Modelling and Simulation of a Radical Chlorination Process of 1,2-Dichloroethane

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ABSTRACT

Tetrachloroethane has been considered. The process has been studied on an experimental installation which consists of a purely chlorination reactor, a r

An industrial process for radical chlorination of 1, 2 – dichloroethane to give 1,1,2 – trichloroethane and 1, 1, 2, 2 – efrigerator, a separator, a heat exchanger and recirculating pump. The reactor has a working volume of 1.6 m^3. In order to describe the kinetics of the reaction, both a model and a numerical solution program were developed. The given work is devoted to the generation of a mathematical model adequately circumscribing the given process. The results obtained with the simulation program were compared with experimental measurements taken at the experimental reactor. It is possible that the proposed mathematical model can be used to calculate various modes of the process for preparing tri-and tetrachloroethane from 1, 2 – dichloroethane.

Key words: 1, 2–Dichloroethane chlorination, 1,1,2 – Trichloroethane production; gas – liquid reaction; Chemical reaction simulation.

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Introduction

Gas – liquid chemical reactions are very important and widely used in the technology of organic and inorganic synthesis for the production of different products. An example of a gas – liquid process of this type is the radical chlorination process of 1,2 – dichloroethane (EDC) up to 1,1,2 – trichloroethane (ETC), 1,1,2,2 – tetrachloroethane (ETeC) and higher chloroethanes in the presence of α,α'–azo-bis-isobutyronitrile (AIBN) as the initiator. ETC and ETeC are valuable chemicals due to their use in the production of vinyl chloride; ethylene trichloride; etc.

Szepvolgyi and Ujhidy (1978) studied liquid phase chlorination of chloroalkanes in a continuous operation and analyzed reaction's products. Wachi & Morikawa (1986) studied the substitution of liquid phase chlorination process of EDC in the presence of traditional initiation methods (UV– radiation, high temperatures, and radical initiators). These authors indicated that this reaction was carried out at low temperatures in the presence of UV- radiation in comparison with radical initiators. Orejas (1999,2001) studied an industrial process for the direct chlorination of ethylene at low temperatures to yield EDC, where ETC is one of the most important secondary products. Rozdkov, Zaidman & Sonin (1991) studied the liquid – phase chlorination of 1,2 – dichloroethane at the presence of ferric chloride. Sokolov, Rodova, Levanova & Fomin (1991) studied the liquid phase chlorination process of EDC at 20-100°C in the presence of vinylchloride as the initiator. These authors indicated that the chlorination process of EDC to ETC in the presence of AIBN at 20-100°C does not fulfill with the environmental requirements. Sedov (1992) studied the kinetics of the reaction of AIBN with reaction mixture. He developed the first model proposed for this reaction. In this work a new mathematical model of a radical chlorination process of EDC has been developed. The model and its numerical simulation program were described and developed on the bases of a series of experiments carried out in an experimental installation. The experimental reactor has a capacity of 1.6 m^{3}. In contrast to the model

proposed by Sedov (1992), this paper presents also mathematical models of interphase mass transfer, and the model of radical chlorination of chloroethanes. Besides, it is important to notice that, the experimental material obtained from our experimental installation clarified that the calculated concentration of chlorine radicals was not enough to carry out the chlorination process of EDC with the same velocity and efficiency, which were observed in the experiments. So, it is possible to use a mathematical model to predict the production of chlorine radicals, which was obtained by a method of discrimination of mathematical models [Sedov, 1992].

Description of experimental installation

The experimental installation (Fig. 1) to study the chlorination process of EDC up to ETeC consisted of purely a chlorination reactor of EDC (1), refrigerator (2), separator (3), heat exchanger (4), and a recirculating pump (5).

The chlorination reactor (1) represents enamed cylindrical means with a diameter of 1304 mm, a height of 2190 mm, an elliptic bottom and a cooling jacket. The working volume of the reactor 1.6 m^3 and the surface of heat exchanger 4.3 m^2.

The chlorination reaction of EDC carried out at a working pressure not exceeding 1.65 atm and a temperature 70-90°C.

