

Boundary conditions for developing a safety concept for an exothermal reaction

Ulrich Hauptmanns*

*Abteilung Anlagentechnik und Anlagensicherheit, Otto-von-Guericke-Universität Magdeburg,
Universitätsplatz 2, 39106 Magdeburg, Germany*

Received 17 July 2006; received in revised form 5 December 2006; accepted 9 February 2007
Available online 15 February 2007

Abstract

Kinetic calculations for an example exothermal chemical process, the production of TCB, are carried out. They address both parameter uncertainties and random failures of the cooling system. In this way, they enable one to establish comprehensive boundary conditions for a safety system in terms of unavailability, the quantities of the undesired by-product (TCDD) produced and the times available before a required intervention, if a pre-determined quantity of TCDD is tolerated. It is shown that accounting for stochastic effects and uncertainties derived from insufficient knowledge provides a broader and more realistic knowledge base for devising a viable safety concept.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Exothermal reaction; Uncertainties; Component failures; TCB; TCDD

1. Introduction

Component failures may have a significant impact on the quantities of substances generated in a chemical process and provoke unwanted side reactions. Data uncertainties will affect the calculational prediction of these quantities. If both are accounted for, more realistic boundary conditions for devising the safety concept and establishing the success criteria for the safety system, i.e. the conditions under which it fulfils its function, are obtained.

Component failures are mostly treated on the basis of deterministic assumptions, e.g. cooling failure at the beginning of the process instead of letting it fail randomly, as occurs in reality.

Data uncertainties have been a concern in the optimization of process plants (cf. [1–3]) but rarely in relation with plant safety [4].

The objective of the present paper is to demonstrate the impact of both effects and their potential for obtaining the boundary conditions for the design of a safety system. This is done by analysing the dynamics of the semi-batch process for the production of trichlorophenol investigated in Ref. [5]. The salient features of this process are described in the next section.

2. Process description and reaction network

2,4,5-Trichlorophenol is used for manufacturing herbicides, antiseptics or as a fungicide in paper and pulp mills. The process used for its production is carried out in a semi-batch reactor at a pressure of approximately 19 bar using methanol as a solvent.

A total amount of 1400 kg of the feed, 1,2,4,5-tetrachlorobenzene (TCB), is suspended in a mashing-tub together with 3.8 m³ of methanol (CH₃OH) and 0.05 m³ of sodium hydroxide. The suspension is introduced into the reactor and heated to 141 °C. After that a total quantity of 0.775 m³ of a 50% aqueous solution of sodium hydroxide (NaOH) is added to the process during a period of time of 60 min. The subsequent time for reaction amounts to 13.5 h. The reaction is exothermal and is held at a temperature of 155 °C by a cooling system once it has been started up by heating the mixture with steam of 156 °C.

The initial volume of the reactor contents amounts to 4825 l reaching 5600 l after the addition of the sodium hydroxide solution, which is fed into the reactor with a temperature of 25 °C.

It is well known that during the process the highly toxic dioxin (TCDD) is produced, albeit in minute quantities, as long as the nominal range of the reaction parameters is maintained. A deviation of the reaction parameters was the cause of the Seveso accident (cf. [6]), in which an estimated quantity between 0.45 and 3 kg of dioxin was released into the environment.

* Tel.: +49 391 6718831; fax: +49 391 6711128.

E-mail address: ulrich.hauptmanns@vst.uni-magdeburg.de.

