text{ K}$

(216.4°C) for $Da_c/Da_{\min} = 5$. The parameters $P_{1,2}$ in the criterion (A10) are $P_1 = 1.00$ and $P_2 = 0.973$ for the average values of $T_c = 503 \text{ K}$ and $\Delta T_{ad} = 0.80$. As $P_1 \approx P_2$ and since ΔT_{ad} is high compared to $(T_{ma} - T_c)$, we will use for P the value $P = 1.00$. We now find with eqn (A10):

$$\frac{U(T_{ma} - T_c)}{d_i C_{AO}} = 1.47 \cdot 10^7 \frac{\text{J}}{\text{kmol.s}}$$

as the design value for the reactor. For standard tube diameters and for $X_{AL} = 0.40$ sets of cooling medium temperatures and reactor lengths are given in Table 2. The overall heat transfer coefficient has been calculated as outlined in [8]. We assumed the reactor to produce

Table 2. Reactor configurations designed according to the selectivity criterion

Oxygen concentration in the feed $C_{AO} = 6.0 \text{ mol per cent}$						
Superficial gas velocity $u_o = 1.3 \text{ m/s}$						
Oxygen conversion $X_{AL} = 0.40$						
$(S'_{XP})_{B,ma} = 0.70$, $T_{ma} = 534 \text{ K}$						
FIRST CRITERION						
d_t	$d_{in} \cdot 10^3$	u	T_c	$Da_c/Da_{\min}$	$l_{0.40}$	S_{PB}
nominal in inches	m	$\text{W/m}^2 \text{ K}$	K	-	m	-
1 "	24.3	298	516	1.85	5.9	0.719
1½ "	38.1	297	506	2.66	7.8	0.740
2 "	49.3	290	497	3.72	11.2	0.766
2½ "	59.0	282	489	5.14	16.4	0.790
3 "	73.7	269	475	8.91	31.5	0.829
SECOND CRITERION						
1 "	"	"	516	1.82	5.7	0.717
1½ "	"	"	507	2.58	7.4	0.736
2 "	"	"	499	3.50	10.1	0.758
2½ "	"	"	491	4.68	13.6	0.778
3 "	"	"	479	7.50	24.9	0.815

steam, so the coolant is boiling water. Figure 1 presents the relationships between the conversion X_A , the reactor temperature T and the integral selectivity S_{PB} as a function of the reactor length for the standard tube diameters. We see from Table 2, that a 2.5" tube already requires a cooling medium temperature of 489 K, which is so low that excessively large tube lengths are required for the conversion chosen. Moreover, we observe that the integral selectivity increases with increasing tube diameters; this is due to the lower average temperature levels in the reactor for the larger diameters, which favours the desired reaction. Further the lower coolant temperatures move the hot spot temperature further away from T_{ma} . For an integral selectivity of $S_{PB} \approx 0.76$ and a feed concentration of 6 mole % of oxygen the allowable nominal tube diameters range from 1.5 to 2.5".

We will select a reactor with 2" tubes of 12 m length for our following considerations. The capacity of the reactor, of course, is determined by the total number of parallel tubes.

In Table 2 also the results obtained are given if the second criterion is used. The difference in the results for the two criteria is rather small; this in general is not the case, but here ΔT_{ad} is so high that the correction term in the second criterion with respect to the first criterion is small.

OPERATION OF THE REACTOR

According to the aforementioned design method based on a selectivity criterion we will consider a reactor design with 2" tubes of 12 m. length operating at a feed concentration of 6 mole % of oxygen and a cooling medium temperature of 473 K.

Fig. 1. Oxygen conversion (a), temperature profiles (b) and integral selectivity (c) as a function of the reactor length and the tube diameter for the ethylene oxide reactor ($C_{A0} = 6.0\%$ mol, $u_0 = 1.3$ m/s, $P = 1.0$ MPa).

