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Dedicated to Professor Liviu Literat, at his 80th anniversary

MASS TRANSFER IN SUBLIMATION PROCESS

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ABSTRACT. This paper is a study of mass transfer in entrainer sublimation, when the solid-gas interface is plane. A mathematical model is established, that allows the calculation of the sublimation process time, or the sublimation front position as a time function. The mathematical model is experimentally checked, using naphthalene cylindrical particles, fixed on special supports, with are offering a plane surface in contact with the entrainer, here is hot air. It is also studied the influence of temperature and entrainer flowrate on sublimation rate.

Keywords: *entrainer sublimation, mass transfer*

INTRODUCTION

The sublimation is a physical process used for separation or purification of solid chemical substances. Although it is a technical process, the literature contains a small number at papers regarding mass and heat transfer [1-17].

Regarding the mass transfer, the existing papers focus both a theoretical and experimental studies [1-6], at a single particle level, or group of particles in fixed or fluidized bed. Some authors [10-17] approach the simultaneous mass and heat transfer in sublimation processes.

The present paper is a study of mass transfer in entrainer sublimation, when the solid-gas interface is plane. A mathematical model is established, that allows the calculation of the sublimation process time, or the sublimation front position as a time function. The mathematical model is experimentally checked, using naphthalene cylindrical particles, fixed on special supports, with are offering a plane surface in contact with the entrainer and here is hot air. It is also studied the influence of temperature and entrainer flow rate on sublimation rate.

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Mathematical model

Figure 1 presents the physical model of entrainer sublimation with plane solid-gas interface. According to this model, the entrainer moves towards the solid surface. At interface it is formed a limit diffusion layer, with δ thickness. The partial pressure of sublimation substance (A) at interface is p_A^i, and the gas phase volume is p_A^∞. The mass transfer direction from the interface to the gas phase volume is Oz.

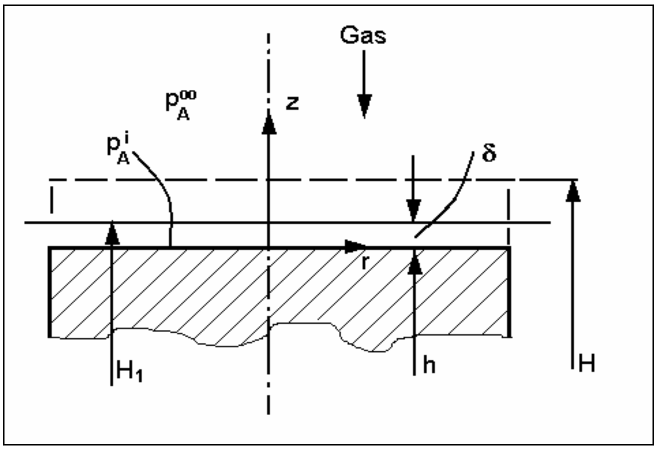

Figure1. The physical model for mass transfer at entrainer sublimation.

Since the mathematical modeling used in this paper looks to find one equation to determine the process time, at the sublimation front position, the starting point is the convective diffusion equation:

$$\frac{\partial p_A}{\partial t} = D_A \frac{\partial^2 p_A}{\partial z^2} \tag{1}$$

The initial and at limit terms, are:

$$t = 0, \qquad h = H \tag{2}$$

$$t > 0, \qquad z = h, \qquad \left| \begin{array}{l} p_A = p_A^i \\ \frac{D_A}{RT}\frac{\partial p_A}{\partial z} = \rho_S \frac{dh}{dt} \end{array} \right. \tag{3}$$

$$t > 0, \qquad z = H_1, \qquad p_A = p_A^\infty \tag{4}$$

In order to simplify solving the differential equation, we adopt pseudo-stationary condition, considering the partial pressure constant on an infinitesimal time interval. Solving the equation (1) under these conditions leads to the following solution:

$$p_A = \frac{p_A^i - p_A^\infty}{h - H_1}(z - H_1) + p_A^\infty \tag{5}$$

Deriving the equation (5) in relation to z it gives:

$$\frac{dp_A}{dz} = \frac{p_A^i - p_A^\infty}{h - H_1} \tag{6}$$

The limiting condition (3) it can be written:

$$\frac{D_A}{RT}\frac{p_A^i - p_A^\infty}{h - H_1} = -\rho_S \frac{dh}{dt} \tag{7}$$

