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# Numerical Simulation and Prediction of Polymer Flammability in Non-Standard Conditions

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Fire safety of plastics is commonly characterized in terms of Oxygen Index (OI), or the limit oxygen concentration in oxidizing atmosphere that supports combustion. OI is determined in normal conditions (atmospheric pressure, room temperature, etc.) according to the procedure prescribing the ambient conditions, number of samples, their dimensions. However, polymer materials and products where they are used meet the variety of ambient conditions ; low and high temperatures, pressures, flow velocities, accelerations, and etc. The methods of prediction of polymer flammability and OI in the wide range of operating conditions have not been available until now. In this study, a mathematical model is worked out and the theory of limits of polymer combustion is developed to predict OI and other critical values in non-standard conditions: pressure 0.1-100 atm ; initial temperature of polymer 250-550 K ; gravity force acceleration 0.1-50 g ; velocity of oxidizing $O_2/N_2$ stream 0-50 m/sec ; different thickness of polymer layers covering the cold base and their simultaneous action. The model involves two-dimensional numerical simulation of the diffusion combustion of a polymer in the presence of heat losses. The main factor to be taken into account is the decrease of flame temperature due to the cooling effect of different agents. Therefore, the extinction criterion and OI are expressed in terms of the relationship between Damköhler and Peclet numbers. Two critical conditions, observed earlier in the experiments on polymer extinction limits, are explained. The predictions of the model were tested for PMMA and were found to be in good agreement with experimental data available.

**Key Words :** Oxygen Index, Flammability, Frank-Kamenetski, Damköhler No., Peclet No., Numerical Simulation

## Nomenclature

$Q$ : $E(T-T_{ad})/RT_{ad}^2$-dimensionless temperature
$\xi$ : $x/l$-dimensionless coordinate
$Da$ : $(lM\Theta_0'/\rho\beta\chi B_o)/2J$-Damköhler number
$M$ : mass combustion rate of the equivalent gas mixture
$\Theta_m$ : $(\Theta_s-\Theta_o)/\{\Psi[\exp(\rho u Pe/M/\Psi)-l]\}$-non-adiabatic combustion temperature for the infinitely fast reaction (corrected for heat losses)
$Pe$ : $Md/\chi\rho$-Peclet number
$\Theta_s$ : $\Theta(T_s)$, $\gamma=RT_{ad}/E$, $\Theta_0'=\beta BE/\tau RT_{ad}^2$, $p=(\rho u)_o d/\rho k$

## 1. Introduction

Numerical simulation of plastics flammability is a powerful research tool to complement or replace time-consuming experiments, which require a great deal of effort in measuring the temperature, the velocity and the concentration of species in combustion gases. Therefore, the devel-

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opment of the adequate models of plastics combustion has attracted much attention. However, the present state of the combustion theory does not allow to bring about the comprehensive calculation of combustion phenomena, even if supercomputers are employed.

Polymer flammability is commonly characterized by Lower Oxygen Index (LOI) and other standard tests. LOI is defined as the limit oxygen concentration in oxidizing atmosphere that supports combustion (Encyclopedia of Polyner Science and Eng., 1987). In volumetric (or mole) fractions:

$$Y^* = [O_2]/([O_2]+[N_2]) \qquad (1)$$
$$\mathrm{LOI} = Y^* * 100\ \%$$

If oxygen concentration is lower than the critical one Y < Y*, combustion is extinguished even after stimulated ignition. The dependence of flame propagation velocity v over a surface of a polymer sample upon Y. With the decrease of Y there is an abrupt extinction limit Y = Y*. This critical limit occurs due to the strong non-linear dependence of chemical reaction rate on temperature. The standard OI is determined in normal conditions (atmospheric pressure, room temperature etc.) according to the procedure prescribing the ambient conditions, number of samples, their dimensions. Various standards are supported in different countries. Widely used is the procedure ASTM D 2863-87 (Annual Book of ASTM Standards; Troitzsch J. 1983) for denoting OI in standard conditions. This standard OI is referred to the most widespread practical circumstances and characterizes the polymer flammability in normal atmospheric conditions, when the velocity of passing air flow is low. Since the major part of the fires are initiated by small ignition sources, this OI test proved to be useful. However, some disadvantages of this test were pointed out (Encyclopedia of Polyner Science and Eng., 1987) : among them the lack of the energy feedback to the specimen ; much combustion heat is carried away from the specimen by convection or radiation. Evidently, the heat loss is the critical factor, which competes to the heat release in course of polymer burning and finally determines the extinction conditions. The polymer with a high standard OI may burn vigorously in a fire, where it can be preheated by other burning objects, so its initial temperature is higher than that in standard LOI test, or it may indicate tendency toward easy burning in other unusual conditions.

Generally the criticality in polymer combustion and limit oxygen concentration in atmosphere are dependent both on polymer composition and on atmospheric pressure P, initial temperature $T_0$, polymer sample size (diameter d, length l or the like), acceleration force g, velocity of by-passing gas flow u, sample orientation (flame propagation "up" or "down") and so on. Therefore in nonstandard conditions oxygen index of a polymer which physics-chemical properties are characterized by a number of parameters $a_1$, $a_2$, ··· is a function of all above parameters:

$$Y^* = Y^*(P,\ T_0,\ d,\ l,\ g,\ u,\ a_1,\ a_2,\ \cdots) \qquad (2)$$

or, in symmetrical form:

$$F(Y^*,\ P,\ T_0,\ d,\ l,\ g,\ u,\ a_1,\ a_2,\ \cdots) = 0 \quad (3)$$

When polymer materials are used in the wide range of ambient conditions, in low and high temperatures, pressures, accelerations, in zero gravity (space flight) etc., the prediction of polymer flammability must be done also for these conditions. The characteristic sizes of polymer specimens can also vary a lot, from thin films and grains to large blocks. As mentioned above, standard OI is referred to normal conditions, when major part of the parameters in Eq. (2) is fixed. One can also resolve Eq. (3) to obtain the critical diameter d* (Y, P, $T_0$, ···), critical velocity u* (Y, P, $T_0$, ···). But it seems impossible to acquire experimentally the comprehensive data array required to derive the relationship Eq. (3) in the whole range of parameters variation, since 5-10 samples are needed to verify one experimental point. Even with the simultaneous variation of pressure, temperature and flow velocity, several thousands tests would be done for each material.

Herein adopted is an alternative approach to prediction of OI in the wide range of parameters based upon the minimal number of test experiments. A mathematical model has been worked out to study the critical phenomena of polymer combustion. The theory has been developed to obtain the main functional relationships between parameters and to predict OI and/or other critical values in nonstandard conditions.

The theory is described in the following chapters of the report. Firstly, the fundamentals of diffusion combustion of polymers are discussed (Chapter 2). Then, a model of extinction of diffusion flame of a burning polymer in the presence of heat losses is developed (Chapter 3). The approach how to develop the procedure of OI calculation and prediction is briefly discussed in Chapter 4 and will be described in subsequent researches.

