



UNIVERSITY OF NIŠ

The scientific journal FACTA UNIVERSITATIS

Series: Working and Living Environmental Protection Vol. 1, No 5, 2000, pp. 1 - 8

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## AN ANALYSIS OF OCCURRENCES IN THE CONDENSED PHASE OF POLYMER FUEL

UDC 665.639.57;678-13

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**Abstract.** *An analysis of the space distribution of temperature in the condensed phase of polymer fuel was carried out. In contrast to the standard approach where it is assumed that the polymer fuel absorbs irreversibly both the mass and energy from the area of the products desintegration, in this paper it is assumed that in addition to the irreversible there is reversible absorption as well which is, in any case, a more realistic assessment of occurrences in the condensed phase. On the basis of this general assumption the dependence of the temperature on the depth of the fuel layer was found out. It is shown that the reversible absorption process gives lower temperatures than those predicted by the standard theory. In practice, it means that the fuel is heated slower than believed and that the fire lasts longer.*

**Key words:** *polymer fuel, combustion, heat, fire, condensed phase, reversible and irreversible absorption.*

### 1. INTRODUCTION

Although organic polymers behave differently in different situations, at burning or heating they can be classified into two groups [1-4].

Under the influence of the thermal energy the first group suffers destruction of the basis polymer chain which desintegrates into low-molecular products which may be either in gaseous or liquid state. They decompose at relatively high temperatures (300°C - 600°C) leaving relatively small coke residue. The process of thermal decomposition is endothermic. Macromolecules of such polymers consist of a great number of monomolecular units of small mass. This group mainly consists of polymers with linear structure (polyethylene, polystyrene, non-stick coating, chloroplast and others).

Since the mass of finite products of desintegration is small, these parts are in gaseous phase at the temperature  $T_p$ .

The second group comprises the polymers in which with the increase of temperature there comes to intramolecular separation of some atoms or atomic groups. This group comprises polyvinyl alcohol, polymers of vinyl series, epoxide resin, polyurethanes and others. As a rule, they all have a gauze structure.

During heating appears gas with particles of great mass, and the interface between the heated and non-heated polymer is rough and contains pores mainly, that is, narrow channels entering into non-heated part of fuel.

The condensed phase consists of two layers: a layer of decomposed fuel (A) and  $T_p$  temperature and a layer of still non-heated fuel (B) which is much thicker than the A layer. Over the A layer, parallel to its upper surface, the heated oxygen passes; it delivers to the A layer the energy required for decomposition of macromolecules of polymers (Figure 1.).

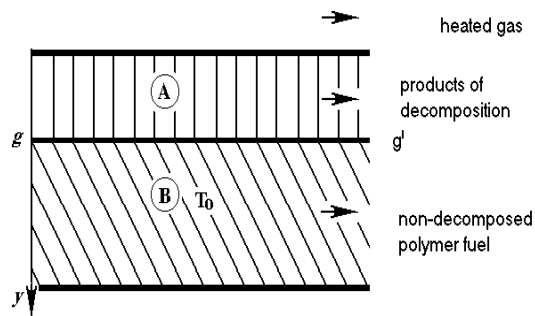


Fig. 1. The condensed phase

The  $gg'$  line separates the area of products of heating (A) from the area of non-decomposed fuel (B). Occurrences in the condensed phase are usually analysed on the basis of equations given and described in detail under [5]. This is a very complex mathematical and physicochemical problem.

The behaviour of the condensed phase shall not be analysed in detail here. However, the temperature field of this phase shall be examined in general, which in theory of mass and thermal energy transfer is presented in papers [6-13].

## 2. IRREVERSIBLE AND REVERSIBLE PROCESSES OF DELIVERY OF THERMAL ENERGY AND MASS

A few decades back it was noticed that the flame temperature at burning had a quasi-oscillating behaviour in time. Because of this, trigonometric functions [ 9] are introduced into the theoretical analysis of flame. Less than one decade back, the micro-theoretical considerations showed that for the quasi-oscillating behaviour of temperature in time the cumulative correction of the equation for changes of temperature in time was essential:

$$\overline{AT}_{(t)} = \frac{A}{t} \int_0^t dtT \quad (2.1)$$

where A is the coefficient of reversible absorption and T is absolute temperature.