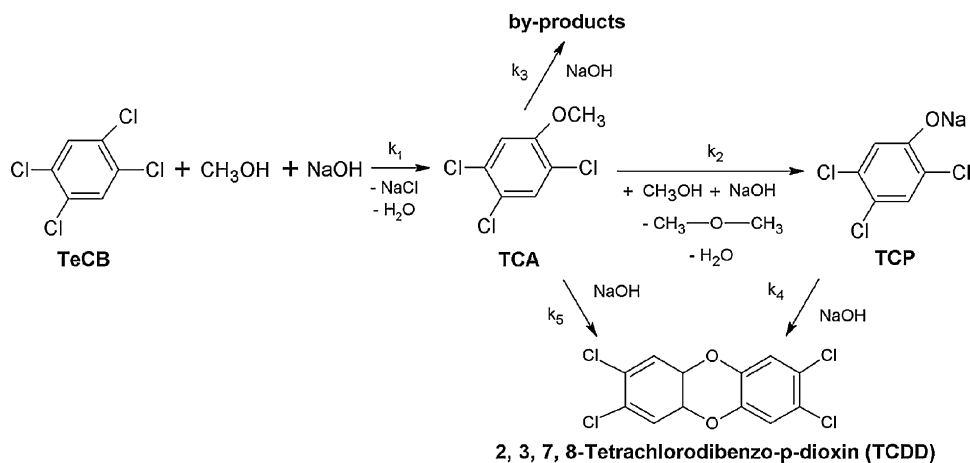


Fig. 1. Reaction network for the synthesis of TCP according to the Boehringer process (after Ref. [5]).

Table 1

Heats of reaction, pre-exponential factors and apparent energies of activation for the reactions of Fig. 1

Reaction <i>i</i>	$\Delta H_{R,i}$ in kJ/mol	k_i (428 K) in $\text{m}^3/(\text{mol s})$	$E_{A,i}$ in kJ/mol
1	-112	2.17×10^{-7}	64.8
2	-50.5	7.70×10^{-8}	146.5
3	-50.5	7.92×10^{-9}	194.3
4	Not determined	7.90×10^{-14}	240
5	Not determined	2.70×10^{-13}	220

The reaction network of the important steps (up to the formation of tetrachlorophenolate) is shown in Fig. 1. The parameters required for describing the reactions mathematically are given in Table 1. The network and parameters stem from a co-operation of the authors of [5] with the Boehringer Company. Simulations based on them agree well with experimental results obtained in a 10l laboratory reactor and values measured in production, as shown in Ref. [5].

3. Process model and deterministic results

The process model described in Ref. [5] is used. A heating (reaction start-up) and cooling system was added. It is modelled by a heat exchange between the reactor contents, whose temperature is assumed constant over the heat exchanger surface, and the heating, respectively, cooling fluid, which is cooled

down, respectively, warmed up whilst passing through the heat exchanger (cf. [7]). The fluid mass flow is controlled by a PI controller adapted from Ref. [8]. Failures of the system during the cooling period are treated based on [9]. The underlying concept is that of a well stirred reactor (cf. [10]). The resulting system of first-order differential and algebraic equations is given in Appendix A. It is solved by a second-order Runge-Kutta scheme with adaptive time steps.

The substances involved in the process and their relevant properties are given in Table 2.

In order to elucidate the process behaviour calculations with and without initial cooling failure and the point values for the input data indicated in Tables 1 and 2 were carried out. They refer to the existing process as well as to a modification extending the time period for NaOH solution feed to 10 h. The results are presented in Table 3.

It is evident that the quantities of TCDD produced during normal operation are minute, whilst cooling failure steps up its production more than a hundred-fold. The critical parameter obviously is the process temperature.

It is interesting to note that extending the feed period to 10 h leads to a much more benign process behaviour. Even after an initial failure of the cooling system quantities of TCDD are produced which are only about four times those from nominal reactor operation. The instant in time of cooling failure vitally affects the quantity of TCDD generated, whilst the variations in TCP yield remain small. This is illustrated by Fig. 2.

Table 2

Substances of the process and relevant properties

Number <i>i</i>	Substance	Chemical formula	Molecular mass M_i	Heat capacity c_p in J/(kg K)
1	1,2,4,5-Tetrachlorobenzene (TeCB)	$\text{C}_6\text{H}_2\text{Cl}_4$	215.9	937.9
2	2,4,5-Trichloroanisole (TCA)	$\text{C}_7\text{H}_5\text{Cl}_3\text{O}$	211.4	953.3 ^a
3	2,4,5-Trichlorophenolate (TCP)	$\text{C}_6\text{H}_2\text{Cl}_3\text{ONa}$	219.42	884.8 ^a
4	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin (TCDD)	$\text{C}_{12}\text{H}_4\text{Cl}_4\text{O}_2$	321.97	889.9 ^a
5	Miscellaneous by-products	–	200 ^b	700 ^b
6	Aqueous solution of sodium hydroxide (50%)	$\text{NaOH} + \text{H}_2\text{O}$	40.0 ^c	3274.0
7	Methanol	CH_3OH	32.04	2541.0

^a Calculated according to Ref. [11].