## 2. Fundamentals of Diffusion Combustion of Polymers

### 2.1 Thin reaction zone, or diffusion approach

In general, polymer combustion involves a lot of different physical and chemical processes : energy, momentum and species transport, chemical reactions, homogeneous and heterogeneous, gasification of solid and so on. At present, there is no comprehensive model accounting for all of the chemical and physical effects which occur during the combustion of polymers. Even the detailed chemical reactions scheme of degradation and further high-temperature oxidation in the flame zone can't be fully represented except the simplest cases. It is well known, that the reaction scheme for methane burning in air includes more than 100 elementary steps (Combustion Chemistry, 1984).

The direct modeling of the chemical kinetics of the diffusion combustion of polymers and their mixtures would involve much more reaction steps and intermediate products and it seems unrealistic in recent days. Moreover, the interpretation of the results of such modeling would be impossible, being a function of hundreds of parameters.

Some of the diffusion flame properties can be obtained in simplified models. The shape of flame, the flame temperature can be calculated via diffusion approach (Williams, 1985; Kuo, 1986), when chemical reactions in gas phase are considered to occur infinitely fast, so that the chemical rate kinetics is no longer a factor. The hydrodynamic and mass transfer equations no longer include chemical reaction term ; and the flame is considered as a thin reaction zone, an interface surface.

This approach, being correct far from quenching limits, is not applicable for the treatment of the critical phenomena, such as OI or critical diameter. These effects are caused by coupling of the chemical kinetics and the mass and heat transfer. The more accurate model of chemical kinetics is required to account for the criticalities in diffusion combustion.

### 2.2 Extinction limits of diffusion flame

In studies of extinction limits of diffusion flame the reaction zone itself and the finite rate of chemical reactions are to be taken into account. Several extinction limits of diffusion gas flame are considered in the modern combustion theory.

a) The kinetic limit of extinction.

In the work by Zel'dovich (Zel'dovich, 1949; Zel'dovich et al., 1985), the kinetic limit of extinction was considered. The kinetic extinction takes place when the mass fluxes of fuel and oxidizer into the reaction zone are intensified to such extent that the chemical reaction rate is insufficient to consume all the substances. The reaction zone is diluted by the cold reactants and the flame comes to extinction. The kinetic limit is the inherent property of the diffusion gas flame. It always exists, even in the absence of heat losses and is attributed to the finite rate of the chemical reaction. The Damköhler number Da, the dimensionless parameter pertaining to the kinetic limit, is the ratio of a characteristic mass transfer time to a chemical reaction time. It is usually considered that the extinction corresponds to a minimum critical value of the Damköhler number which involves the overall kinetic parameters of the fuel combustion. That is the case for the commonly considered kinetic limit. However, it was found that in the presence of heat losses the diffusion-kinetic limit appears so the Peclet number is also to be taken into account.

The most essential result which was established in previous theoretical studies is that at the extinction limit the intensity of non-premixed combustion approaches to its maximal value in extinction limit and that is proportional to the intensity of stoichiometric combustion in premixed gases.

b) The diffusion-kinetic limit.

In the presence of heat losses the maximal temperature in the reaction zone is lowered. For the extinction to occur, the chemical reaction rate must be reduced enough to be of the order of the diffusion rate, i. e. the chemical reaction must be transferred from diffusion regime into diffusion-kinetic regime. Further increase of heat losses would result in the flame extinction. These qualitative considerations are developed in the Chapter 3, where the mathematical model of polymer combustion near extinction limits is formulated, and the extinction limits are obtained in terms of the main dimensionless parameters : Damköhler and Peclet numbers. The principal conclusion of the modern theory for the limits of extinction of diffusion gas flame can be summarized as follows : the maximal combustion rate of non-premixed gases $M_{max}$ is proportional (with a proportionality coefficient of the order of 1) to the combustion rate of stoichiometric mixture of fuel and oxidizer. This result, originally stated by Zel'dovich (Zel'dovich, 1949; Zel'dovich et al., 1985) and Spalding (Spalding, 1954), had been validated for "symmetrical" case, when the chemical reaction rate w is proportional to the one and the same (generally first) order of the fuel [a] and oxidizer [b] concentrations

$$w \sim [a][b]\exp(-E/RT)$$

In the research (Margolin and Krupkin, 1981a), that this result remains valid for non-symmetrical case also, when the chemical reaction rate is proportional to the different powers of fuel and oxidizer concentrations :

$$w \sim [a]^n[b]^m\exp(-E/RT)$$

$n \neq m$, as well as for different initial concentrations of fuel and oxidizer, $[a_0]=[b_0]$.

At the extinction limit of the non-premixed flame, the characteristic thickness S of the boundary layer between fuel and oxidizer is proportional to the width of the premixed flame reaction zone :

$$Sc\rho u(T)/\lambda=\text{const}$$

Here u(T) is the premixed combustion velocity of stoichiometric mixture.

This condition can be satisfied in two main cases :

a) If S decreases and approaches its critical value S*, the diffusion flame velocity will increase; when S becomes lower than S* the combustion comes to extinction (the kinetic limit) ;

b) If S=const but the heat losses from the reaction zone increase, the maximal temperature and chemical reaction rate are lowered. When the temperature reduces so that the characteristic combustion zone length l of the stoichiometric equivalent mixture $l=\lambda/(c\rho u(T))$ (which increases with the temperature reduction) becomes equal to S, the critical condition will be achieved. Further increase of heat losses results in the flame extinction (the diffusion-kinetic limit).

In the first mechanism, the extinction occurs in the region of the most thin boundary layer (the front edge of the flame), in the second case this process may begin at the region the flame zone far from the front edge. This result was also proved by experiments (Margolin et al., 1984).

The above considerations concerning the extinction limits of gas diffusion flame are also valid for polymer combustion. In this case the maximum combustion rate $M_{max}$ must be understood as the combustion rate of the stoichiometric mixture of the products of polymer gasification with oxidizing atmosphere. The value of $M_{max}$ is referred to as the equivalent premixed combustion rate and can be estimated numerically or measured experimentally.

As shown later, the value of maximal combustion rate $M_{max}$ could be the characteristic parameter for constructing a theory of extinction limits for polymers. In general, $M_{max}$ is a function of the full set of system parameters :

$$M_{max}=M_{0max}+\varepsilon(RT_{ad}/E,\ T_{ad}/T_o,\ D_{ik}/\chi_{ik},\cdots)$$

where $\varepsilon$ is a small correction pertaining to the dependencies of pre-exponents on temperature, heat diffusivities $\chi_{lk}$ and diffusion coefficients $D_{lk}$ on temperature and so on. But for practical purposes we can restrict ourselves to consider only the first term, so $M_{max}=M_{0\ max}$ for a specific gaseous mixture.

## 3. Mathematical Model of Polymer Combustion near Extinction Limits

### 3.1 Combustion in a boundary layer

The combustion of solid fuels in the oxidizing gas flow may be treated within the framework of a boundary-layer theory. Let us consider a steady two-dimensional flow over a flat plane of a polymer material (Fig. 1).