Runaway

We first check on runaway at design conditions by increasing the oxygen concentration in the feed and keeping $U(T_{ma} - T_c)/d_i$ constant. Results are given in Fig. 2, which shows that runaway occurs at 7.9 mole % O_2 in the feed. Hence, at the proposed design conditions the reactor operates completely safe. Moreover, the integral selectivity S_{PB} is the highest at the oxygen concentration of 6 mol % as can be seen from Fig. 2(c).

Varying reactor loads

Another important operation problem are the reaction conditions to be chosen at varying loads. We will con-

sider two reactor load changes of 50 and 150% of the design rate $u_0 = 1.30$ m/s. We should be aware that a variation in reactor load results in a change in the overall heat transfer coefficient. According to selectivity criterion (A10) a proper reactor operation requires keeping the term $U(T_{ma} - T_c)/d_i C_{A0}$ constant and in our case equal to 1.47×10^7 J/kmol.s in order to maintain the required selectivity and safe operation. Therefore the cooling medium temperature should be adjusted for the change in the heat transfer coefficient as a result of the change in the reactor load. In Table 3 cooling medium temperatures calculated from $U(T_{ma} - T_c)/d_i C_{A0} = 1.47 \times 10^7$ J/kmol.s are given for the new reactor loads. In

Fig. 2. Oxygen conversion (a), temperature profiles (b) and reactor selectivity (c) in the ethylene oxide reactor as a function of the tube length; effect of oxygen inlet concentration ($d_i = 2''$, $u_0 = 1.3$ m/s, $P = 1.0$ MPa).

Table 3. Selectivity and conversion in an ethylene oxide reactor with 2" tubes of 12 m length, keeping $U(T_{ma} - T_c)d_i C_{A0}$ constant and at varying reactor loads.

u_0 m/s	U $W/m^2 K$	T_c K	x_{AL} —	s_{PB} —
0.65	196	480	0.39	0.815
1.30	290	497	0.42	0.766
1.95	368	505	0.40	0.744

Fig. 3 is shown what the new conditions are—the solid lines—and also what would happen—the dotted lines—if the coolant temperatures were not adjusted according to the criterion and were kept constant at $T_c = 497$ K. It can be seen from the solid curves that operation of the reactor adhering to criterion (A10) leads to safe operation without runaway and with high selectivities. For the lower load of $u_0 = 0.65$ m/s the conversion is decreased (Fig. 3a) due to lower average temperature level (Fig. 3b) despite the longer residence time. On the other hand at the higher load of $u_0 = 1.95$ m/s the conversion is

Fig. 3. Oxygen conversion (a), temperature profiles (b) and reactor selectivity (c) as a function of the reactor length and its load for the ethylene oxide reactor (solid lines calculated according to criteria, dotted lines—keeping T_c constant); $d_i = 2$ ", $C_{A0} = 6\%$ mol, $P = 1$ MPa).

decreased (Fig. 3a) due to shorter residence time and despite the higher average temperature level (Fig. 3b). If the coolant temperature is not adjusted, decreasing the load to 50% leads to immediate runaway because of the reduction of the overall heat transfer coefficient at lower gas flow rates.

This may seem an unexpected result because reducing the load also results in a reduction of the total heat production in the reactor, so we would expect less severe conditions and a more safe operation. This is not true. At reducing the flow rate the hot spot moves towards the

entrance of the reactor and consequently the length of the tube—or cooling area—available to remove heat at the highest heat production rates is also reduced. But also the heat transfer coefficient is reduced at the lower flow rate. The combination of these two effects in the first part of the reactor results in conditions which are not adequate anymore to keep the hot spot within acceptable limits and to prevent runaway.

Figure 3 demonstrates the strong influence of the gas flow rates through the reactor. Temperature profiles, conversions and integral selectivities are all affected in a

Fig. 4. Oxygen conversion (a), temperature profiles (b) and integral selectivity (c) as a function of the reactor pressure and its length ($d_t = 1.5''$, $C_{A0} = 6\%$ mol, $u_0 = 1.3$ m/s).