^b Assumed values.

^c NaOH only.

Table 3
Substances generated and process parameters (without considering uncertainties)

Operating regime	NaOH feed during 1 h		NaOH feed during 10 h	
	Cooling	No cooling	Cooling	No cooling
Maximum quantity of TCDD in mol/in kg	0.0201	2.275	0.0209	0.0750
	0.0065	0.732	0.0093	0.0241
Maximum quantity of TCP in mol/in kg	4708	4791	4687	5304
	1033	1051	1028	1164
Maximum temperature in K	428.15	478.2	428.15	444.5
Final temperature in K	394.2	420.4	414.8	426.5
Time of start of cooling in min	25.0	–	190.0	–
Heat removed by coolant in kJ	768,968	–	288,583	–

Considering by way of example a level of approximately 110% of the final level in case of correct functioning of cooling as tolerable, viz. 0.022 mol of TCDD (7.1 g), a critical period for a cooling failure may be derived. This is the period during which a cooling failure leads to a quantity of TCDD a larger than that stated above. It amounts to the first 2.04 h for 1 h feed and to 7.9 h in case of 10 h feed.

4. Data uncertainties

Most of the data involved in predicting the behaviour of chemical processes are uncertain. These uncertainties may either be due to a lack of knowledge (epistemic) or derive from the stochastic nature of important events for process behaviour such as the failure of operational components (aleatory).

Normally, the data are treated as unknown fixed quantities which may be determined by experiment within specified confidence bounds. But the latter are rarely specified.

In order to account for uncertainties the data are no longer considered to be fixed but their behaviour is assumed to be random as a consequence of uncertainty. Random variables are treated by statistical distributions, whose parameters are normally estimated on the basis of experimental results.

The input data with largest influence on the calculation results in the present case are the rate constants and heats of reaction (cf. Table 1). Unfortunately, no information on their uncertainties is available in the present case. Therefore, a generic approach was adopted. It consists in (a) the choice of a distribution and (b) the fixing of the distribution parameters.

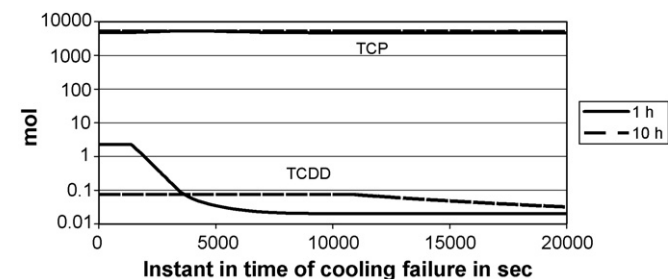


Fig. 2. Production of TCDD and TCP as a function of the instant in time of cooling failure (feed periods 1 and 10 h).

The distribution chosen in this particular case is the log-normal distribution (cf. [12]). It is well suited for quantities defined on the positive axis.

Its probability density function (pdf) is given by

$$f(x) = \frac{1}{\sqrt{2\pi sx}} \exp\left(\frac{-(\ln x - \mu)^2}{2s^2}\right), \quad x > 0 \quad (1)$$

where x is the random variable in question, e.g. the heat of reaction, μ the mean value of the logarithms of that variable and s is the corresponding standard deviation. The distribution is characterized by its expected value

$$E[X] = \exp\left(\mu + \frac{s^2}{2}\right) \quad (2)$$

its median or 50th centile (50% of the values lie below and 50% above)

$$x_{50} = e^\mu \quad (3)$$

and its 5th and 95th centiles denoted by x_{05} , respectively, by x_{95}

$$x_{05} = \frac{x_{50}}{K_{95}}, \quad \text{and} \quad x_{95} = x_{50}K_{95} \quad (4)$$

K_{95} is the uncertainty factor defined as follows:

$$K_{95} = e^{1.6449s} \quad (5)$$

where the value of 1.6449 is the argument of the standard normal distribution corresponding to a probability of 0.95. Hence, as is frequently done, the factor is chosen such that 90% of the values of x lie between x_{05} and x_{95} .