In general, however, there are two boundary layers, hydrodynamic and thermal, appearing in the flow. Their thickness lh and lt are considered to be much smaller than the length of the plate, L ; that is $l/L \ll 1$. The equations of the stationary boundary-layer reacting laminar flow can be written in Schwab-Zel'dovich approximation as follows(Willams, 1985) :

(continuity)

$$\frac{\partial \rho u}{\partial x}+\frac{\partial \rho v}{\partial y}=0 \tag{4}$$

(momentum)

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\frac{1}{\rho}\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right) \tag{5}$$

(energy and species)

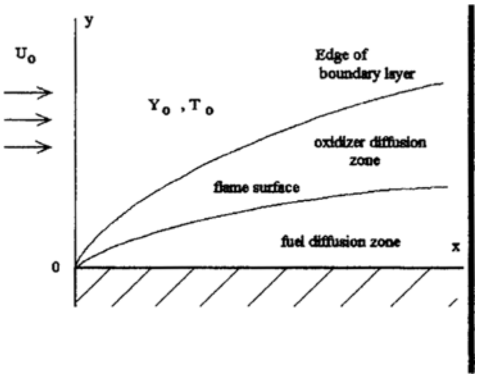

**Fig. 1** Combustion of a polymer material plate in boundary layer

$$L(j)=\frac{\partial}{\partial x}(\rho uj)+\frac{\partial}{\partial y}(\rho vj)-\frac{\partial}{\partial y}\left(D\frac{\partial i}{\partial y}\right)$$
$$=J \tag{6}$$

where $\rho$-density ; u, v-flow velocity components along the axes x and y of the Cartesian coordinate system ; $\mu$-viscosity ; D-diffusion coefficient. The equations of energy and species conservation are written in the unified form, when the chemical reaction is described by one-stage irreversible process, where $A_i$ stands for species i :

$$\sum_{i=1}^{N} n_i' A_i \rightarrow \sum_{i=1}^{N} n_i'' A_i$$

in Schwab-Zel'dovich approximation the value of J

$$J=W_i/(M_i(n_i''-n_i')) \quad i=1\cdots N \tag{7}$$

is the same for all of the species. Here N is the total number of species ; $W_i$-the mass reaction rate of the formation of species i, $M_i$-it's molecular weight.

The value of j is as follows :

For the energy equation :

$$j=\int_{T_0}^{T} c_p dT \Big/ \left(\sum_{i=1}^{N} h_i^o M_i (n_i'-n_i'')\right) \tag{8}$$

where $c_p$-specific heat capacity ; $h_i^o$-specific standard formation enthalpy of species i ;

For the species conservation equations:

$$j=Y_i/(M_i(n_i''-n_i') \tag{9}$$

where $y_i$-mass fractions for species i ;

The boundary conditions for the equations at the gas-solid interface are as follows :

For the continuity and momentum equations, the nonslip conditions :

$$y=0 : u=0,\ v=0 \tag{10}$$

The boundary conditions for the energy equation, energy-flux balance:

$$y=0 : \lambda \mathrm{grad}\ T=M(L+Q) \tag{11}$$

where M-mass combustion rate of the polymer ; L-specific heat of gasification ;

Q-specific heat losses from the unity of surface per unity of mass of gasified fuel.

The boundary conditions for the species conservation equations, mass-flux balance :

$$y=0 : \rho D\ \mathrm{grad}\ y_i=M_i \tag{11}$$

where $M_i$-the mass rate of generation of species i at the surface.

At the edge of the boundary layer the conditions are as follows :

$$y=l : u=U_0 ; T=T_0 ; y_i=y_{i0} \quad i=1\cdots N \tag{12}$$

Diffusion combustion in boundary layers was studied by many authors(Fendell, 1965; De Ris, 1969; Sirigrano, 1972; Fernandez-Pello and Williams, 1977; Freyand Tien, 1979; Krishamurthy et al., 1976; Tien et al., 1978).

The conditions for existence of automodel combustion regimes are among the principal problems. This is of particular concern as regards the limit conditions of combustion.

In case when the gravity force is significant, the relevant term should be added into the Eq. (5). Since the full equation system is very complicated, at the first stage we have developed the mathematical model, allowing to treat the system in 1-D approximation and to obtain the qualitative dependencies between the dimensionless parameters.

The analysis of the equation system shows that in common used assumptions the problem becomes automodel when $(u=0, g=0)$ or $(u=0, g=0)$. So the problem is simplified to give one-dimensional equations treated in the Sec. 3.3. However, some comments must be added to the common assumptions as stated above.

In general, the boundary-layer approximation is not good in the region of the formation of the boundary layer. But the extinction often occurs namely in this region, and this contradiction is intrinsic to all the researches done by now. To provide more accurate consideration, the full system of Navier-Stokes equations together with the diffusion and energy equations must have been studied. Such consideration would yield the "exact" extinction conditions as concerns the hydrodynamics of the reacting flows.

But we doubt that this "exact" consideration would give more accurately the oxygen index, due to the uncertainties of chemical kinetics that can not be overcome. At least at the first stage, it is expedient to develop the simplified models with the minimal number of empirical parameters obtained from test experiments.

### 3.2 The mechanism and kinetics of combustion of polymers containing C, H, O, N. the combustion rate of the equivalent gaseous mixture

During the polymer combustion in an oxidizing atmosphere, the products of polymer destruction and gasification are consumed in the exothermic reaction occurring in gas phase. The concept of the equivalent gas mixture for the products of polymer decomposition is not so easy to be introduced. However, for C-H-O-N polymers, the problem of the complexity of the chemical kinetics may be solved due to the peculiarities of the key step of combustion. It is known(Frank-Kamenstski, 1987), that during the combustion of gaseous hydrocarbons in oxygen nitrogen atmosphere, the process of oxidation can be approximately accounted for by the reduced mechanism. The first stage involves numerous reactions of preliminary oxidation of $C_xH_y$ into CO and $H_2O$. Unless all CH and $CH_2$ free radicals are consumed, CO can not be oxidized further to $CO_2$. These preliminary reactions are relatively fast and result in the accumulation of CO in the reacting mixture.

