Simulation of the evaporation process of 1.2-dichloroethane into nitrogen

E V Podoplelov, A V Balchugov, A I Dementev and A S Ryabov
Angarsk State Technical University, 60 Tchaikovsky Str., Angarsk 665835, Russia
E-mail: uch_sovet@angtu.ru

Abstract. The interaction of gas and liquid phases in some cases is accompanied by the spontaneous occurrence of convective flows and turbulent pulsations at the phase boundary and in adjacent areas. Hydrodynamic instability allows to accelerate the interfacial transfer of matter and leads to an increase in mass transfer coefficients. Research in this field is not only theoretical, but also practical, since surface convection can be artificially created in apparatus for intensifying the mass exchange process.

1. Introduction
In gas-liquid processes under certain conditions in the liquid convective currents [1, 2] may occur usually leading to a significant increase in the mass transfer coefficient. The phenomenon of fluid surface instability can significantly accelerate the process of interfacial transfer [3-6]. The paper studies the mechanism of surface convection in a chemical reaction with a large thermal effect in the gas-liquid system. Liquid phase chlorination of ethylene in the process of producing 1.2-dichloroethane may be an example of such a process. The process of evaporation of 1.2-dichloroethane into nitrogen containing in the exhaust gas chlorine takes place in the process of liquid-phase chlorination of ethylene. Graphical dependences that theoretically confirm the possibility of surface convection are obtained by solving differential equations that describe the convective diffusion of 1.2-dichloroethane vapor in nitrogen and the temperature distribution in a 1.2-dichloroethane film.

2. Numerical simulation
The evaporation of 1.2-dichloroethane into nitrogen containing in the exhaust gas chlorine takes place in the process of liquid-phase chlorination of ethylene. Theoretically let's find out the possibility of convective structures on the surface during the evaporation of hot 1.2-dichloroethane into nitrogen. Let a laminar nitrogen flow pass over the horizontal surface of a layer of fixed 1.2-dichloroethane (figure 1). The nitrogen speed is constant – w, m/s. The length of the contact surface of 1.2-dichloroethane and the nitrogen stream is l, m. The height of the nitrogen layer is h, m. The height of the 1.2-dichloroethane layer is d, m. The width of the surface of 1.2-dichloroethane is b, m. The initial concentration of 1.2-dichloroethane vapor in nitrogen is C₁ (mol/m³). The equilibrium concentration of 1.2-dichloroethane vapor in nitrogen is C*. Since the nitrogen flow is laminar, the vapor transfer of 1.2-dichloroethane in the direction of y axis is carried out only by molecular diffusion. The liquid surface is the origin of coordinates along the y axis.

The vapor diffusion in nitrogen is described by the equation of convective diffusion in a dimensionless form:
\[
\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = \alpha \frac{\partial c}{\partial x},
\]

where \(\alpha = \frac{w l}{D_c}\) is the dimensionless concentration \(c = \frac{C}{C_0}\); \(x = X/l\), \(y = Y/l\).

Boundary conditions: for \(x=0\) and for any \(y\) \(c=0\); for \(y=0\) and for \(x>0\) \(c=1\); for \(x=1\) and for any \(y\) \(\frac{\partial c}{\partial x} = 0\); for \(y=1\) and for any \(x\) \(\frac{\partial c}{\partial y} = 0\).

**Figure 1.** Diagram of the movement of nitrogen over the surface of 1.2-dichloroethane.

We shall apply the finite difference method [7] to equation (1). This method is based on replacing the derivatives included in the differential equation with approximate values expressed in terms of the difference in the values of the function at individual points (nodes) of the grid.

On the nitrogen stream we apply a grid (figure 2). Point O will have \(x\) and \(y\) coordinates. At point O, as well as at grid nodes 1, 2, 3, 4, we denote the concentration of \(c_0, c_1, c_2, c_3, c_4\), respectively.

**Figure 2.** To the conclusion of the equation of diffusion of vapors of 1.2-dichloroethane in nitrogen.

The O' point concentration derivative will be recorded as follows:

\[
\left( \frac{\partial c}{\partial x} \right)_{x+\Delta x, y} \approx \frac{c_0 - c_3}{\Delta x}.
\]

The accuracy of equality (2) increases with decreasing value of \(\Delta x\).