In view of indications contained in Refs. [13,14] $K_{95} = 1.25$ was chosen for the rate constants and $K_{95} = 1.05$ for the enthalpies of reaction. This means that 90% of the values are comprised within intervals of $\pm 25\%$ for rate constants and $\pm 5\%$ for reaction enthalpies, respectively. The K_{95} factors for rate constants in Ref. [13] lie between 1.16 and 10 and in Ref. [15] between 1.41 and 3.16, albeit for different reactions.

The choice is somewhat supported by the indication in Ref. [16] that the target for uncertainties of rate constants should be 15%.

By the same token the heat capacities of the substances involved in the process (cf. Table 2) are not well known with the

Table 4
Components of a typical cooling system and corresponding failure rates from Ref. [18]

Component	<i>i</i>	Expected value of failure rate λ_i per 10 ⁶ h	Uncertainty factor K_{95}
Temperature sensor	1	28.6	1.5
Signal transducer	2	13.9	3.3
Controller	3	25.7	2.5
Pneumatic control valve	4	19.8	1.7

exception of those for water, methanol and the sodium hydroxide solution, which are considered to be virtually exact. They were therefore obtained using the atomic element contribution method, which provides data affected by average errors in the 9–10% range (cf. [11]). This information can be used to specify a log-normal distribution for the heat capacities concerned with the mean values indicated in Table 2 and an uncertainty factor $K_{95} = 1.11$.

The same uncertainty factor is assigned to the enthalpy of mixing between NaOH and TeCP, which amongst others may be affected by random variations in lye concentration.

5. Calculation of component lifetimes

The probabilistic analysis of a typical chemical reactor [9] has shown that the control system of the cooling circuit is the weakest link for reactor safety. Such a control system typically consists of the components contained in Table 4. They are arranged in series in the sense of reliability (cf. [17]), i.e. the failure of any one of them would make the cooling system break down and call for the safety system (i.e. emergency cooling) to operate.

The random lifetimes of the components are calculated based on the exponential distribution, which is the only one applying to constant failure rates, using the following relationship:

$$\tau_i = \frac{1}{\lambda_i} \ln u \quad (6)$$

where u is a random number uniformly distributed on [0,1]. Since the system is a semi-batch reactor, the instants of time of cooling failure are calculated using the following relationship:

$$t_{\text{fail}} = \min_{i=1,\dots,4} (\tau_i) - \left\lfloor \frac{\min_{i=1,\dots,4} (\tau_i)}{T_r} \right\rfloor T_r \quad (7)$$

where T_r is the cycle time, i.e. duration of the reaction (14.5 h) plus 2 h for discharging the reactor and preparing the resumption of production. $\lfloor \cdot \rfloor$ denotes the integral part of the quotient. Should the component failure occur during the preparation period for the next charge, it is supposed that the failed state is discovered before operation is resumed and that the component is repaired. This assumption may easily be relaxed, if necessary.

6. Uncertainty propagation

Both epistemic and aleatory uncertainties are treated using the Monte-Carlo method (cf. [19]). In order to keep the num-

ber of trials low, Latin Hypercube sampling was used for the epistemic uncertainties. The straight Monte-Carlo approach was employed for component lifetimes. A total number of 2500 trials were made, leading to an average temporal spacing between the moments of cooling failure of 24 s, which is considered to be adequate.

7. Calculations accounting for uncertainties

Table 5 repeats the calculations presented in Table 3 taking into account the parameter uncertainties. The results show a marked influence of the uncertainties, which, however, have different impacts depending on the parameter considered. The K_{95} factors are largest in the cases where temperature is not controlled due to cooling failure. They are especially large for the quantity of TCDD produced. This shows that the predictions made with point values (cf. Table 3) may considerably underestimate the quantity of TCDD present in the reactor. This fact should be accounted for in elaborating the safety concept.

Additional calculations reveal a strong sensitivity of TCDD production on the enthalpy of mixing. Its variations, which may result from both deficiencies in knowledge and fluctuations in the composition of the aqueous solution of sodium hydroxide, strongly influence the process temperature. Hence, the composition should be carefully controlled.