The subsequent oxidation of CO to $CO_2$ is the rate-controlling stage (the key steps are : $CO+OH \rightarrow CO_2+H$ and $CO_2+H \rightarrow CO+OH$, the forward and the reverse reactions). Therefore, as far as the combustion velocity is concerned, all hydrocarbons behave themselves as similar way. The experimental data on the combustion velocities in the oxygen nitrogen stoichiometric mixtures with hydrocarbons show that the overall chemical kinetics of the hydrocarbons oxidation can be summarized by one effectively bimolecular equation for the reaction rate :

$$w=Z[a]^n [b]^m \exp(-E/RT),$$

with a universal effective activation energy E approximately equal to 20-25 Kcal/mole, and the order of reaction $r=n+m=1.5$. The pre-exponential factor Z is different for different substances and can be determined from one exper-

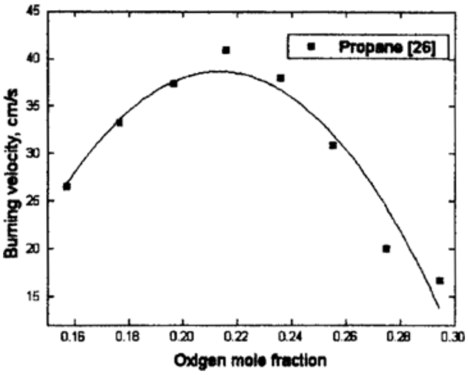

**Fig. 2** Combustion velocity upon oxygen index for propane/$O_2$/$N_2$ mixtures

imental point. The calculated dependence of the combustion velocity upon oxygen index for stoichiometric propane/$O_2$/$N_2$ mixtures is shown on Fig. 2. Plotted also are the experimental points by using data from reference (Metgalchi and Keck, 1982).

Less experimental data are available on polymers combustion kinetics. Sohrab and Williams (Sohrab and Williams, 1981) indicated that their experiments on diffusion flame extinction could be a means of evaluating the kinetic parameters of gas-phase stage of polymer combustion, though the extracting of numerical values of activation energy for polymers proved to be an ambitious task. The reported value of the effective activation energy for polymethylmetacrylate (PMMA) (Krishmamurthy, 1975), based on the experimental results for extinction of diffusion flames in the stagnation-point boundary layer, is equal to 21 Kcal/mole, in accordance with our considerations. However, this is not a common point of view.

The authors (Sohrab and Williams, 1981) noted that the values of the effective activation energies obtained depend greatly on the way of taking into account the radiant losses, melting and dripping, so they may vary, according to literature, from 20 to 50 Kcal/mole. The composition of the gasification products of C-H-O-N polymers on the final stages of the oxidation is obviously containing the same species as during the oxidation of gaseous hydrocarbons.

This concept results in the overall equation of the combustion rate of the equivalent gaseous mixture of the products of polymer oxidation with the ambient oxidizing atmosphere, similar to that for gaseous hydrocarbons, with the universal activation energy E and specified parameter Z for each polymer or the mixture of polymers.

Two of the three parameters, characterizing the overall chemical kinetics, for C-H-O-N containing polymers can be adopted in the first approximation to be universal : $r=m+n=1.5$, $E=20\text{-}25$ Kcal/mol. Only one individual parameter Z remains to be determined from the test experiments. In the high-order approximations $n+m$ and E could also be obtained from experimental data. That would involve more than one experimental point to be required. We consider that it would be unnecessary. For the purposes of the present work, that is for OI or critical diameter calculation, we can easily adopt the simplified procedure. According to our experience, the accuracy of the first approximation is sufficient. Later we shall compare the predictions of OI as provided by the approach developed with the experimental data on extinction of polymers in various conditions. One must note that for polymers of different composition, e.g., Cl-containing, the overall chemical kinetics is not accounted for by two-stage scheme and the values of $n+m$ and E are different.

### 3.3 Limits of diffusion combustion in the presence of heat losses

In this section, the diffusion combustion of polymers near extinction limits is considered. It is shown that two extinction limits exist : the first one is the kinetic limit as it is the case in gas diffusion flame (see 2.2) ; the second one is accounted for the heat losses from the reaction zone due to external cooling agent. Let us consider the diffusion flame formed during the combustion of a polymer slab of thickness d in an oxidizing atmosphere. The polymer slab is cooled by a cold base of a constant low temperature $T_0$. The reaction between fuel A and oxidizer B is assumed to be described by the following equation :

$$n_A A + n_B B \rightarrow \text{products} \tag{13}$$

where $n_A$ and $n_B$-the relevant stoichiometric coefficients.

The components, as it is for diffusion flame, are supplied to the reaction zone in the stoichiometric ratio. The relationships of the mass flux of oxidizer to the reaction zone $(\rho u)_{ok}$, the mass combustion rate of the polymer $(\rho u)$ and the total rate of reactants consumption in the chemical reaction $M = (\rho u)_0$ are expressed in terms of the coefficients $n_A$ and $n_B$ as follows :

$$(\rho u)_0 = (\rho u) \Psi = (\rho u)_{ok} \Psi / (\Psi - 1),$$

where $\Psi = \alpha\beta B_0 / (\alpha + \beta B_0)$

; $B_0$-oxygen concentration in the ambient atmosphere,

$$\alpha = (n_A M_A + n_B M_B) / n_A M_A \ ;$$
$$\beta = (n_A M_A + n_B M_B) / n_B M_B \ ; \tag{14}$$

The equations for temperature and species concentration distributions can be written as follows :

$$\frac{d^2(\tau T)}{dx^2} - D^{-1} u \frac{(d(\tau T)}{dx} = -F$$
$$\frac{d^2(\alpha A)}{dx^2} - D^{-1} u \frac{d(\alpha A)}{dx} = F$$
$$\frac{d^2(\beta B)}{dx^2} - D^{-1} u \frac{d(\beta B)}{dx} = -F \tag{15}$$

where A and B-mass concentrations of fuel and oxidizer, $F = zAB\exp(-E/RT)$-the Arrhenius reaction rate ; z-pre-exponential factor ; E-effective activation energy ;

D and $\chi$-diffusion and heat diffusivity coefficients ; $\tau = \alpha c M_A / Q$, Q-heat of reaction per mole of component A ; c-specific heat capacity of gas. The boundary conditions for the Eq. (15) is as follows :

at $\chi = 0$ :

$$\lambda_g dT/dx = L\rho u + \lambda_p \varphi \ ;$$
$$\rho u = \rho u A - \rho D dA/dx \ ;$$
$$0 = uB - D \ dB/dx \ ;$$
$$T = T_S$$

and at $\chi = 1$ : $A = 0$ ; $B = B_0$, $T = T_0$

where $\varphi = (dT/dx)_S$-surface temperature gradient in solid phase, $\lambda_p$ and $\lambda_g$-heat conductivity of the polymer and the gas, L-heat of polymer gasification.

In the limit case of stationary combustion of the infinitely thick polymer slab, there is a natural temperature gradient $\varphi_0 = \lambda_p (T_S - T_0) / c\rho u$ in the solid phase. In the absence of heat losses, the temperature in reaction zone is equal to the adiabatic combustion temperature $T_{ad}$ of the mixture of the gaseous products of the polymer gasification and the oxidizing atmosphere. For a finite polymer thickness d the surface temperature gradient $\varphi$ is more than $\varphi_0$. This effect results in cooling of the reaction zone even when the reaction in gas phase is assumed to occur infinitely fast (the effect of cold base).

There are different ways of presenting the kinetics of thermal destruction of a burning polymer. Here we consider the following case: the surface temperature is related with the mass combustion rate by the Arrhenius law of thermal destruction $\rho u = z \exp(-E_1/2RT)$, where z is the pre-exponent, $E_1$-the effective activation energy of thermal destruction of the polymer.