Similarly the temperature gradient for the point O' has the form:

\[
\frac{\partial^2 c}{\partial x^2} \approx \frac{1}{\Delta x} \left[ \left( \frac{\partial c}{\partial x} \right)_{x+\Delta x, y} - \left( \frac{\partial c}{\partial x} \right)_{x-\Delta x, y} \right] = \frac{1}{\Delta x^2} \left( c_1 + c_3 - 2c_0 \right).
\]

The second derivative on the \(y\) coordinate at the point O is determined in the same way:
\[
\frac{\partial^2 c}{\partial y^2} \approx \frac{1}{\Delta y^2} (c_2 + c_4 - 2c_0).
\]

The approximate expression for the first derivative of the concentration on the coordinate \(x\) at point \(O\) takes the form:

\[
\frac{\partial c}{\partial x} = \frac{c_1 - c_3}{2\Delta x}.
\]

Substituting the obtained approximate expressions (3, 4, 5) into equation (1), we obtain:

\[
\frac{1}{\Delta x^2} (c_1 + c_2 + c_3 + c_4 - 4c_0) = \alpha \frac{c_1 - c_3}{2\Delta x}.
\]

Where the concentration at point \(O\) comes from:

\[
c_0 = \frac{1}{4}(c_1 + c_2 + c_3 + c_4) - \frac{1}{8} \alpha \cdot \Delta x (c_1 - c_3).
\]

From the latter equation, it is obvious that the concentration at point \(O\) (figure 2) depends on the concentrations at four adjacent points (1, 2, 3 and 4), as well as on the value of \(\alpha\) and the pitch of the grid \(\Delta x\).

The solution of the last equation (6) together with the boundary conditions makes it possible to calculate the values of vapour concentrations of 1.2-dichloroethane at any point in the nitrogen flow (figure 2). The values of the obtained vapour concentrations of 1.2-dichloroethane in nitrogen will be more accurate, the smaller the grid pitch value. A small pitch grid will require a large number of calculations that are difficult to perform manually. Therefore, a program in MathCad has been developed to calculate vapour concentrations of 1.2-dichloroethane in nitrogen. The calculations were carried out at the following parameters: the nitrogen velocity above the surface of 1.2-dichloroethane 0.03 cm/s, the diffusion coefficient of vapors of 1.2-dichloroethane in nitrogen \(D=1.033 \times 10^{-5}\) m²/s, the gas flow height \(h=0.02\) m, the length of the evaporation surface \(l=0.07\) m, the initial concentration of 1.2-dichloroethane vapor in the nitrogen stream is zero, the temperature of nitrogen is 79 °C, and the pressure is 1 at. The grid pitch is chosen is 0.5 mm. 40 cells arranged over the gas layer height, 140 cells placed over the evaporation surface length.

The results of the computer program calculation make it possible to determine the change in driving force along the evaporation surface (figure 3) by the following expression:

\[
\left( \frac{\partial c}{\partial y} \right)_{y=0} \approx \frac{c_H - c_i}{\Delta y},
\]

where \(c_H\) is the equilibrium concentration of vapors of 1.2-dichloroethane near the evaporation surface, \(c_i\) is the concentration of vapors of 1.2-dichloroethane at the grid nodes, \(\Delta y\) is the grid pitch.
The graphical dependence of the driving force on the length of the evaporation surface (figure 3) cannot be approximated with sufficient accuracy by any simple equation. Since the main amount of 1.2-dichloroethane evaporates at the very beginning of the surface, we found the following equation:

\[
\left( \frac{\partial c}{\partial y} \right)_{y=0} = f(x),
\]

for the initial surface plot \(0 < x < 0.3\).

The approximating equation on the initial plot has the form:

\[
\left( \frac{\partial c}{\partial y} \right)_{y=0} = 7.9042x^{-0.5213}. \tag{7}
\]

The last equation describes a graphical dependence (figure 3) with an error of 0.34%.

The lines of constant vapour concentrations of 1.2-dichloroethane in the nitrogen stream (figure 4) can be constructed from the calculations of equation (6). The plotted dependencies make it possible to spatially assess the change in vapour concentrations of 1.2-dichloroethane in a steady state nitrogen stream.
As a result of evaporation, the upper layer of 1.2-dichloroethane is cooled and a temperature difference occurs in the film of 1.2-dichloroethane, which can lead to convection caused by thermogravity [8-11]. The temperature change in the fixed film of evaporating 1.2-dichloroethane is investigated. Let nitrogen flow pass over the 1.2-dichloroethane film, the movement mode is laminar.