In working volume of the reactor a bubbler is built for feeding gaseous chlorine into the reaction mixture. EDC and initiator, both in liquid state, are fed to the reactor through different distributers. The most important secondary product is hydrogen chloride (HCl) which leaves the reactor with the waste gases.

Originally the chlorination reactor of EDC is fed with 1700 L of liquid EDC. The heatcarrier heats the reaction mixture up to working temperature 75°C within 3 hours.

After reaching working temperature in the reactor, 7 L of a solution of the initiator was fed to the reactor. The initiator was made of 7.5% solution of AIBN in EDC. Immediately the gaseous chlorine is opened in the bubbler. The flow rate of chlorine is 25-60 m^3/hour.

usual time of the reaction is 5-7 hours. The quantitative analysis of all components in the reaction mixture was carried out on the reactor contents. The composition of the gas phase (waste gases) was determined by a gas analyzer.

During the experiment, the initiator is periodically added to the reaction mixture whereas the working parameters of the chlorination process were varied one by one. However, in some experiments, the working parameters vary considerably such as: flow rate of chlorine, temperature of the reaction mixture, concentration of chlorine in waste gases.
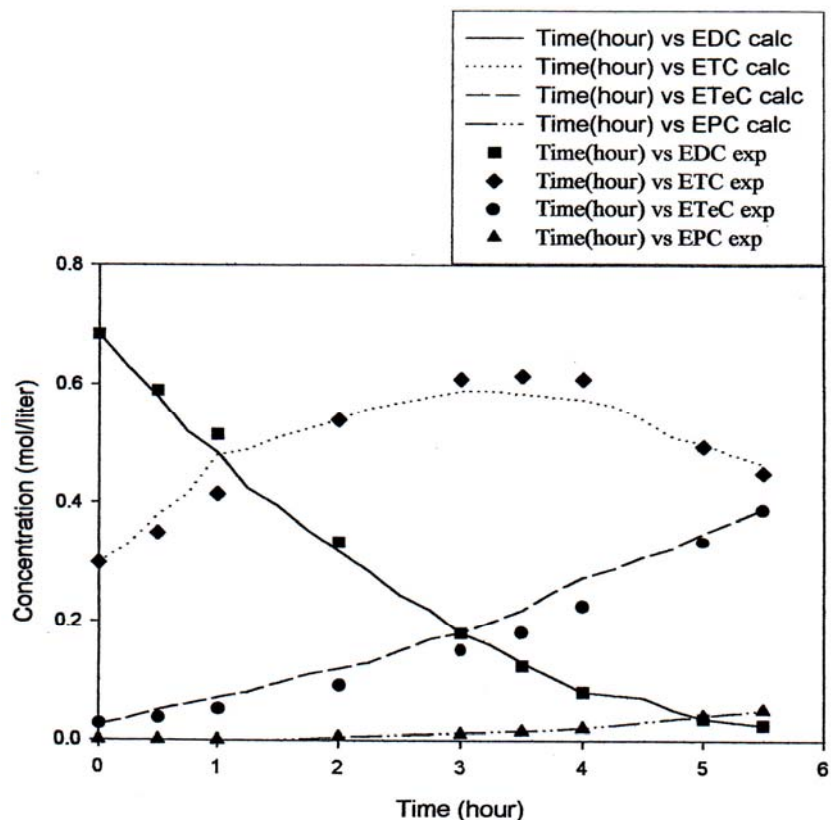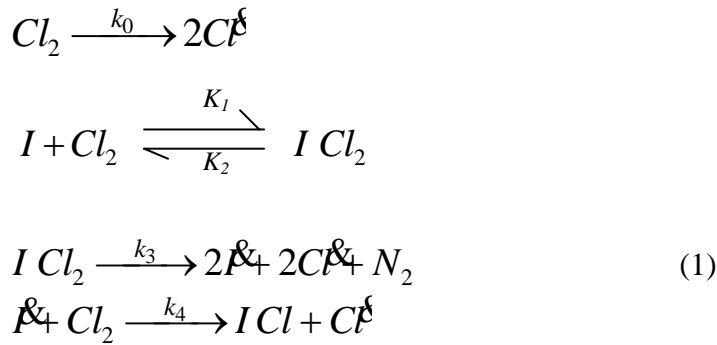
Fig. 1. Experimental installation of the chlorination process of 1<2-dichloroethane.