The Eq. (15) in case of the frequently used assumption of the unity Lewis number: $Le = D/\chi = 1$ can be reduced to the following equation:

$$\frac{d^2\Theta}{d\xi^2} - \Psi^{-1} p \frac{d\Theta}{d\xi} = Da[\Theta_0 - \Theta - \xi(\Theta_m - \Theta_0)$$
$$(\exp[p(\xi - 1)/\Psi] - 1)] * [\Theta_0 + \Theta_0' - \Theta$$
$$- \Psi(\Theta_m - \Theta_0 - \Theta_0')(\exp[p(\xi - 1)\Psi] - 1)] \cdot$$
$$\exp(\Theta / (1 + \gamma\Theta)) \tag{16}$$

with the boundary conditions:

$$\xi = 0 : \Theta = \Theta_S, \ \text{grad}\Theta = P(\Theta_S + (\Psi - 1)$$
$$(\Theta_0 + \Theta_0') / \Psi - \Theta_m)$$
$$\xi = 1 : \Theta = \Theta_0. \tag{17}$$

where $(\rho u)_o / M = C \exp[E_1/2E(\Theta_S / (1 + \gamma\Theta_S))]$

The Eqs. (16) and (17) were solved by numerical iterative integration.

Depending on the parameters Da and Pe, there exist two, or one or no solutions (Margolin and Knupkin, 1983).

Only high-temperature solutions can represent real combustion regimes.

The results of the calculations are presented on the Fig. 3. In the absence of heat losses (Pe≫1) with the increase of Da, the combustion temperature tends to the adiabatic combustion temperature of the equivalent gas mixture ($\Theta_m \rightarrow 0$).

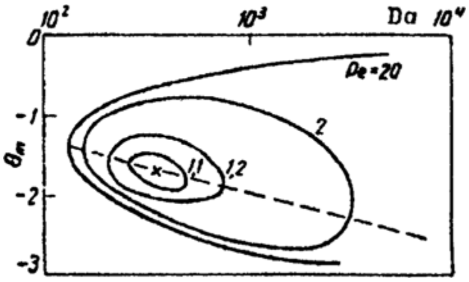

**Fig. 3** Depending $Q_m$ on the parameters Da and Pe

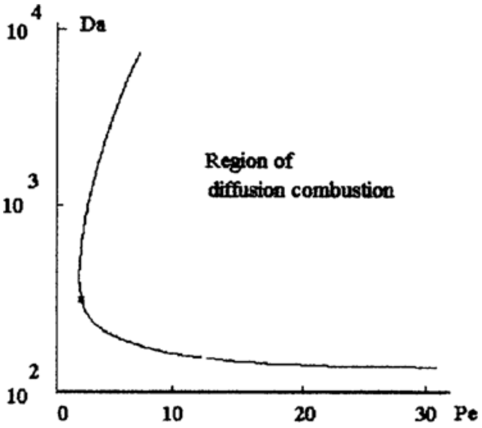

**Fig. 4** The extinction curve Da(Pe)

With the decrease of Da, the combustion temperature decreases due to the over-intensification of the combustion, high- and low-temperature solutions approach each other and then merge at $\mathrm{Da} = \mathrm{Da}^*$. If $\mathrm{Da} < \mathrm{Da}^*$, no solutions exist.

In the presence of heat losses, with the lower Pe numbers, the combustion temperature decreases with the increase of Da even for the infinitely fast reaction. Two critical Da numbers exist when $\mathrm{Pe} > \mathrm{Pe}^*$. When $\mathrm{Pe} = \mathrm{Pe}^*$, the two Da's merge, that is the condition of the total extinction.

In Da-Pe coordinates, the extinction curve $F(\mathrm{Da}, \mathrm{Pe}) = 0$ separates the regions of successful combustion and extinction (Fig. 4). The combustion can occur only inside the curve Da(Pe), which is similar to the relevant curve for the extinction of premixed flames in tubes. However, they are different; for premixed flames the combustion is related only with the upper branch of the curve, while for diffusion flames - with the region inside the curve. The critical condition of the total extinction is the same for both curves and corresponds to the condition $\mathrm{Da} = \mathrm{Da}(\mathrm{Pe}^*)$.

So, the extinction limits of the polymer diffusion flame are determined in terms of the dimensionless parameters Da and Pe. The equations to give the numerical values of $\mathrm{Da}^*$ and $\mathrm{Pe}^*$ are to be solved by an iterative procedure.

## 4. Calculation of Oxygen Index

This project is intended to develop the model of polymer flammability in non-standard conditions and the prediction of OI. One should note that all methods of theoretical prediction of some value are always based upon some theoretical insight. The quality of a model for describing some effect is assessed according to how much empirical parameters are involved into the model.

The better understanding of the physics and chemical processes, the less parameters are required to account for the effects. In this project, we have attempted to satisfy all the requirements by minimal number of test experiments : *one value* - standard Oxygen Index is employed.

The theoretical considerations in the previous sections now can be summarized to outline a procedure of calculation of OI based upon minimal number of test experiments for determining the empirical parameters involved into the equations.

The most stable flame zone in diffusion combustion of polymers is the front edge of the flame. At the extinction limit, the ratio of heat losses from the flame zone to the overall heat release is proportional to $RT_{ad}/E$. This equation in terms of the relationship between dimensionless parameters - Da and Pe numbers has been introduced previously.

The general equation, involving Pe number, must be specified concretely for the heat losses due to various factors, including acceleration (which enhances natural convection), natural and forced convection, cold base of the polymer itself, cold walls, surrounding the flame zone, radiation etc.

In any case, from the analysis of the diffusion combustion limits, we have seen that it is necessary to choose the characteristic combustion velocity. As it was shown in Sec. 3.2, the combustion velocity of the equivalent stoichiometric gas mixture may be taken as the characteristic velocity.

The critical conditions of extinction of diffusion flame due to the simultaneous action of the various factors were described by the system of equations, the heat losses due to the various cooling factors taken into account as follows (Margolin and Krupkin, 1981b):

$$\left[\frac{g\chi_g}{Z_o^3 f^3(Y^*, P, T_o)}\left(\frac{P}{P_0}\right)^2\right]^{\frac{1}{3}} + K_1\left[\frac{\nu\chi_g}{\delta_0 Z_0^2 f^2(Y^*, P, T_0)}\left(\frac{P}{P_0}\right)^2\right]^{\frac{1}{2}} + K_2\frac{(T_s - T_0)\rho_s\chi_s}{T_{ad}\rho_g\delta_0\partial Z_0 f(Y^*, P, T_0)} + K_3\frac{\chi_g^2}{h^2 Z_0^2 f^2(Y^*, P, T_0)} + K_4\frac{T_{ad}^3}{Z_0^2 f^2(Y^*, P, T_0)}\frac{P}{P_0} = 1 \tag{18}$$

Each term in (18) represents the heat losses by five various factors ; free and forced convection, cold base, cold walls, radiation respectively, $K_1$ ··· $K_4$-are numerical coefficients, pertinent to the relative importance of each heat loss. In general, when critical conditions are calculated, only one or two terms from (18) are sufficient.

