Calculation of temperatures in condensed phase of burning PMMA by equation of Michelson, Mullar and Le Chatelier

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Abstract. Results of studying an aerosol of the dioxide of sulfur and pentoxide of phosphorus released into the atmosphere by the chemical company for processing of phosphorit are presented. Influence of the direction and speed of wind on sulfur dioxide distribution and pentoxide of phosphorus in a ground layer of the atmosphere is studied, and the points of the direction of wind leading to pollution of the atmosphere of the nearby city are allocated. The statistical analysis of environmental pollution is carried out by the method of the correlation and regression analysis. The equations of dependence of the amount of the sulfur dioxide and pentoxide of phosphorus, released into the atmosphere, on the volume, released by the enterprise of production, are defined. The obtained results are recommended for control, regulation and management of the environment.

1. Introduction
A modern chemical industry produces several tens of thousands of products. In the laboratories, hundreds of new technological processes are being developed. It is unrealistic to set the task of studying the mechanism of the course of all these processes, whereas the task of optimizing and managing these processes must be solved.

2. Methods.
Distribution of temperatures in the condensed phase of the burning PMMA according to the equation of Michelson, Mullar and Le Chatelier.

Polymer under the influence of heat coming from the flame decomposes to form combustible products, which, falling into the gas zone, support combustion. This process is divided into several stages: heating and pyrolysis of the condensed phase, ignition of volatile degradation products; the combustion zone, where the maximum flame temperature is reached, and the afterburning zone behind the combustion front. The heat absorbed by the polymer is consumed to heat the polymer from the initial temperature to the surface temperature, the phase transitions are melting, evaporation and decomposition of the polymer. The depth of heating of the condensed phase depends on the thermophysical properties of the polymer and the burning rate. The source of heat is a flame that transfers heat energy to the polymer by both convection and radiation.
It should be noted that the pyrolysis of polymers under combustion conditions takes place with unilateral action of heat and significant heating rates. These factors can significantly affect the mechanism of thermal decomposition of solids.

To study such processes, the method of linear pyrolysis was developed [1]. Its essence lies in the decomposition of the material under one-sided heating. In the combustion of condensed substances, it is possible to distinguish between linear velocity (I_{\text{lin}}), which fixes the change of the sample length in time and is measured in cm/s, and mass velocity (I_{\text{m}}), which determines the amount of burned material per unit area per unit time g/cm² s. In the simplest case, these quantities are connected by $I_{\text{m}} = I_{\text{lin}} \cdot \rho$, where $\rho$ is the density of the material.

3. Results.
The burning rate and the thermophysical characteristics of the polymer determine the depth of heating and the temperature field in the condensed phase, and for the case when reactions with insignificant thermal effects occur, the temperature distribution can be calculated from the equation of Michelson, Mullar and Le Chatelier [2-9]:

$$T_x = T_o + (T_s - T_o) \cdot e^{-\frac{U_h \cdot x}{H}}$$  \hspace{1cm} (1)

where $T_x$ is the temperature of the substance at distance $x$ from the surface; $T$ is the initial temperature; $T_s$ is the surface temperature; $H$ is the thermal diffusivity.

The depth of heating of the condensed phase is 0.5-0.6 cm. In general, the trend of the curves indicating the change in the temperature of the condensed phase coincides with that calculated by Eq. (1). It has been established that the depth of heating of the condensed phase is considerably less as compared with free burning under the action of flame.

Quantitative data on the mechanism of thermal transformations of different classes of polymers are absent.

4. Discussion
The amount of monomer formed in the depth of the burning polymer was calculated from the known kinetic data [9]. Calculations [9] show that at a slow burning rate, the polymer degradation proceeds to deeper degrees of decomposition than at fast burning rates, as is observed in the case of combustion under the action of a propane-air flame. Accordingly, with free combustion, the dispersion process proceeds to a greater extent than with the action of the flame of the burner. It is shown that the distribution of the molecular weight and temperature over the depth of the condensed phase is identical with the same power of the combustion flux, regardless of the geometric positions of the sample: the burning surface downward or upward. It has been established that under the action of the flame of a propane-air burner with a temperature of 1100 °C, when PMMA burns, the molecular mass is reduced by 50% at a depth of the condensed phase 0.6 mm from the burning surface. A study of the cutoff of the extinguished PMMA sample by ultramicrotomes revealed that the depth of the bubbles is 0.75 mm in the condensed phase during combustion, depending on the geometric location of the sample at diametrically opposite positions of the sample, i.e. the degree of dispersion is negligible. It was found that pyrolysis processes take place in a considerable thickness of the condensed phase during self-combustion; PMMA bubbles are visible at a distance of 3.5-3.65 mm from the surface, a decrease in the molecular weight of 3500000 by 50%, i.e. 1750000 is observed at a depth of 1.85 mm. The distribution of the molecular weight of PMMA and the temperature over the depth of the condensed phase are identical. It is found that with diametrically opposite conditions for the location of the sample for the combustion of PMMA, the initial temperature of the sample and the induction period during polymer pyrolysis significantly affect the sample. Critical conditions of ignition and combustion.
An estimation of the fraction of the dispersion process was carried out when studying the burning of PMPA in an atmosphere with different oxygen content, and it was shown that this fraction in the total burning rate can amount to 70% [10].