8. Calculations with stochastic cooling failures

The above cases were treated once again. The cooling now fails at a random point in time. One set of calculations accounts for failures alone and the other one additionally considers the epistemic uncertainties of the input data. Table 6 provides the details.

It is clearly visible that, considering the stochastic nature of component failures, on the average lower quantities of TCCD are to be expected than after initial cooling failure. If data uncertainties are accounted for, the predicted quantities are somewhat higher.

9. Boundary conditions for a safety system

The above calculations provide the basis for devising a safety system for the reactor which accounts for both the demand frequency and the quantity of TCDD involved.

The total expected frequency of the initiating event “cooling failure” is calculated as the sum of the data of Table 4 to be 0.8 year⁻¹. However, only 13.4% of the cooling failures occur during the critical first 2.22 h of the process, so that 0.11 year⁻¹ critical demands on the safety system are to be expected, in case the feed is completed within 1 h. Should the feeding process be spread over 10 h, 26.0% of the cooling failures would be expected during the corresponding critical period so that 0.21 critical demands on the safety system would be expected per year. However, the quantity of TCDD involved is considerably smaller in the latter case, no matter when cooling failure occurs.

Table 5
Calculations accounting for parameter uncertainties (quantities in mol and kg)

Operating regime		NaOH feed during 1 h				NaOH feed during 10 h			
		Cooling	K_{95}	No cooling	K_{95}	Cooling	K_{95}	No cooling	K_{95}
Maximum quantity of TCDD in mol/in kg	Expected value	0.0203		4.346		0.0210		0.0853	
	95th centile	0.0065	1.20	1.399	9.53	0.0068	1.21	0.0275	1.90
		0.0242		16.19		0.0253		0.1617	
		0.0078		5.212		0.0081		0.0521	
Maximum quantity of TCP in mol/in kg	Expected value	4692		4575		4662		5217	
	95th centile	1030	1.05	1004	1.41	1023	1.06	1145	1.12
		4905		6304		4935		5831	
		1076		1383		1083		1279	
Maximum temperature in K		428.15		491.1		428.15		454.6	
Final temperature in K	Expected value	394.3		420.5		414.8		426.5	
	95th centile	395.3	1.0025	423.7	1.01	415.9	1.003	430.1	1.01
Time for start of cooling in min	Expected value	18.3		–		133.4		–	
Heat removed by coolant in kJ	Expected value	769,411		–		290,479		–	
	95th centile	769,817	1.0005	–		290,875	1.001	–	

Table 6
Calculations accounting for stochastic cooling failures with and without data uncertainties

Operating regime		Stochastic cooling failure without parameter uncertainties				Stochastic cooling failure including parameter uncertainties			
		NaOH feed during 1 h	K_{95}	NaOH feed during 10 h	K_{95}	NaOH feed during 1 h	K_{95}	NaOH feed during 10 h	K_{95}
Maximum quantity of TCDD in mol/in kg	Expected value	0.1042		0.0363		0.1409		0.0368	
	95th centile	0.0335	14.5	0.0117	1.61	0.0454	9.36	0.0118	3.20
		0.4030		0.0775		0.5233		0.0917	
		0.1298		0.0250		0.1685		0.0295	
Maximum quantity of TCP in mol/in kg	Expected value	4749		4929		4718		4882	
	95th centile	1042	1.04	1082	1.01	1035	1.09	1071	1.12
		4957		5386		5142		5446	
		1088		1182		1128		1195	
Maximum temperature in K		478.2		444.5		485.8		452.6	
Final temperature in K	Expected value	395.8		418.7		395.8		418.5	
	95th centile	404.8	1.02	426.6	1.001	404.5	1.02	426.3	1.02

The above frequencies of demand enable one to fix the targets for the unavailability of the safety system (i.e. emergency cooling). This may be done, for example, in accordance with a safety goal. Should this, by way of example, be 10^{-5} year $^{-1}$ this unavailability would have to be of the order of 10^{-4} .

Another important aspect is the time which is available before an intervention, e.g. emergency cooling, is needed. The results obviously depend on the instant of cooling failure; they are given in Fig. 3. The underlying requirement was that the quantity of TCDD should not exceed 0.022 mol.