The integration of equation (7) comes to:

$$t = \frac{\rho_S RT}{k(p_A^i - p_A^\infty)}(H - h) \tag{8}$$

The distance from the interface, h, can be represented as a function of the sublimation degree, defined by the relation:

$$\eta_A = \frac{m_A^0 - m_A}{m_A^0} = \frac{V_S^0 - V_S}{V_S^0} = 1 - \frac{h}{H} \tag{9}$$

$$h = H(1 - \eta_A) \tag{10}$$

Replacing relation (10) in (8) gets to:

$$t = \frac{\rho_S RTH}{k(p_A^i - p_A^\infty)}\eta_A \tag{11}$$

Using equation (9) and (11), one can calculate the duration of sublimation process function of h and η_A, or the sublimation front position (expressed by h) as a function of time.

RESULTS AND DISCUSSIONS

It was experimentally determined the mass variation of each naphthalene support in time, at variable temperature and air flow rate values. The results are presented in Table 1.

Using those data and equation (9), was determined the variation of sublimation degree for the naphthalene from supports, in time. The results are presented in Table 2.

Table1. Mass variation at three temperatures (50°C, 60°C and 70°C) and entrainer flow rate in the range 1.5 -3.5 m^3/h

Mv (m^3/h)	T (°C)	t (min)				
		5	10	15	20	25
1.5	50	0.0057	0.0130	0.0153	0.0367	0.0394
	60	0.0059	0.0348	0.0384	0.0716	0.1119
	70	0.0200	0.0844	0.1234	0.1701	0.2336
2.0	50	0.0154	0.0198	0.0337	0.0389	0.0537
	60	0.0220	0.0404	0.0537	0.786	0.1151
	70	0.0358	0.0740	0.1117	0.1518	0.2360
2.5	50	0.0163	0.0176	0.0264	0.0280	0.0657
	60	0.0136	0.0264	0.0592	0.0782	0.1254
	70	0.0410	0.0790	0.1208	0.1620	0.2395
3.0	50	0.0094	0.0196	0.0306	0.0416	0.0592
	60	0.0209	0.0480	0.0655	0.0916	0.1311
	70	0.0386	0.0829	0.1420	0.1763	0.2511
3.5	50	0.0106	0.0217	0.0343	0.0437	0.0666
	60	0.0215	0.0488	0.0795	0.0945	0.1547
	70	0.0481	0.0920	0.1313	0.1934	0.2886

Table 2. Degree of sublimation at three temperatures (50°C, 60°C and 70°C) and entrainer flow rate in the range 1.5 -3.5 m^3/h

Mv (m3/h)	T (°C)	t (s)				
		300	600	900	1200	1500
1.5	50	0.0063	0.0144	0.0170	0.0408	0.0438
	60	0.0065	0.0386	0.0420	0.0796	0.1244
	70	0.0224	0.0938	0.1372	0.1890	0.2597
2.0	50	0.0171	0.0220	0.0370	0.0432	0.0597
	60	0.0244	0.0449	0.0597	0.0874	0.1279
	70	0.0398	0.0822	0.1241	0.1688	0.2624
2.5	50	0.0181	0.0195	0.0293	0.015	0.0730
	60	0.0151	0.0293	0.0658	0.0869	0.1394
	70	0.0455	0.0878	0.1343	0.1801	0.2663
3.0	50	0.0104	0.0217	0.0340	0.0462	0.0658
	60	0.0232	0.0533	0.0728	0.1018	0.1457
	70	0.0429	0.0921	0.1579	0.1960	0.2792
3.5	50	0.0117	0.0241	0.0381	0.0485	0.0740
	60	0.0239	0.0542	0.0884	0.1050	0.1720
	70	0.0534	0.1023	0.1460	0.2150	0.3209

The variation of sublimation degree for naphthalene is a measure for the time evolution of the sublimation process.