Development of the model equations

The model considered in this work consists of three main sections: the dissolution process of chlorine, the interaction of AIBN with the reaction mixture and the chlorination process of chloroethanes.
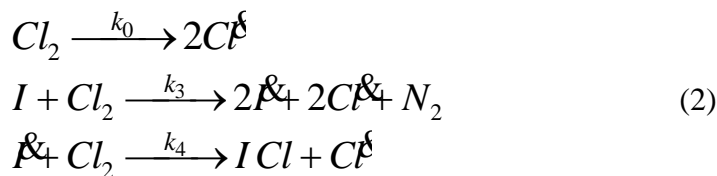
The following scheme of interaction of the AIBN with the reaction mixture was proposed by Sedov (1992).

$$Cl_2 \xrightarrow{k_0} 2Cl^{\bullet}$$

$$I + Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I\,Cl_2$$

$$I\,Cl_2 \xrightarrow{k_3} 2\overset{\bullet}{R} + 2C\overset{\bullet}{l} + N_2 \tag{1}$$
$$\overset{\bullet}{R} + Cl_2 \xrightarrow{k_4} I\,Cl + C\overset{\bullet}{l}$$

Where Cl_2: molecular chlorine dissolved in EDC; $C\overset{\bullet}{l}$: chlorine radical; I: initiator (AIBN); $I\,Cl_2$: an activated complex; $\overset{\bullet}{R}$: initiator-radical; $I\,Cl$: initiator dissociation product.

According to Sedov, the second reaction occurs very fast and it is practically, in equilibrium. Therefore, it can be eliminated and we can consider a generalized reaction (sum of second and third reactions).

In our work the following system of the kinetic equations circumscribing the interaction of AIBN with molecular chlorine, dissolved in EDC.

$$Cl_2 \xrightarrow{k_0} 2Cl^{\bullet}$$
$$I + Cl_2 \xrightarrow{k_3} 2\overset{\bullet}{R} + 2C\overset{\bullet}{l} + N_2 \tag{2}$$
$$\overset{\bullet}{R} + Cl_2 \xrightarrow{k_4} I\,Cl + C\overset{\bullet}{l}$$
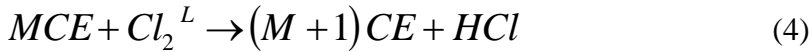
The kinetic equations circumscribing the radical chlorination process of EDC, ETC and ETeC have an identical aspect.

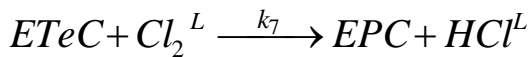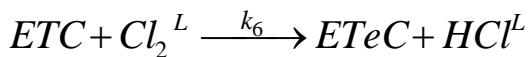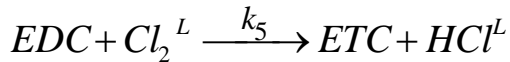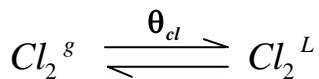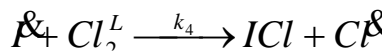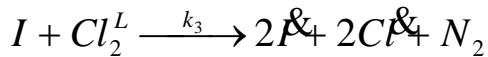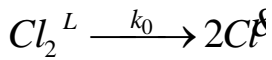$$MCE + Cl_2{}^L \rightarrow (M+1)CE + HCl + Cl^\bullet \qquad (3)$$
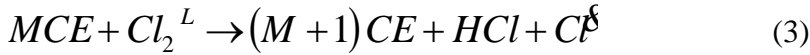
Where MCE: di(tri, tetra) chloroethane; $(M+1)CE$: tri (tetra, penta) chloroethane; $Cl_2{}^L$: dissolved molecular chlorine.