Fig. 3 indicates that the time before intervention required is always more than half an hour, even if the statement is based on the 5th centile of the results. This shows that an automatic emergency cooling system may be supplemented by human emergency interventions. Sufficient time is available for the latter. Credit may be taken from this fact when deciding on how to meet the unavailability target of the emergency cooling system.

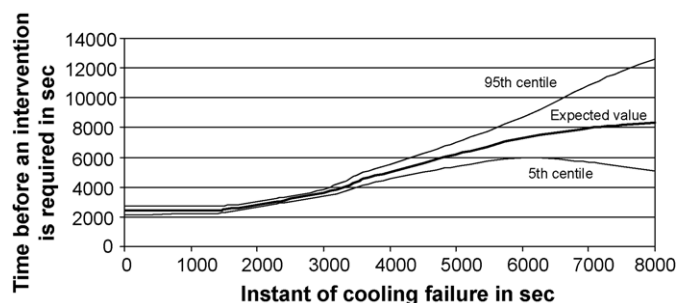


Fig. 3. Times available for intervention after cooling failure (including 5th and 95th centiles).

10. Summary and conclusions

The time behaviour of a chemical reaction with a critical dependence on process temperature was presented in detail. The calculations enable one to

- assess the quality of the results by including data uncertainties and to estimate the expected maximum quantity of the hazardous side product;
- identify the time frame for necessary interventions;
- assess the expected frequencies of demand for the safety system or additional interventions and to thereby derive unavailability targets for the safety system.

Hence, it may be concluded, that calculations which account for data uncertainties and the stochastic nature of component failures provide more comprehensive and realistic boundary conditions for the design of a safe process.

Appendix A. Process and reactor model

TeCB

$$\frac{dn_1}{dt} = -k_1(428 \text{ K}) \exp \left[-\frac{E_{A1}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_1 n_6}{V} \quad (\text{A.1})$$

TCA

$$\begin{aligned} \frac{dn_2}{dt} = & k_1(428 \text{ K}) \exp \left[-\frac{E_{A1}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_1 n_6}{V} - k_2(428 \text{ K}) \\ & \times \exp \left[-\frac{E_{A2}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} - k_3(428 \text{ K}) \\ & \times \exp \left[-\frac{E_{A3}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} - k_5(428 \text{ K}) \\ & \times \exp \left[-\frac{E_{A3}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \end{aligned} \quad (\text{A.2})$$

TCP

$$\begin{aligned} \frac{dn_3}{dt} = & k_2(428 \text{ K}) \exp \left[-\frac{E_{A2}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \\ & - k_4(428 \text{ K}) \exp \left[-\frac{E_{A4}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_3 n_6}{V} \end{aligned} \quad (\text{A.3})$$

TCDD

$$\begin{aligned} \frac{dn_4}{dt} = & k_5(428 \text{ K}) \exp \left[-\frac{E_{A5}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \\ & + k_4(428 \text{ K}) \exp \left[-\frac{E_{A4}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_3 n_6}{V} \end{aligned} \quad (\text{A.4})$$

By-products

$$\frac{dn_5}{dt} = k_3(428 \text{ K}) \exp \left[-\frac{E_{A3}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \quad (\text{A.5})$$

NaOH

$$\begin{aligned} \frac{dn_6}{dt} = & -k_1(428 \text{ K}) \exp \left[-\frac{E_{A1}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_1 n_6}{V} \\ & - k_2(428 \text{ K}) \exp \left[-\frac{E_{A2}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \end{aligned}$$

$$\begin{aligned} & -k_3(428 \text{ K}) \exp \left[-\frac{E_{A3}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \\ & -k_5(428 \text{ K}) \exp \left[-\frac{E_{A5}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} \\ & -k_4(428 \text{ K}) \exp \left[-\frac{E_{A4}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_3 n_6}{V} + \frac{\rho_6 \dot{V}_{in}}{2M_6} \end{aligned} \quad (\text{A.6})$$

CH₃OH

$$\begin{aligned} \frac{dn_7}{dt} = & -k_1(428 \text{ K}) \exp \left[-\frac{E_{A1}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_1 n_7}{V} \\ & - k_2(428 \text{ K}) \exp \left[-\frac{E_{A2}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_7}{V} \end{aligned} \quad (\text{A.7})$$