When the flame of the torch is applied from the bottom upwards to the PMMA plates, the upper part of the flame cone, contacting the polymer surface, helps to reduce the oxygen supply from the sides, while the reverse position of the sample shows stable combustion, which is caused by significant diffusion of oxygen on the surface. The change in the temperature profile in the gas and condensed phase of the burning PMMA is completely dependent on the power of the flame source. According to Landau's views, the mass burning rate is proportional to the force of gravity [11]. Consequently, the burning rate of the sample located by the combustion surface downwards for equal thermal and aerodynamic parameters should be greater than for the sample burning down from the top. However, the experimental data show the opposite (U1 = 0.043 mm / s, U2 = 0.003 mm / s). Furthermore, forced combustion of the plate, facing the combustion surface downwards, requires forced air blowing. The decomposition products of the polymer that fall into the combustion zone experience two oppositely directed forces - the gravity and lifting force of the combustion products due to their low density due to high temperatures. Calculations show that the lifting force of heated gases significantly exceeds the gravitational forces. When the sample is burned from the top down, the combustion products are carried upward, creating favorable conditions for the diffusion of oxygen. When the sample burns in the opposite direction, the combustion products rise to the surface, shielding it from access to oxygen, resulting in damping.

In the case of burning PMMA under the action of a propane-air flame, when the diffusion of oxygen does not matter, the linear combustion rates, temperature profiles and surface temperatures (Ts) are the same regardless of the location of the samples. It was shown that the burning rate of polymers is determined by the processes of evaporation from the surface and the dispersion of the decomposition products from the depth of the condensed phase, while an increase in the burning rate leads to a decrease in the contribution of the dispersing process and an increase in evaporation.

When burning from the bottom up, the molecular mass of PMMA does not change at a depth of 4.35 mm. From a comparison of the curves, it is established that with self-combustion of PMMA, a deeper thermal destruction occurs in deeper layers compared to forced burning under the action of a propane-air flame. Apparently, this is explained by the slow heating of the surface to the substrate at a low combustion rate of 0.0068 mm / s with combustion from top to bottom, and with combustion from the bottom up, the velocity is 0.0052 mm / s. It should be noted that the combustion of the PMMA sample from the bottom up requires a considerable induction period.

5. Conclusion

1. It is found that for diametrically opposite conditions for the location of the sample for the combustion of PMMA, the initial temperature of the sample and the induction period during the pyrolysis of polymers influence significantly the sample.
2. The molecular weight of the initial polymer varies with the temperature distribution, but it should be noted that the fragmentation of macromolecules begins at relatively low temperatures (160 °C), and near the burning surface, the molecular mass of the destroyed polymer is of great importance. Therefore, under combustion conditions, PMMA does not have time to destruct completely to the monomer. Thus, the surface temperature is higher than the boiling point of the monomer and, apparently, an increase in the burning rate should lead to an increase in the surface temperature.
3. The coefficient of thermal diffusivity was calculated from the Michelson equation, assuming that the temperature does not change with time, i.e. steady-state conditions are realized, the combustion rate and surface temperature are taken from the experimental data.
4. It is found that the experimental value of PMMA combustion in a propane-air flame from top to bottom obeys the Mikhelson equation; the coefficient of thermal conductivity is 0.0848 mm$^2$/s, and the calculated coefficient is 0.0900 mm$^2$/s.
References

[1] Shteinberg A S, Ulybin V B, Dolgov E I, Manelis G B 1972 The effect of dispersion in the processes of linear pyrolysis and combustion of polymers. Combustion and Explosion. Materials of the Third All-Union Symposium on Combustion and Explosion. (Moscow: Nauka) pp. 124-127

[2] Shaklein A A, Karpov A I, Korepanov M A 2013 Propagation of a flame on the surface of a solid fuel at different angles of inclination. Chemical Physics and Mesoscopy 4-15 497-501

[3] Kokovina E S 2016 Modeling of flame propagation taking into account pyrolysis of combustible material. (Magician. diss. SP)

[4] Gibov K M, Abdikarimov M N 1983 Pyrolysis of polymers during combustion. Proceedings of the Institute of Chemical Technology of the Academy of Sciences of the Kazakh SSR "Synthesis and study of monomers and polymers". Vol. 58 (Alma-Ata: Science) pp. 151-167

[5] Abdikarimov M N, Turgumbaeva R Kh 1986 Influence of burning conditions on pyrolysis processes PMMA. "Polymer materials in machine building." Theses of the report of the republican conference (Izhevsk) pp. 41-42

[6] Abdikarimov M 1997 About the Influence of Thermal Streams and Oxygen on the Combustion of Polymethylmethacrylate International Symposium "Chemistry of Flame Front" (Almaty, Kazakhstan) pp. 37-39

[7] Abdikarimov M I 2005 Mikhelson's equation in the study of degradation processes in the condensed phase of burning polymethylmethacrylate under various conditions and geometric positions. Bulletin of KazNPU them. Abay, a series of physical and mathematical. Science 2 (13) 9-13

[8] Abdikarimov M I 2005 Study of the pyrolysis processes of PMMA during combustion. Proceedings of KSTU 218-220

[9] Abdikarimov M N 2007 Pyrolysis processes of PMMA at combustion. IX International Symposium on Self-propagating High-temperature Synthesis, V 5. (Dijon, France) pp. 15

[10] Hauser, Peck M 1967 Heterogeneous combustion (Moscow: Mir)

[11] Isaacs I K 1974 The oxygen index flammability test. Flammability Solid. Plast. V.7 (Westpost Conn) pp. 1-12

[12] Landau L D 1944 Toward a Theory of Slow Burning (Zh. Eksp)