Table 4. Selectivity and conversion in an ethylene oxide reactor with 1.5" tubes of 12 m length, keeping $U(T_{ma} - T_c)/d$; $C_{A0} u_0 = 1.3$ m/s, $T_{ma} = 534$ K.

P	ΔT_{ad}	U	T_c	$L_{0.40}$	$X_{A,12}$	$S_{PB,12}$
MPa	-	W/m ² K	K	m	-	-
1.0	0.79	297	506	7.8	0.53	0.743
2.0	0.81	441	497	11.4	0.41	0.767
3.0	0.82	553	489	15.6	0.33	0.787

different way. It is a matter of overall plant economics which combination of conversion and selectivity is best or in other words which gas flow rate (number of tubes in the reactor for a desired production) represents an economic optimum.

The influence of the reactor pressure

In our previous calculations we used a reactor pressure of 1.0 MPa. It is known that in industrial practice frequently higher reactor pressures are applied. In Fig. 4 and Table 4 therefore results are given for design pressures of 2.0 and 3.0 MPa and compared with the 1.0 MPa case. In these figures a nominal tube diameter of 1.5 in. and a length of 12 m are taken and conditions are chosen according to criterion (A10). In this case 2 in. tubes would give far too low conversions at the higher reactor pressures. We see that the reactor selectivity is improved at higher pressures at the expense of the conversion obtained. We conclude from these figures that the reactor pressure is a very important variable, but a correct choice can only be made on economic grounds taking a.o. compression costs, reactor construction costs and selectivities obtained into account.

CONCLUDING REMARKS

From the discussions presented we may conclude that the criterion $U(T_{ma} - T_c)/d$; $C_{A0} = \text{constant}$ leads to very useful results for the design of reactors for multiple, parallel reactions and also for the operation of existing reactors in order to achieve optimum operating conditions. In all cases where according to the criterion the coolant temperature has to be lowered the reactor selectivity is improved at the expense of the total conversion. Moreover, we can observe from the results given that the ratio of the integral to the differential selectivity is strongly influenced by the ratio Da_c/Da_{min} or T_{ma}/T_c .

The method outlined in part I is restricted to parallel reactions for which the kinetics are of the first order or can be fitted reasonably well by first order kinetics. For consecutive reactions we soon will publish a similar treatment.

NOTATION

For the symbols we used we refer to Part I[1]. New symbols, introduced in this part, are:

- S_{PB} selectivity based on B as a key-reactant (P -desired product)
 S'_{PB} differential selectivity based on B as a key-reactant (P -desired product)

- S'_{XP} differential reciprocal selectivity ratio (based on A as a key-reactant)
 $(S'_{XP})_B$ differential reciprocal selectivity ratio (based on B as a key-reactant)
 ν stoichiometric coefficient

Subscripts

B reactant

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APPENDIX

We consider reactions of the following type:

Both reactions are irreversible, exothermic and of the first order in reactant A . The heat balance for the pseudo-homogeneous model of the cooled, tubular reactor is:

$$u \frac{dT}{dz} = - \left(\frac{\nu_A}{\nu_P} \Delta H_P R_{wP} + \frac{\nu_A}{\nu_X} \Delta H_X R_{wX} \right) \frac{\rho_B}{\rho_g c_P} - \frac{4U}{d \rho_g c_P} (T - T_c) \quad (A2)$$

Here the heats of reactions ΔH_P and ΔH_X of both reactions are now based on the conversion of one kmole of key-reactant A . We introduce the conversions to the products P and X with respect to reactant A , which are defined by:

$$X_P = \frac{\nu_A}{\nu_P} \frac{C_P - C_{P0}}{C_{A0}} \quad \text{and} \quad X_X = \frac{\nu_A}{\nu_X} \frac{C_X - C_{X0}}{C_{A0}} \quad (A3)$$