We consider the bottom of the layer of 1.2-dichloroethane as the origin along the y axis. Since the liquid is stationary, until convection occurs, the main method of heat transfer is thermal conductivity.

The heat transfer mode is stationary therefore the medium temperature does not change during time. Then

\[ \frac{\partial^2 T}{\partial X^2} + \frac{\partial^2 T}{\partial Y^2} = 0. \] (8)

Boundary conditions: at \( Y=d \) (on the liquid surface), the heat balance has the form:

\[ \lambda \frac{\partial T}{\partial Y} = rD \frac{\partial C}{\partial Y}. \] (9)

There is a heat source with a constant initial temperature \( T_0 \) on the liquid film bottom (\( Y=0 \)). We take on that the fluid layers adjacent to the lower wall have a temperature \( T_0 \) at \( X=1 \), the temperature change along the \( X \) axis stops and can be written \( \frac{\partial T}{\partial X} = 0 \),

(10)

at \( X=0 \) (at the beginning of the liquid layer) temperature change \( \frac{\partial T}{\partial X} = 0 \).

(11)

The last two conditions indicate that the side walls of the cell are thermally insulated. We bring the Laplace equation (8) to a dimensionless form by making a replacement.

Dimensionless temperature:

\[ t = \frac{T - T_0}{T_0}, \]

where \( T_0 = 200 \, ^\circ\text{C} \) is the initial liquid temperature and the lower facet temperature of the liquid film.

Laplace equation in dimensionless form:

\[ \frac{\partial^2 t}{\partial X^2} + \frac{\partial^2 t}{\partial Y^2} = 0. \] (12)

Boundary conditions in dimensionless form:

for \( y=1 \), \( \lambda \frac{T_0}{l} \frac{\partial t}{\partial Y} = rD \frac{\partial C}{\partial Y} ; \)

(13)

when \( y=0, t=0 \); (14)

for \( x=0 \) and \( x=1 \), \( \frac{\partial t}{\partial X} = 0. \)

(15)

It is apparent from condition (13) that the cooling intensity of the surface of 1.2-dichloroethane depends on the driving force of the process of evaporation of 1.2-dichloroethane into nitrogen \( \frac{\partial C}{\partial Y} \). To determine the driving force of the process of evaporating 1.2-dichloroethane into nitrogen, equation (7) is applicable.

When it is considered that...
\[
\frac{\partial C}{\partial Y} = \frac{C'}{l} \left( \frac{\partial c}{\partial y} \right)_{y=0},
\]

then the boundary condition (13) takes the form:

\[
\lambda \frac{T_0}{l} \frac{\partial t}{\partial y} = 7.9042 r D \frac{C'}{l} \chi^{-0.5213}.
\] (16)

Let us solve the Laplace equation (12) by the method of finite differences by substituting the boundary conditions (13), (14) and (15). The grid nodes deposited on the nitrogen stream are described using the Laplace equation. According to the Laplace equation, the temperature at any node of the grid is equal to the arithmetic mean value of the values at the four adjacent nodes of the grid, therefore:

\[
t_0 = \frac{t_1 + t_2 + t_3 + t_4}{4}.
\] (17)

The temperature at the bottom of the grid is zero.

Let us write down equation (16) in finite differences:

\[
\lambda \frac{T_0}{l} \frac{t_1 - t_0}{\Delta x} \approx 7.9042 r D \frac{C'}{l} (\kappa \cdot \Delta x)^{-0.5213},
\]

where \( \Delta x \) is the grid pitch (\( \Delta x = \Delta y \), that is the grid pitch in the direction of the x and y axes is the same), \( \kappa \) is the node number, \( t_i \) is the temperature in the second row of the grid from the surface of 1.2-dichloroethane. Taking into account the last equation, the equation of the temperature distribution at the grid nodes on the surface of 1.2-dichloroethane will be:

\[
t_0 = t_1 - b \cdot \kappa^{-0.5213} \cdot \Delta x^{0.4787},
\] (18)

here \( b = 7.9042 r D \frac{C'}{\lambda T_0} \).

The temperatures at the grid nodes were determined by equation 17 and 18. To calculate temperatures in grid nodes, a computer program in MathCad is compiled. During the calculations, the following assumptions were made: the equilibrium concentration of \( C' \) and the surface temperature of the \( T_0 \) along the surface of 1.2-dichloroethane do not change. For calculations, a grid spacing of 0.2 mm was selected. As a result of calculations in MathCad, a temperature distribution on the surface of 1.2-dichloroethane (figure 5) was obtained.