Process energy balance

$$\begin{aligned} & \left(C_R + \sum_{i=1}^5 M_i c_{pi} n_i + 2c_{p6} M_6 n_6 + c_{p7} M_7 n_7 + C_P \right) \frac{dT}{dt} \\ & = k_1(428 \text{ K}) \exp \left[-\frac{E_{A1}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_1 n_6}{V} |\Delta H_1| \\ & + k_2(428 \text{ K}) \exp \left[-\frac{E_{A2}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} |\Delta H_2| \\ & + k_3(428 \text{ K}) \exp \left[-\frac{E_{A3}}{R} \left(\frac{1}{T} - \frac{1}{428} \right) \right] \frac{n_2 n_6}{V} |\Delta H_3| \\ & - \rho_6 c_{p6} \dot{V}_{in} (T - T_{in}) + \frac{\rho_6}{2M_6} \dot{V}_{in} |\Delta H_{mix}| - \dot{Q}_{cool} - \dot{Q}_{loss} \end{aligned} \quad (\text{A.8})$$

- Feed:

$$\dot{V}_{in} = \frac{V_f - V_i}{T_d}$$

- Heat capacity C_P (accounts for heat capacity of residual products, which produces an increase of the total heat capacity from 15,600 to 20,100 kJ/kg after feed):

$$C_P = 116.82(n_{7,i} - n_7)$$

- Heat loss from the reactor (which varies with reaction temperature and amounts to 21 kW at 155 °C) [5]:

$$\dot{Q}_{loss} = 0.15556(T - 293.15)$$

Coolant energy balance and PI controller

$$\dot{Q}_{cool} = \dot{m} c_{p,w} (T - T_{c,in}) \left[1 - \exp \left(-\frac{A k_w}{\dot{m} c_{p,w}} \right) \right] \quad (\text{A.9})$$

$$\frac{d\dot{m}}{dt} = \frac{K_1}{\tau} (\dot{Q} - \dot{Q}_{cool}) + \frac{K}{\tau} s_h, \quad \dot{m}(t^*) = a \quad (\text{A.10})$$

$$\frac{ds_i}{dt} = \frac{K_0}{p_i} (u_c - K_{mV/T} T), \quad s_i(0) = 0 \quad (\text{A.11})$$

$$s_h = k_c (u_c - K_{mV/T} T) + s_i, \quad s_h(0) = 0 \quad (\text{A.12})$$

General process conditions		
k_w	Heat transfer coefficient	0.5 kW/(m ² K)
A	Area for heat exchange	12 m ²
T_{in}	Temperature of sodium hydroxide feed	25 °C
ΔH_{mix}	Enthalpy of mixing (NaOH/TeCB)	–30 kJ/mol
V_i	Initial volume	4825 l
V_f	Final volume	5600 l
T_d	Dosification period for NaOH	60 min
$n_{1,i}$	Tetrachlorobenzene (TeCB) (initial quantity)	6161 mol
$n_{4,i}$	Miscellaneous by-products (initial quantity)	368 mol
$n_{6,i}$	Sodium hydroxide (initial quantity)	950 mol
$n_{7,i}$	Methanol (initial quantity)	93,827 mol
ρ_6	Density 50% aqueous solution of sodium hydroxide	1521.7 × 10 ⁻³ kg/l
ρ_7	Density of methanol	773.2 × 10 ⁻³ kg/l
C_R	Heat capacity of the reactor	6800 kJ/K
Cooling system including control		
\dot{Q}	Net heat generation (reaction + mixing – \dot{Q}_{loss} – feed)	kW
$T_{c,in}$	Coolant inlet temperature	20 °C
$c_{p,w}$	Coolant heat capacity (water)	4.179 kJ/(kg K)
a	Coolant/steam mass flow at time t^* (when $T=428.15$ K is reached)	2 kg/s
τ	Cooler time constant	100.0 s
K	Cooler gain	5.0 kg/(s mV)
u_c	Command signal	428.15 mV
k_c	Proportional gain	10.0
$K_{mV/T}$	Gain of temperature in mV transducer	1.0 mV/K
K_0	Gain	10.0
K_1	Gain	1 kg/(s kW)
p_i	Integrator coefficient	5.0 s