The Figures 2 and 3 are graphical representation for h=f(t) functions, with the specified values for temperature and different air flow rate. As one can see, the height of sublimation front drops in time, regard less the temperature and entrainer flow rate values. As temperature rise, the height of sublimation front gets small, the reduction being pronounced at greater temperatures. The entrainer flow rate determines a positive influence on sublimation front height.

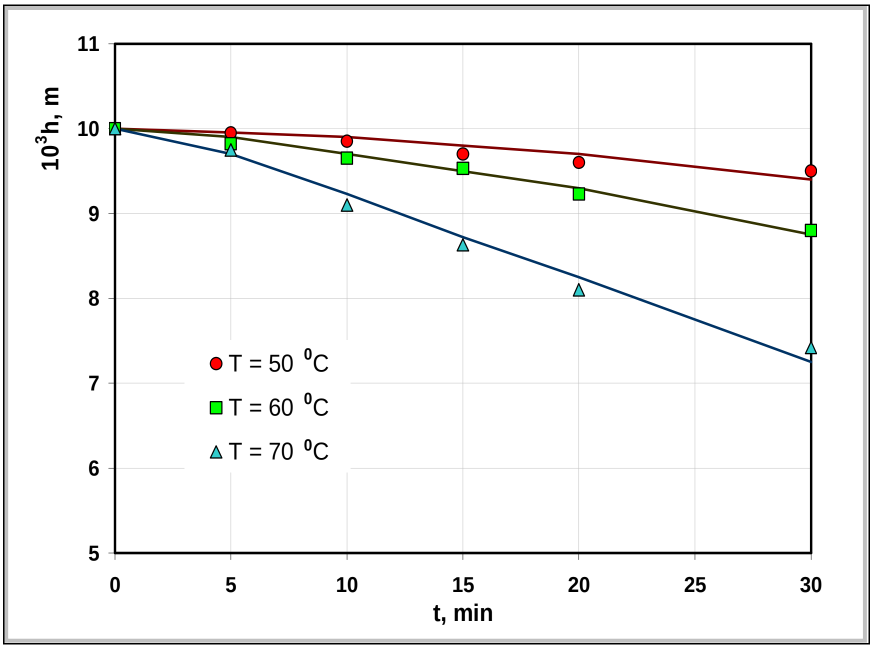

Figure 2. Sublimation front vs time at three temperatures (50°C, 60°C and 70°C) and entrainer flow rate M_V =1.5 m^3/h.

In continuation, was determined the average sublimation rate, using the relation:

$$v_s = \frac{1}{t}\int_0^t v_s(t)dt \tag{12}$$

The sublimation rate $v_s(t)$ were computed with the relation:

$$v_s(t) = -\frac{dm}{S \cdot dt} \tag{13}$$

Figures 4 and 5 contain the dependencies v_s=f(M_v) for many different temperatures, and v_s =f(T) at different entrainer flow rate values. One can note that both entrainer debit and temperature have a positive influence on average sublimation rate. In the entrainer flow rate variation range between 1.5-3.5 m^3 /h, which is equivalent to entrainer velocity values through sublimation room between (0.409-0.955) m/s, the entrainer flow rate has a low influence on the sublimation rate. Temperature ranging from 50-70^0 C has a greater influence.

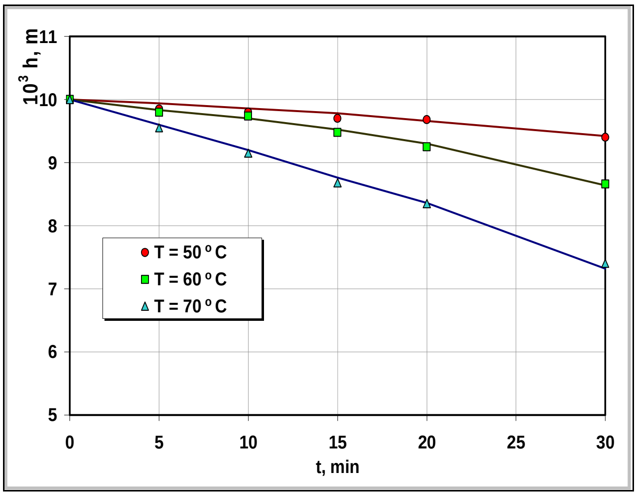

Figure 3. Sublimation front vs time at three temperatures(50°C, 60°C and 70°C) and entrainer flow rate M_V =3.5 m^3/h.