![Figure 5. Temperature on the surface of 1.2-dichloroethane.](image-url)
The isotherms in the 1.2-dichloroethane layer are shown in figure 6. It can be seen from the graph that the temperature gradient over the thickness of the 1.2-dichloroethane film is the largest in the initial section (figure 6).

![Figure 6. Temperature gradient in a liquid film.](image)

3. Results and discussion

Let’s find out if there is thermocapillary convection in the liquid film, that is, convection caused by a gradient of surface tension. To determine the critical temperature gradient in the 1.2-dichloroethane film, use the Marangoni number:

\[
Ma = \frac{\Delta T \varepsilon h^2}{\mu a},
\]

(19)

where \(\Delta T\) is the temperature gradient by film height of 1.2-dichloroethane, \(K\), \(h\) is the film height of 1.2-dichloroethane, \(m\), \(\mu\) is the dynamic viscosity coefficient of 1.2-dichloroethane, \(Pa\cdot s\), \(a\) is the temperature conductivity coefficient of 1.2-dichloroethane, \(m^2/s\), \(\varepsilon\) is the temperature gradient:

\[
\sigma(T) = \sigma_0 - \varepsilon T.
\]

From the literary data [12] the critical value of the number Marangoni. With this Marangoni number, thermal capillary convection will occur in the 1.2-dichloroethane layer. From formula (19), having previously substituted the critical value of the Marangoni number, it is possible to determine the critical temperature gradient in the 1.2-dichloroethane film leading to thermocapillary convection. At \(\mu_g = 0.44 \cdot 10^{-3} Pa\cdot s\), \(a = 7.49 \cdot 10^{-8} m^2/s\), \(\varepsilon = 1.35 \cdot 10^{-4}\) \(J/m^2\cdot s\), \(h = 0.007\) \(m\) the critical temperature gradient will be \(\Delta T_{cp} = 0.4\) grad. From figure 5 it can be seen that such a temperature difference exists on the surface (at \(0 < x < 21\) mm). Therefore it can be approved that the convection caused by thermocapillary forces takes place on a surface plot of 21 mm long.

4. Conclusion

The calculations indicate that at a nitrogen velocity of 0.03 m/s, the evaporation surface is unstable and thermocapillary convection takes place in the 1.2-dichloroethane film accelerating the mass transfer process in the process of producing 1.2-dichloroethane.

This model can be useful for calculation in other gas-liquid systems and the results of calculations are used in the design of heat and mass exchangers.
References

[1] Gershuni G Z and Zhukhovitsky E M 1972 *Convective stability of an incompressible liquid* (Moscow: Nauka) p 392

[2] Balasubramanian S N, Rihani D N and Doraissamy L K 1966 *Ind. Eng. Chem. Fund.* B 5 184

[3] Getling AV 1999 *Rayleigh-Benard convection. Structures and dynamics* (Moscow: URSS Editorial) p 248

[4] Buevich Yu A and Rabinovich L M 1984 *Hydrodynamics of interfaces* (Moscow: World) p 209

[5] Grymzin Yu N, Kvashnin S Yu, Lothov V A and Malyusov V A 1982 *Theoretical Foundation of Chemical Engineering* B 16 p 251

[6] Dilman V V, Kulov N N and Naydenov V I 1999 *Theoretical Foundation of Chemical Engineering* B 33 p 495

[7] Yudaev B N 1973 *Heat transfer* (Moscow: Graduate School) p 359

[8] Balchugov A V, Semenov I A and Podoplelov E V 2005 *Collection of scientific papers of the Angarsk State Technical University* B 1 pp 38–45

[9] Podoplelov E V, Balchugov A V, Rakhmanin V Yu and Podoplelova A V 2013 *Mathematical methods in engineering and technology (MMTT-26)* B 1 pp 59–61

[10] Balchugov A V 2009 *Highly selective gas-liquid chemical processes with a large thermal effect and their instrumentation (thesis for the degree of Doctor of Technical Sciences)* (Tomsk: Tomsk Polytechnic University) p 384

[11] Podoplelov E V, Balchugov A V, Ulyanov B A and Sviridov D P 2006 *Collection of scientific papers of the Angarsk State Technical Academy* B 1 pp 180–186

[12] Kutateladze S S, Volchkov E P and Terekhov V I 1987 *Aerodynamics and heat and mass transfer in limited vortex flows* (Novosibirsk: Institute of Thermophysics) p 282