The dimensionless equations, which describe the reactor behaviour are:

$$\frac{dX_P}{dZ} = \frac{\nu_A}{\nu_P} Da \kappa (1 - X_P - X_X) \quad (A4)$$

$$\frac{dX_X}{dZ} = \frac{\nu_A}{\nu_X} Da \kappa^p (1 - X_P - X_X) \quad (A5)$$

$$\frac{dT}{dZ} = Da \Delta T_{ad} \left(\frac{\nu_A}{\nu_P} \kappa + \frac{\nu_A}{\nu_X} H \kappa^p \right) (1 - X_P - X_X) - Da U^* (T - T_c) \quad (A6)$$

After introducing the total conversion of the reactant A ($X_A = X_P + X_X$) the relation between the reaction temperature and the conversion X_A can be found

$$\frac{dT}{dX_A} = \Delta T_{ad} \frac{1 + \frac{\nu_P}{\nu_X} H \kappa^{p-1}}{1 + \frac{\nu_P}{\nu_X} \kappa^{p-1}} - U^* \frac{(T - T_c)}{\left(\frac{\nu_A}{\nu_P} \kappa + \frac{\nu_A}{\nu_X} \kappa^p \right) (1 - X_A)} \quad (A7)$$

The differential reciprocal selectivity ratio for the reactions (A1) is found by dividing eqn (A5) by (A4):

$$\frac{dX_X}{dX_P} = S'_{XP} = \frac{\nu_P}{\nu_X} \kappa^{p-1} \quad (A8)$$

The maximum allowable differential selectivity ratio $(S'_{XP})_{ma}$ is related to the maximum allowable temperature T_{ma} , which is now defined by:

$$T_{ma} = \frac{\gamma_p(p-1)}{\gamma_p(p-1) - \ln \left[\frac{\nu_X}{\nu_P} (S'_{XP})_{ma} \right]} \quad (A9)$$

and the selectivity criteria by:

$$\frac{U(T_{ma} - T_c)}{d_i C_{A0}} \geq - \frac{k_R \rho_B \Delta H_P}{4} * \frac{\nu_A}{\nu_P} \left[\frac{\nu_X}{\nu_P} (S'_{XP})_{ma} \right]^{1/(p-1)} * [1 + H(S'_{XP})_{ma}] * P_{1,2} \quad (A10)$$

in which $P_1 = 1$ for the first criterion and for the second one holds:

$$P_2 = 1 - \frac{T_{ma} - T_c}{\Delta T_{ad}} * \frac{1 + \frac{\nu_P}{\nu_X} \kappa_c^{p-1}}{1 + \frac{\nu_P}{\nu_X} H \kappa_c^{p-1}} \quad (A11)$$

Similarly the minimum coolant temperature can be found by solving the implicit equation:

$$\frac{Da_c}{Da_{min}} = \frac{\left[\frac{\nu_X}{\nu_P} (S'_{XP})_{ma} \right]^{1/(p-1)} * [1 + (S'_{XP})_{ma}]}{\kappa_c \left(1 + \frac{\nu_P}{\nu_X} \kappa_c^{p-1} \right)} \quad (A12)$$

in which $T_c = [1 - (\ln \kappa_c) / \gamma_p]^{-1}$ and further a practical value has to be inserted for Da_c / Da_{min} . The differential selectivity ratio S'_{XP} as used in the criteria is based on reactant A as key component. If the second reactant B is the more valuable raw material, then B should be chosen as key-reactant. The differential reciprocal selectivity ratio $(S'_{XP})_B$ based on B is given by:

$$(S'_{XP})_B = \left(\frac{\nu_{B2}}{\nu_{B1}} \right) \left(\frac{\nu_P}{\nu_X} \right) \kappa^{p-1} \quad (A13)$$

The relation between the two selectivities S'_{XP} and $(S'_{XP})_B$ can directly be obtained from eqns (A8) and (A13):

$$S'_{XP} = \left(\frac{\nu_{B1}}{\nu_{B2}} \right) (S'_{XP})_B \quad (A14)$$