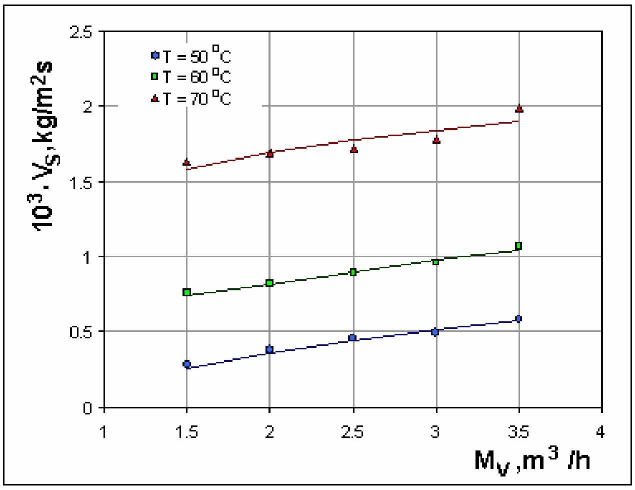

Figure 4. Sublimation rate as function of air flow rate at three temperatures (50°C, 60°C and 70°C).

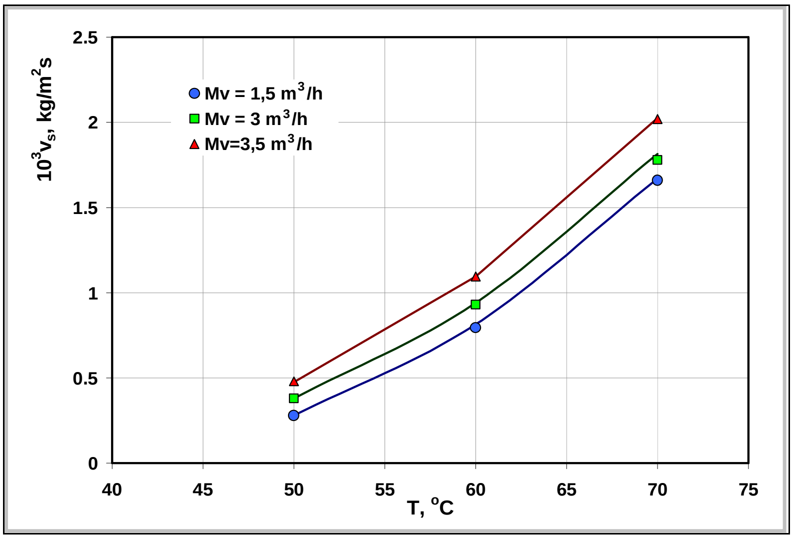

Figure 5. Sublimation rate as function of temperature at three air flow rates (1.5, 3.0 and 3.5 m^3/h).

Based on average sublimation rate values, was determined the individual mass transfer coefficient, using mass transfer equation:

$$v_s = \frac{k}{RT}(p_A^i - p_A^\infty) \tag{14}$$

The calculation of mass transfer coefficient involves knowledge of partial pressure values at gas-solid interface, which depends on the temperature at interface T_i. In order to determine the temperature at interface, the following equations were used:

$$\alpha(T_\infty - T_i) = \frac{k}{RT}(p_A^i - p_A^\infty)\Delta H_s \tag{15}$$

$$\ln p_A^i = 31.2352 - 8587 / T_i \tag{16}$$

$$Nu = \left(\frac{Pr}{Sc}\right)^{0.4} Sh \tag{17}$$

$$D_A = 8.177 \cdot 10^{-7} \cdot T^{1.983} \tag{18}$$

The equations (16), (17) and (18) were taken from literature [12].