If we consider that the concentration of radicals is quasistationary, then equation (3) becomes less complicated and yields:

$$MCE + Cl_2{}^L \rightarrow (M+1)CE + HCl \qquad (4)$$

Foundation for such supposition is that the chlorine radicals are consumed, and produced during chemical interaction.

Through merging the kinetic equations of interaction of a gas and liquid phase, and the radical chlorination of chloroethanes, the kinetic equations of the gas-liquid process are summarized as follows:

$$Cl_2{}^L \xrightarrow{k_0} 2Cl^\bullet$$

$$I + Cl_2^L \xrightarrow{k_3} 2\overset{\bullet}{R} + 2Cl^\bullet + N_2$$

$$\overset{\bullet}{R} + Cl_2^L \xrightarrow{k_4} ICl + Cl^\bullet$$

$$Cl_2{}^g \underset{\longleftarrow}{\overset{\theta_{cl}}{\rightleftharpoons}} Cl_2{}^L$$

$$HCl^g \underset{\longleftarrow}{\overset{\theta_{Hcl}}{\rightleftharpoons}} HCl^L \qquad (5)$$

$$EDC + Cl_2{}^L \xrightarrow{k_5} ETC + HCl^L$$

$$ETC + Cl_2{}^L \xrightarrow{k_6} ETeC + HCl^L$$

$$ETeC + Cl_2{}^L \xrightarrow{k_7} EPC + HCl^L$$

The system of kinetic equations is described in these differential equations (6).

$$\frac{dI}{dt} = -k_3 \cdot I \cdot Cl_2^L$$

$$\frac{dC\dot{l}}{dt} = \sqrt{k_0 \cdot Cl_2^L} + \sqrt{k_3 \cdot I \cdot Cl_2^L} + k_4 \cdot \dot{R} \, Cl_2^L$$

$$\frac{d\dot{R}}{dt} = \sqrt{k_3 \cdot I \, Cl_2^L} - k_4 \cdot \dot{R} \, Cl_2^L$$

$$\frac{d\, Cl_2^g}{dt} = Q_{in} - \theta_{Cl}\left(Cl_2^* - Cl_2^L\right) - Q_{out} \cdot Cl_2^g$$

$$\frac{d\, Cl_2^L}{dt} = \theta_{Cl}\left(Cl_2^* - Cl_2^L\right) - Cl_2^L\left(k_0 + k_3 I + k_4 \dot{R} + k_5 EDC + k_6 ETC + k_7 ETeC\right)$$

$$\frac{d\, EDC}{dt} = -k_5 \cdot EDC \cdot Cl_2^L$$

$$\frac{d\, ETC}{dt} = Cl_2^L \cdot \left(k_5 \cdot EDC - k_6 \cdot ETC\right)$$

$$\frac{d\, ETeC}{dt} = Cl_2^L \cdot \left(k_6 \cdot ETC - k_7 \cdot ETeC\right) \qquad (6)$$

$$\frac{d\, EPC}{dt} = k_7 \cdot ETeC \cdot Cl_2^L$$

$$\frac{d\, HCl^g}{dt} = \theta_{HCl}\left(HCl^g - HCl^*\right) - Q_{out} \cdot HCl^g$$

$$\frac{d\, HCl^L}{dt} = \frac{d\, ETC}{dt} + \frac{d\, ETeC}{dt} + \frac{d\, EPC}{dt} - \theta_{HCl}\left(HCl^g - HCl^*\right)$$

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$$Cl_2^* = \frac{1}{He_{cl}}$$

$$HCl^* = HCl_{out}$$

$$k_5 = k_5\left(Q_{in}, I, T\right)$$

$$k_6 = k_6\left(Q_{in}, I, T\right)$$

$$k_7 = k_7\left(Q_{in}, I, T\right)$$

Where: Q_{in}, Q_{out} : are flowrate of input and output respectively; θ : is mass transfer coefficient; Cl_2^* : is equilibrium concentration of chlorine; He_{Cl} : is Henry's constant.