References

- [1] N. Watanabe, Y. Nishimura, M. Matsubara, Optimal design of chemical processes involving parameter uncertainty, *Chem. Eng. Sci.* 28 (1973) 905–913.
- [2] N. Nishida, A. Ichikawa, E. Tazaki, Synthesis of optimal process systems with uncertainty, *Ind. Eng. Chem. Process Des. Dev.* 13 (1974) 209–214.
- [3] R. Henrion, P. Li, A. Möller, M.C. Steinbach, M. Wendt, G. Wozny, Stochastic Optimization for Operating Chemical Processes Under Uncertainty, ZIB-Report 01-04, Konrad-Zuse-Zentrum für Informationstechnik, Berlin, 2001.
- [4] U. Hauptmanns, Uncertainty and the calculation of safety-related parameters for chemical reactions, *J. Loss Prev. Process Ind.* 10 (4) (1997) 243–247.
- [5] R. Braun, A. Schönbacher, Simulation von Semibatchprozessen am Beispiel einer komplexen chemischen Reaktion, in: G. Kreysa, O.-U. Langer, V. Pilz (Hrsg.), *Chemische Reaktionen – Erkennung und Beherrschung sicherheitstechnisch relevanter Zustände und Abläufe, Praxis der Sicherheitstechnik*, vol. 4, DECHEMA, Frankfurt am Main, 1997.
- [6] F.P. Lees, *Loss Prevention in the Process Industries*, vol. 3, Butterworth Heinemann, Oxford, 1996.
- [7] V.P. Isachenko, V.A. Osipova, A.S. Sukomel, *Heat Transfer*, Mir Publishers, Moscow, 1980.
- [8] K. Watanabe, I. Matsuura, A. Masahiro, M. Kubota, D.M. Himmelblau, Incipient fault diagnosis of chemical processes via artificial networks, *AIChE J.* 35 (11) (1989) 1803–1811.
- [9] U. Hauptmanns, Fault tree analysis for process plants, in: A. Kandel, E. Avni (Eds.), *Engineering Risk and Hazard Assessment*, vol. I, CRC Press, Boca Raton, 1988.
- [10] K.R. Westerterp, W.P.M. van Swaaij, A.A.C.M. Beenackers, *Chemical Reactor Design and Operation*, John Wiley & Sons, Chichester, July 1995.
- [11] R.H. Perry, D.W. Green (Eds.), *Perry's Chemical Engineering Handbook*, McGraw Hill, New York, 1998.
- [12] N.L. Johnson, S. Kotz, N. Balakrishnan, *Continuous Univariate Distributions*, John Wiley & Sons, 1995.
- [13] S. Balakrishnan, P. Georgopoulos, I. Banerjee, M. Ierapetriou, Uncertainty considerations for describing complex reaction systems, *AIChE J.* 48 (December (12)) (2002) 2875–2889.
- [14] D. Salvatierra, J.D. Taylor, P.A. Marrone, J.W. Tester, Kinetic study of hydrolysis of methylene chloride from 100 to 500 °C, *Ind. Eng. Chem. Res.* 38 (1999) 4169–4174.
- [15] M.T. Reagan, H.N. Najm, P.P. Pébay, O.M. Knio, R. Ghanem, Quantifying uncertainty in chemical system modelling, *Int. J. Chem. Kinet.* 37 (2005) 368–382.
- [16] T.F. Edgar, D.A. Dixon, G.V. Reklaitis, Vision 2020: computational needs of the chemical industry, *Natl. Acad. Sci.* 23 (2) (1999) 74–90.
- [17] R.E. Barlow, F. Proschan, *Statistical Theory of Reliability and Life Testing—Probability Models*, Holt, Rinehart and Winston, New York, 1975.
- [18] U. Hauptmanns, Reliability Data for Process Plants, Prepared for the “Technical Committee on Installation Safety and Major Hazard Commission Working Group on Land-Use-Planning”, Report No. IAUT-AS 0103, Magdeburg, July 2003.
- [19] J.E. Gentle, *Random Number Generation and Monte Carlo Methods*, Springer-Verlag, New York, 2003.