The values for individual mass transfer coefficient obtained, are presented in Table 3. The results from this table show similar dependencies of coefficient K, similar to sublimation rate.

Table 3. Individual mass transfer coefficient $10^2 \cdot k,\ (m/s)$ calculated at three values of temperature and air flow rate in the range 1.5 – 3.5 m^3/h

T (°C)	*M_V (m^3/h)*				
	1.5	*2.0*	*2.5*	*3.0*	*3.5*
50	5.611	7.647	9.356	8.430	9.485
60	7.393	7.604	8.285	8.662	10.222
70	7.712	7.793	7.904	8.291	9.529

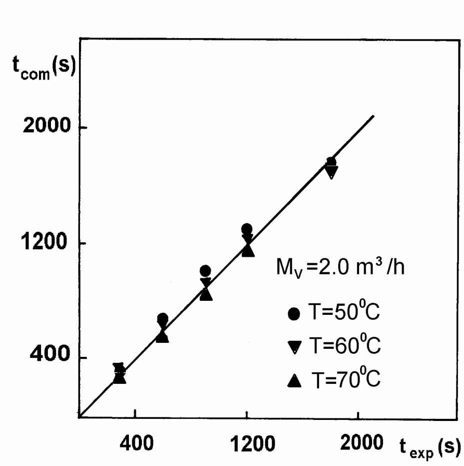

Figure 6. Comparison between experimental and calculated data at three temperatures (50°C, 60°C and 70°C) and air flow rate M_V =2.0 m^3/h.

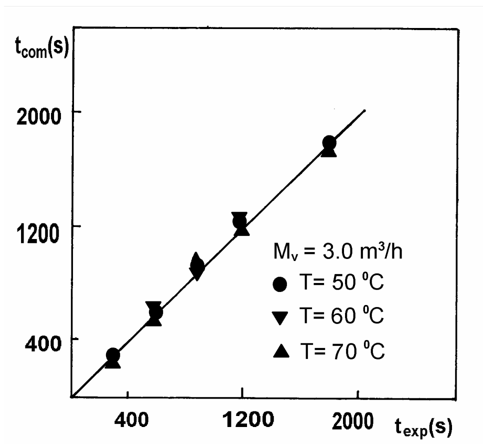

Figure 7. Comparison between experimental and calculated data at three temperatures (50°C, 60°C and 70°C) and air flow rate M_V =3.0 m^3/h.

In this paper was studied the mass transfer at entrainer sublimation on plane solid-gas interface. A mathematical model for the sublimation process was established, which allow determination of process duration, or sublimation front height, or sublimation degree as a function.

Using naphthalene filled supports, which provide plane surface in contact with the entrainer, it was experimentally determined the variation of sublimation degree and sublimation front height in time, at numerous values for entrainer (air) temperature and velocity. It was also determined the average sublimation rate, and individual mass transfer coefficient, both on the same values for entrainer temperature and flow rate.

The results show that flow rate and temperature have a positive influence on sublimation rate and individual mass transfer coefficient.

By comparing the experimental data with these calculated using the mathematical model, a good concordance is obtained.

List of symbols

p_A - component A partial pressure, N/m^2
D_A - component A diffusion coefficient, m^2/s
t - time, s
H -support slot height, m
h -sublimation front height, m
R - universal gas constant, J/kgK
ρ_s -component a density in solid state, kg/m^3
δ -limit diffusion layer thickness, m
k - individual mass transfer coefficient, m/s
m^0_A – component A mass at the initial moment, kg
m_A- component A mass at the given time t=t, kg
η_A- component A sublimation grade
i -symbol for interface
∞ -symbol for gas phase volume
V_S^0- initial solid phase volume, m^3
V_S –solid phase volume at t=t, m^3
S -mass transfer surface area, m^2
Δm –naphthalene support mass variation, kg
Δt -time interval, s
α - heat transfer individual coefficient, W/m^2 K
ΔH_S- latent sublimation heat, J/kg
T -temperature
$Nu = \frac{\alpha l}{\lambda}$ - Nusselt number
$Sh = \frac{kl}{D_A}$ - Sherwood number
$Pr = \frac{C_p \eta}{\lambda}$ - Prandtl number
$Sc = \frac{\eta}{\rho D_A}$ - Schmidt number
η -gas phase dynamic viscosity, Pa*s
ρ -gas phase density, kg/m^3
C_p -gas phase specific heat, J/kg K