Here ; g-acceleration
; $\chi_g$, $\chi_s$-heat diffusivities of gas and polymer
; P-pressure
; $P_0$-atmospheric pressure
; $T_0$-initial temperature
; v-gas flow velocity
; $Y^*$-oxygen mole fraction in the atmosphere, $Y^* = [O_2]/([O_2]+[N_2])$
; $\delta_0$-characteristic size of a polymer sample (if based upon a cold base of temperature $T_0$)
; h-distance between flame zone and cold walls (if any)
; $Z_0$-numerical coefficient (of dimension cm/sec), specific for each polymer, $f(Y^*, P, T_0)$ a function related to the dependence of the combustion rate of the equivalent stoichiometric gas mixture in the form of Zel'dovitch and Frank-Kamenetski (Zel'dovich et al., 1985), which is presented as follows (Margolin and Krupkiu, 1981b):

$$f(Y^*, P, T_0) = \left(\frac{\lambda}{\lambda_0}\right)^{\frac{1}{2}}\left(\frac{P}{P_0}\right)^{\frac{1}{2}}\left(\frac{T_{ad}}{T_{ad} - T_0}\right)^{1} + \frac{r}{2} \left(\frac{Y^*}{Y^* + v}\right)^{\frac{r}{2}}\exp\left(-\frac{E}{2RT_{ad}}\right) \tag{19}$$

where, $Z_0 = \left[\frac{\lambda_0\mu q Z_0 P_0^r R}{(r_0^2 c^2 E^{r+1})}\right]^{\frac{1}{2}}$

A specific for each polymer constant factor of the dimension of cm/sec, $Y^*$-oxygen index, r -total order of reaction (equal to 1.5 for hydrocarbon + oxygen + nitrogen mixtures, see 3.2), $\lambda_0$, $\rho_0$-heat conductivity and density of combustion products in air at $P_0 = 1$ atm.

Adiabatic combustion temperature $T_{ad}$ also depends upon Y, P, $T_0$ and is to be determined via calculations of thermodynamical equilibrium of combustion products.

The Eq. (18) relating the decrease of the adiabatic flame temperature due to heat losses and (19) together form the equation system to be solved numerically to give the oxygen index as a function of different parameters. The parameter $Z_0$ is the only one to be obtained from the experiments, since E and r may be assumed to be constant for C-H-O-N containing polymers.

The results of the calculation of oxygen index for polymers are presented in the wide range of nonstandard conditions :

- pressure 0.1-10 atm;
- initial temperature 250-500 K;
- gravity force acceleration 1-50 g;
- velocity of by-passing flow of oxidizing $O_2/N_2$ stream 0-50 m/s;
- different oxygen mole fractions for polymer layers covering the cold base.

The input parameters involve the chemical composition of a polymer, its formation enthalpy and standard oxygen index. The overall chemical kinetics is represented by the parameter $Z_0$, the one to be calculated from the input data

## 5. Results

### 5.1 Dependence of oxygen index on pressure

The calculations showed that with the increase of pressure at lower subatmospheric pressures OI is significantly decreased, while at the pressures more than 1 atm the dependence is rather weak. The boundary pressure, at which the character of dependence is changed, depends on the polymer type. For the majority of studied polymers, OI becomes less dependent on pressure at the pressures greater than 0.2-0.3 atm.

The theoretical curves, Figs. 5. and 6 were calculated as it was already noted, based upon the polymer composition, formation enthalpy and standard oxygen index.

On the Fig. 6, the dependence is shown for PMMA and Polypropylene, on the Fig. 5-for two different grades of ABS plastic, which have different flame retardant admixtures and different standard oxygen index.

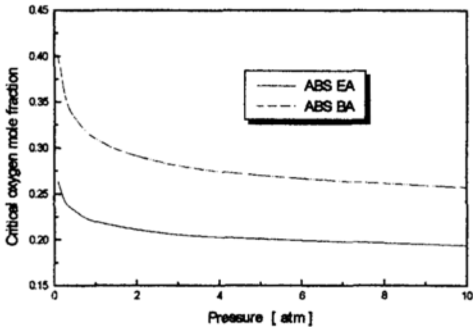

**Fig. 5** Dependence of oxygen index on pressure for flame retardant and non-retardant polymer

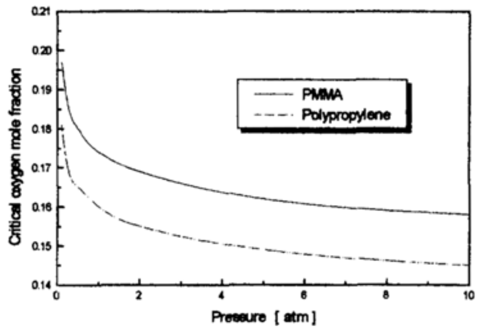

**Fig. 6** Dependence of oxygen index on pressure for PMMA and polypropylene

The dependence of OI on pressure can be explained as follows. The existence of the critical oxygen concentration in this case is due to the presence of heat losses by natural convection and radiation. Relatively low effect of the heat losses to the solid phase is proved below, where the dependence of OI on initial temperature is presented. With the increase of pressure the concentration of oxygen (at the given oxygen mass fraction $Y^*$) in the atmosphere is increased.

Therefore, the flame is stabilized closer to the polymer surface, ensuring the intense heat transfer to the solid, less losses by natural convection, and therefore more vigorous gasification of the polymer. Thus, the region of stable combustion is expanded. In general, one can expect that the theoretical curve goes somewhat lower than the experimental one at pressures less than 0.3 atm.

One can account this effect for the onset of radiation losses which at low pressures and higher combustion temperatures would become relatively more important. As it is seen, for $P > 0.4$-$0.5$ atm, the law of dependence of OI on pressure can be approximately described as $Y^* = P^{-0.1}$.

### 5.2 Dependence of oxygen index on initial temperature

The dependence of OI upon initial temperature is presented in Figs. 7 and 8. The Figs. 7 and 8 show the calculated theoretical curves. In Fig. 8 the dependence is shown for PMMA and Polypropylene and the Fig. 7 shows the two different grades of ABS plastic. With the increase of initial

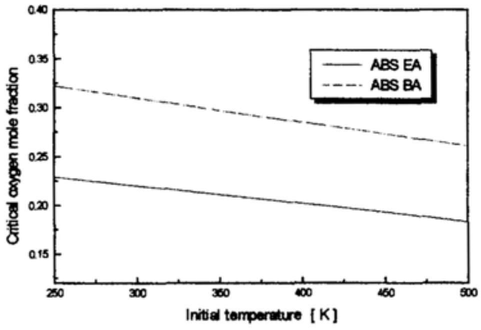

**Fig. 7** Dependence of oxygen index on initial temperature for flame retardant and non-retardant polymer

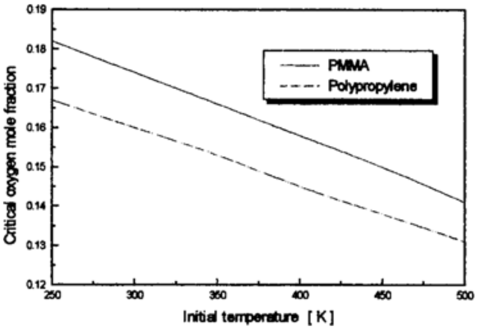

**Fig. 8** Dependence of oxygen index on initial temperature for PMMA and polypropylene

temperature, OI is slightly decreased. The dependence is almost linear and rather weak. From the effect, it is proved that the main factors for the existence of critical conditions are the heat losses from the gas phase. In general, the more the flame temperature at the extinction limit, the less dependent on initial temperature OI is.