The system of the differential equations (6) describes variations of concentration of chemical species with time. For increasing the accuracy of calculations all concentrations are necessary to be divided by a normalization coefficient, which is calculated by the condition:

$$\zeta = \sum_{\forall_i} C_i \qquad (7)$$

Where C_i : Concentration of all components in a liquid phase.

Similarly, it is necessary to evaluate the concentration of components in a gas phase.

Evaluation of the model parameters

The model in this work is used to determine the model parameters (using experimental data), and for the optimization of the chlorination process of EDC.

The rate constants of reactions for, di-, tri-, terta-, and higher chloroethanes depend on flow rate of the initiator, chlorine, and temperature of the reaction mixture. For each group of parameters (flow rate of chlorine, flow rate of the initiator, temperature in

reactor), the rate constants of reactions were evaluated. And by using a method of multiple correlation, the regression equation can be formulated for rate constants of reactions [Westertrep & others, 1984].

$$d_1 = \sum_{i=0}^{N-1} \frac{K_{0i}}{K_{1i}}$$

$$d_2 = \sum_{i=0}^{N-1} \frac{K_{0i}}{K_{2i}} \qquad\qquad (8)$$

$$d_3 = \sum_{i=0}^{N-1} \frac{K_{0i}}{K_{3i}}$$

Where N: number of experiments with constant values of temperature, flow rate of chlorine and initiator; $K_0 \ldots K_3$: rate constants of EDC, ETC, ETeC, EPC respectively, which were found from experimental data; $d_1 \ldots d_3$: averaged ratios for the evaluation of rate constants.

In this case the regression equation can be formulated as:

$$\langle K_0 \rangle = A_0 + A_1 \cdot \mathrm{In}(t + 273) + A_2 \cdot Q_{CL} + A_3 \cdot Q_{in}$$

$$\langle K_1 \rangle = \frac{\langle K_0 \rangle}{d_1}$$

$$\langle K_2 \rangle = \frac{\langle K_0 \rangle}{d_2} \qquad\qquad (8)$$

$$\langle K_3 \rangle = \frac{\langle K_0 \rangle}{d_3}$$

Where $\langle K_0 \rangle$: Rate constant of reaction for EDC, which is found by regression equation; $\langle K_1 \rangle \ldots \langle K_3 \rangle$: Rate constants of reactions for ETC, ETeC, EPC, respectively, which were found from the averaged ratios.

In this proposed model, the constants (A_0; A_1; A_2; A_3) are defined as follows:

$A_0 = -28.34985$; $A_1 = 4.800739$; $A_2 = 1.2318E-2$; $A_3 = 4.552E-3$

The data used for the formulation of the regression equation are shown in the table.