l -characteristic length, m

λ -gas phase thermal conductivity coefficient, W/m K

EXPERIMENTAL SECTION

In order to make the experiments, we used the laboratory installation presented in the Figure 8. According to Figure 8, the installation is composed from a cylindrical column (1), made from heat resistant glass, and which represents the sublimation chamber, the air heating room (the entrainer) (2), the fan for air transportation (3), the rotameter for air flow rate measurements (4), the thermometers (5) and (6), the valve which regulates the air flow rate (7), and the autotransformer used to adjust the temperature in sublimation chamber. The sublimation chamber is equipped inside with a device (1a) to hold the support on which the sublimation particle will be fixed. The entrainer (air) gets in the sublimation chamber through a coupling positioned in upper side, and gets out through the existing at lower side. The heating room makes the entrainer warm using an electrical resistance powered by the current supply through autotransformer (8).

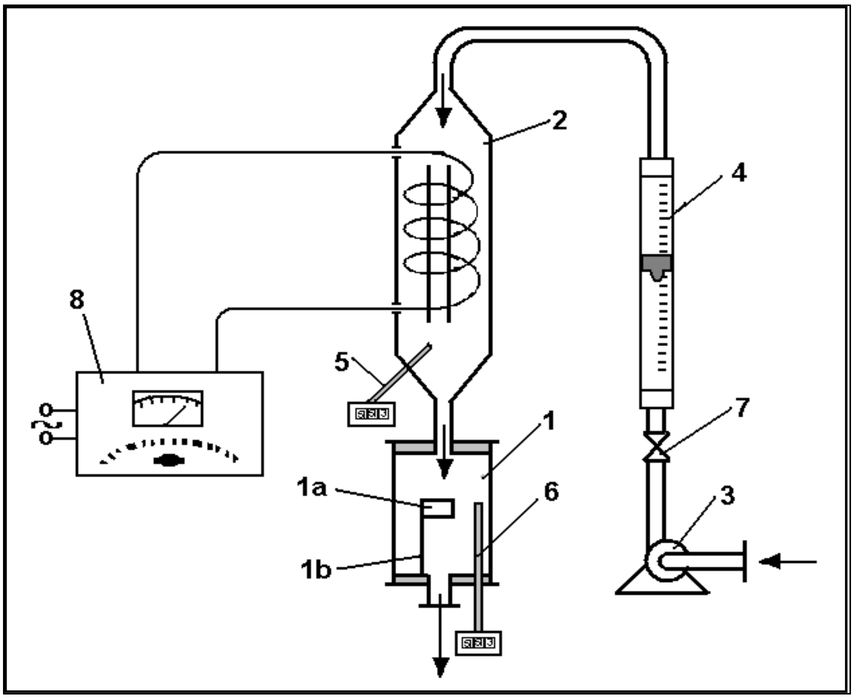

Figure 8. Experimental setup. 1 - cylindrical column, 2 –, air heating room 3 – fan, 4 –rotameter, 5, 6 – thermometers, 7 – valve, 8 – autotransformer.

For the experiments it was used naphthalene, with air as entrainer. The naphthalene was inserted melted in the cylindrical slot of each support. The support allows the contact with the gaseous entrainer only on the frontal side of the naphthalene cylinder solidified in the slot. This has a diameter d=10 mm and height H=100 mm.

In each of the experiments a single naphthalene support was used. The temperature in sublimation room during each experiment was kept constant. Three temperatures were used: 50^0 C, 60^0 C, 70^0 C and several values of entrainer flow rate (air):1.5, 2.0, 2.5, 3.0 and 3.5 m^3/h.

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