### 5.3 Dependence of oxygen index on acceleration force

The increase of acceleration force a with the reference to the gravity force acceleration $g(a/g > 1,\ g=981\ \text{cm/s}^2)$ results in the increase of oxygen index. The Figs. 9 and 10 show the calculated theoretical curves. On the Fig. 10, the dependence is shown for PMMA and Polypropylene, on the Fig. 9 - for two different grades of ABS plastic.

In these cases, the dependence of oxygen index on acceleration force is due to the heat losses by natural convection. With the increase of gravity, the convective heat losses are increased, and the oxygen index is also increased.

In the first approximation, OI is proportional to the one third power as $Y^* \sim (a/g)^{1/3}$. This relationship holds for the accelerations down to $a/g=0.2$-$0.4$. In microgravity conditions, $a/g \ll 1$, which take place in space flight, for example, the relationship will be more complex, but here we did not consider this subject.

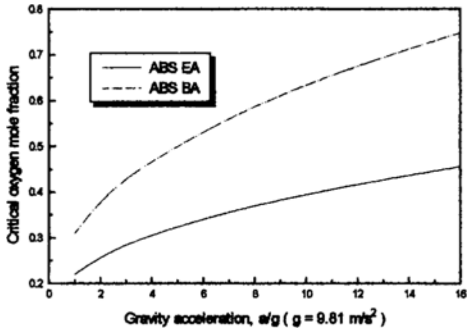

**Fig. 9** Dependence of oxygen index on gravity acceleration for flame retardant and non-retardant polymer

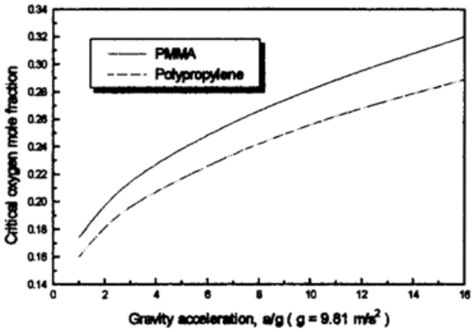

**Fig. 10** Dependence of oxygen index on gravity acceleration for PMMA and polypropylene

Our model does not correspond to microgravity conditions, and we performed no calculations for that case. Since in microgravity the heat losses by natural convection are impossible, heat conduction and radiation heat losses would become more significant.

There are no principal obstacles to extend our model for microgravity conditions also, but this requires special study and one would take into account more empirical parameters in addition to OI.

### 5.4 Dependence of oxygen index on flow velocity

With the increase of the flow velocity of by-passing gas stream, OI is increased. The effect of flow velocity depends greatly on the size of the sample, its orientation and the conditions of flow, since all of these parameters determine the boundary layer and hence the characteristics of forced convection.

The Figs. 11 and 12 show the calculated theoretical curves. On the Fig. 12, the dependence is shown for PMMA and Polypropylene, on the

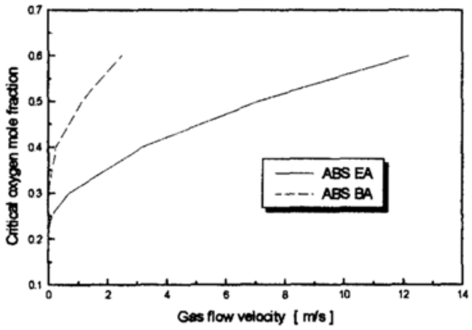

**Fig. 11** Dependence of oxygen index on oxidizing $O_2/N_2$ stream velocity for flame retardant and non-retardant polymer

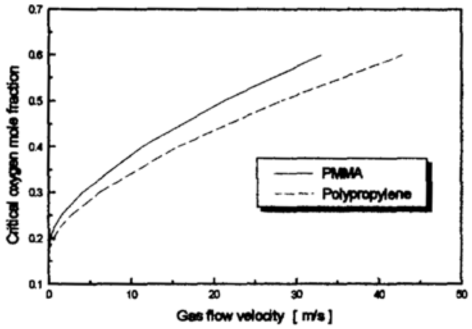

**Fig. 12** Dependence of oxygen index on oxidizing $O_2/N_2$ stream velocity for PMMA and polypropylene

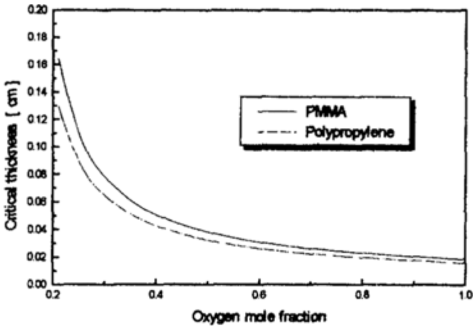

**Fig. 13** Dependence of critical thickness on oxygen mole fraction for PMMA and polypropylene

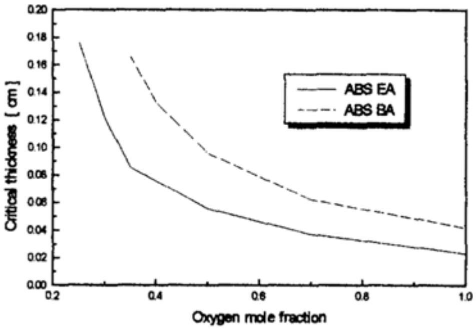

**Fig. 14** Dependence of critical thickness on oxygen mole fraction for flame retardant and non-retardant polymer

Fig. 11 for two different grades of ABS plastic.

The increase of the oxygen index with the increase of velocity is due to the intensification of heat losses by forced convection. This effect is known as the blowout of the flame by the convective heat losses.