Results and discussion

In order to describe the reaction's kinetics, a numerical simulation program was developed in Pascal language. The model described in the previous section was implemented and solved. At mathematical exposition of such process we face a class of tasks, which, in applied mathematics are named "poorly stipulated". The difference in concentration between the initiator and other components of reaction can be of two – three orders, and the use of a standard software generates significant errors. The dissolution process of chlorine and the interaction of AIBN with the reaction mixture are fast comparing with the chlorination process of chloroethanes. So these two processes are at steady state. The system of the differential equations (6) splits into three independent systems of differential equations: first that describes the dissolution process of a gas phase, second – interaction of AIBN with the reaction mixture, and third – the chlorination of EDC. From a numerical viewpoint, this model represents a system of nonlinear differential equations of fourth order. The model can be solved using Newton – Raphson algorithm [Finlayson, 1980]. Fig.2 shows a comparison between the predictions calculated by means of the simulation program and the experimental data. As shown in fig.2, the mathematical model predicts satisfactorily the experimental data. The given model adequately circumscribes the chlorination process of 1,2 – dichloroethane. Hence it is suggested that the given model can be used to optimize the system and to calculate various modes of instrument settings of the process.
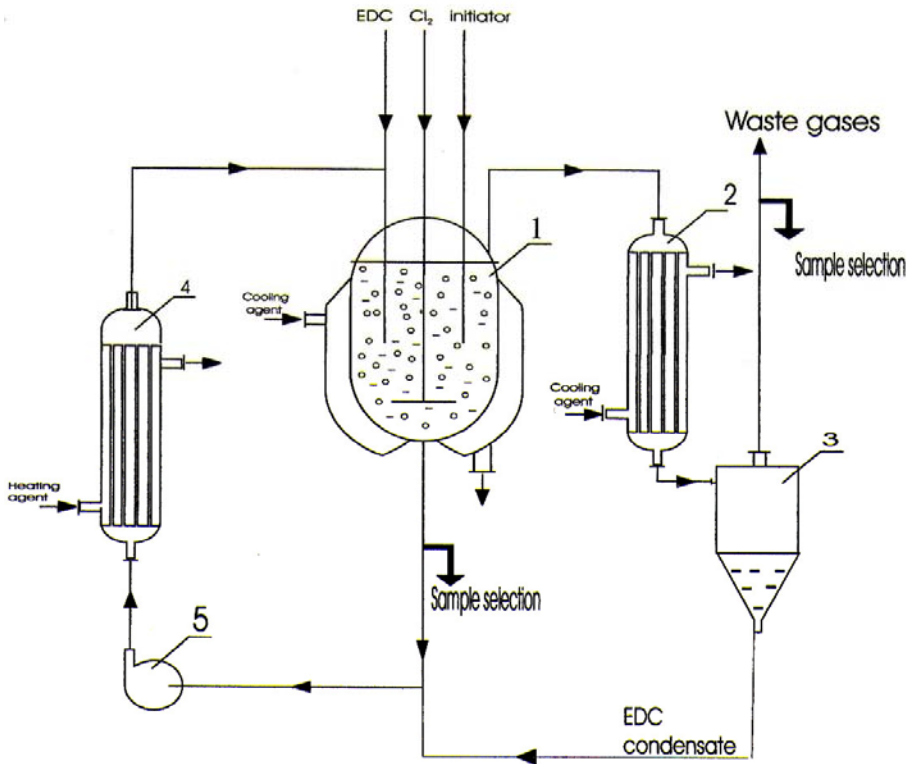
Fig.2. Comparison between experimental and calculated values of concentration

Conclusions

A mathematical model and a numerical simulation program that describe the kinetics of reaction for the production of 1,1,2-trichloroethane, 1,1,2,2- tetrachloroethene and higher chloroethanes by the radical chlorination process of 1,2 – dichloroethane has been developed. It has been shown that, the mathematical model is adequately circumscribing the given process. The predictions obtained from the simulation program were compared with the experimental reactor measurements taken at the experimental reactor. It is possible to calculate various modes of instrument settings of the process of deriving tri and tetrachloroethane from, 1,2- dichloroethane.

Table (1) Data used for the formulation of the regression equation

Experiment	T (°C)	Qc_1 (m³/hour)	Qin (L/hour)	k_0	k_1	k_2	k_3	d_1	d_2	d_3
1	76	40	2.56	0.23796	0.05121	0.0512	0.000145	4.6487	4.64766	1641.1
2	90	63	2.56	0.72784	0.25344	0.08258	0.00001	2.8718	8.81376	73157.1
3	85	45	2.56	0.31355	0.06889	0.00992	0.00992	4.5514	31.6078	31.6049
4	82	35	3.51	0.230	0.0478	0.1827	0.00001	4.8117	1.25589	23000
5	82	37	2.56	0.37025	0.0839	0.00454	0.2365	4.4114	81.5529	1.56553
6	86	47	2.56	0.56136	0.1875	0.0694	0.000011	2.9947	8.08876	51032.7
7	88	63	0.9575	0.65776	0.2438	0.0757	1.32E-6	2.6978	8.68858	499059
8	86	25	3.681	0.10363	0.0353	0.3228	0.2826	2.9332	0.32095	0.36689
							Average	3.7399	18.122	80990

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