### 5.5 Dependence of the polymer thickness layer based upon cool surface on oxygen mole fraction

Polymer covers and layers are widely used in applications. This subject is of principal concern for the industrial applications of polymers, because the flammability of polymer products depends not only on the material properties itself, but also upon the construction design, where polymers are used together with metals and other materials. The thickness of polymer layer is as important as the peculiarities of its thermal interaction with metal or stone elements of construction. Despite its importance, this problem has not been fully studied yet. The Figs. 13 and 14 show the calculated theoretical curves. On the Fig. 13 the dependence is shown for PMMA and Polypro-pylene, the Fig. 14 shows the two different grades of ABS plastic. The calculations showed that with the increase of OI at atmospheric pressure critical thickness d* is decreased approximately inversely proportional to Y ; the dependence being rather sharp when approaching Y* -standard oxygen index. It is evident, that the existence of such critical thickness is due to the competition between the heat loss to the solid phase and the heat release in combustion. The former in the studied case becomes the relatively important factor of heat losses. As the thickness of the polymer layer becomes very small, the heat losses to the solid phase are increased, and the flame extinguishes. One can expect that the flame should become very unstable at the limit of extinction and the mechanism of the polymer decomposition is changed. Therefore, the calculated curves are to be considered as qualitative trends rather than quantitative. However, there have been no estimations of this value in the literature before the present studies.

## 6. Conclusions

The theory of the combustion limit of polymers in an oxidizing atmosphere is developed.

The mathematical model of the extinction limits of boundary-layer polymer combustion in the presence of heat losses is developed. The heat transfer by conduction, convection of forced and natural, radiation, the heat losses into cold base and due to acceleration forces are taken into account. One of the most crucial points of the model is the treatment of the chemical kinetics of combustion. Since the detailed reaction kinetics is extremely complicated and as a rule not available, the overall reaction scheme is presented by a generalized physics-chemical characteristics: the mass combustion rate of the equivalent stoichiometric mixture of the polymer decomposition products and the oxidizing atmosphere. The equivalent mixture combustion rate is expressed in the form by Zel'dovich and Frank-Kamenetski. The adiabatic combustion temperature required for the above is determined via the calculations of the thermodynamic equilibrium. The empirical parameters involved in the model are concerned with the equivalent mixture combustion rate. For C-H-O-N containing polymers, only one parameter is required. It may be found, e.g., from the measured oxygen index in standard conditions or from the critical diameter. The procedure of calculation of Lower Oxygen Index for C-H-O-N containing polymers and their mixtures in non-standard conditions (as a function of pressure, initial temperature, gravity acceleration, flow velocity) is developed and the calculations of LOI for several plastics were made in the various conditions.

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## References

Annual Book of ASTM Standards, *The American Society for Testing and Materials*, Philadelphia, Pa., published annually.

*Combustion Chemistry*, 1984, Ed. by Gardiner, W. C., Jr., Springer-Verlag.

De Ris, J. N. 1969, "Spread of a Laminar Diffusion Flame," *In: 12th Symp. (Int.) on Combustion*, p. 241.

Encyclopedia of Polymer Science and Engineering. 2-nd ed., 1987, Vol. 7. Wiley-Interscience.

Fendell, F. E. 1965, "Ignition and Extinction of Combustion of Initially Unmixed Reactants," *J. Fluid Mech.*, Vol. 21, No. 2, p. 281.

Fernandez-Pello, A. and Williams, F. A., 1977, "A Theory of Laminar Flame Spread over Flat Surfaces of Solid Combustibles," *Combustion Flame*, Vol. 28, No. 3, p. 251.

Frank-Kamenetski, D. A., 1987, *Diffusion and Heat Transfer in Chemical Kinetics*, 3-rd Ed., Moscow, Nauka Publ.

Frey, A. E. and Tien, J. S., 1979, "A Theory of Flame Spread over Solid Fuel Including Finite-Rate Chemical Kinetics," *Combustion Flame*, Vol. 36, No. 3, p. 263.

Krishnamurthy, L., 1975, "Diffusion Flame Extinction in the Stagnation Point Boundary Layer of PMMA in $O_2/N_2$ Mixtures," *Combust. Sci. Technol.*, Vol. 10, Nos. 1-2, p. 21.

Krishnamurthy, L., Williams, F. A. and Seshadry K., 1976, "Asymptotic Theory of Diffusion Flame Extinction in the Stagnation Point Boundary Layer," *Combustion Flame*, Vol. 26, No. 3, p. 363.

Kuo, K. K., 1986, Principles of Combustion.

Margolin, A. D., Krupkin, V. G. 1981a, "On the Critical Conditions of the Diffusion Combustion," *Fizika Goreniya i Vzryva*, Vol. 17, No. 2, p. 3.

Margolin, A. D., Krupkin, V. G. and Valeev, I. N. 1984, and "Diffusion Gas Flame in the Presence of Heat Losses," *Khim. Fizika*, Vol. 3, No. 6, p. 874.

Margolin, A. D. and Krupkin, V. G., 1983, "Effect of Heat Losses on the Extinction Limits and the Structure of the Diffusion Flame During the Polymer Combustion," *Fizika Goreniya i Vzryva*, Vol. 19, No. 5, p. 25.

Margolin, A. D. and Krupkin, V. G. 1981b, "Critical Conditions of Polymer Combustion in Oxidizing Atmosphere," *Dokl. Acad. Sci. USSR*, Vol. 257, No. 6, p. 1369.

Margolin A. D. and Krupkin V. G., 1982, "Effect of the Thermal Boundary Layer of the Solid Phase on the Stability of Polymer Combustion," *Khim. Fizika*, Vol. 1, No. 7, p. 994.

Metgalchi, M., and Keck, J. C., 1982, "Burning Velocities of Mixtures of Air with Methanol, Isooctane, and Indolene at High Pressure and Temperature," *Combustion Flame*, Vol. 48, pp. 191~210.

Sirignano, W. A., 1972, "A Critical Discussion of Theories of Flame Spread Across Solids and Liquid Fuels, *Combust. Sci. Technol.*, Vol. 6, No. 2, p. 95.

Sohrab, S. H. and Williams, F. A., 1981, Extinction of Diffusion Flames Adjacent to Flat Surfaces of Burning Polymers," *J. Polymer Sci., Polym. Chem. Ed.*, Vol. 19, No. 11, p. 2955.

Spalding, 1954, D. B. A theory of the extinction of diffusion flame. *Fuel*, Vol. 33, p. 255.

Thermodynamic Properties of Individual Substances., 1978, Reference Book, Vol. 1-4; (Gurvich L. V., Weitz I. V., Medvedev V. A. et. al.) 3rd Ed., Moscow, "Nauka" Publ.

Tien, J. S., Singhai, S. N., Harrold, D. P. and Prahl J. M., 1978, "Combustion and Extinction in the Stagnation Point Boundary Layer of a Condensed Fuel," *Combustion Flame*, Vol. 33, No. 1, p. 55.

Troitzsch J., 1983, *International Plastics Flammability Handbook: Principles, Regulations, Testing and Approval*, Hanser Publ.

Williams, F. A., 1985, *Combustion Theory*. 2-nd ed., Benjamin/Cummings, Menlo Park, CA.

Zel'dovich, Ya. B. "On the Theory of Non-Premixed Combustion," *Sov. J. Tech. Fiz.*, 1949, Vol. 19, No. 10, p. 1199.

Zel'dovich Ya. B., Barenblatt G. I. and Librovitch V. B., Makhviladze G. M., 1985, *The Mathemati- cal Theory of Combustion and Explosions*. Consultants Bureau, New York.