In the paper [7] the microtheory of coefficient A is presented; it is based on the tunnelling effects of gaseous particles into the intermolecular surfaces of vessel walls. Not going into details of the mentioned calculations we shall emphasize that the explanation of the quasi-oscillating behaviour of temperature is in the fact that only a part of gaseous molecules (with their energy) is irreversibly absorbed into the vessel walls. A part of gaseous molecules is squeezed back by action of intermolecular forces into the walls (desorption) and this part can again get through the wall upon expiration of a certain time interval. These processes are, *de facto*, the processes of reversible absorption of particles and their energy. At irreversible absorption, the change of temperature in time is proportional to the term type PT where P is the coefficient of irreversible absorption.

So, for the convective type of heat transmission, formulated in [6] and [7], a generalized absorption equation is given

$$\frac{dT}{dt} = -PT - \frac{A}{t} \int_0^t dtT \quad (2.2)$$

where the cumulative, integral term represents the correction of the standard equation  $\frac{dT}{dt} = -PT$ , which comes from the process of the reversible reaction.

Some time later, measuring changes of the overpressure of CO<sub>2</sub> in a vessel with water [8] it was found out that the overpressure can drop to zero value and pass to underpressure which can also be explained by the fact that the absorption of CO<sub>2</sub> molecules is both irreversible and reversible. For the overpressure,  $\Delta\sigma$  of the isothermal-isochoric system is formulated according to the analogy with (I. 2. 3) equation:

$$\frac{d}{dt} \Delta\sigma = -P\Delta\sigma - \frac{A}{t} \int_0^t dt\Delta\sigma \quad (2.3)$$

which fitted well in the experiment with the absorption of CO<sub>2</sub> from [8]. Later on, reasoning concerning the gas overpressure was transferred to the number of particles in a room with the absorbent and the equation of (2. 3) type along with transition  $\Delta\sigma \rightarrow \Delta n$  and the adequate changes of P and A parameters, was even used in some court and social problems [10-12]. The situation in the condensed phase of the polymer fuel, described in introduction, is similar to the cases noted here because gaseous products of decomposition from the (A) layer can be absorbed both reversibly and irreversibly from the solid polymer fuel from the (B) layer. In order to be able to compare the generalized theory with the current theories from [5] and [14] in the equation of (2.2) type, it is necessary to go from the time variable t to the space coordinate y. Since the theories from [5] and [14] refer to the quasi-stationary solutions when the front of the decomposed layer gg' moves at a constant speed V<sub>0</sub>, it can be assumed that:

$$t = \frac{y}{V_0} \quad (2.4)$$

and an equation is obtained which regulates the space dependence of temperature.

3. TEMPERATURE IN THE CONDENSED PHASE  
WITH EFFECTS OF REVERSIBLE ABSORPTION INCLUDED

Since for the condensed phase the coordinate  $y$  starts from the value  $S_{(\tau)}$ , where  $\tau$  is the time for establishing the stationary regime, in the equation (2.2) we shall go to the variable  $y = Y - S_{(\tau)}$ , where  $Y$  starts from zero.

The integro-differential equation

$$\frac{dT}{dt} = -PT - \frac{A}{t} \int_0^t dtT = 0 \quad (3.1)$$

we shall by differentiation transfer into the differential equation of the second order:

$$\frac{d^2T}{dt^2} + P \frac{dT}{dt} + \frac{A}{t} - \frac{A}{t^2} \int_0^t dtT = 0 \quad (3.2)$$

Since, on the basis of (3.1)

$$-\frac{A}{t} \int_0^t dtT = \frac{dT}{dt} + PT \quad (3.3)$$

replacing (3.3) in (2.2) we get the equation:

$$\frac{d^2T}{dt^2} + \left( \frac{1}{t} + P \right) \frac{dT}{dt} + \frac{A+P}{t} T = 0 \quad (3.4)$$

After replacement

$$t = \frac{y}{V_0}; \quad \frac{dT}{dt} = V_0 \frac{dT}{dy}; \quad \frac{d^2T}{dt^2} = V_0^2 \frac{d^2T}{dy^2} \quad (3.5)$$

the equation (3.4) becomes:

$$\frac{d^2T}{dy^2} + \left( \frac{1}{y} + p \right) \frac{dT}{dy} + \frac{a+p}{y} T = 0 \quad (3.6)$$

where:

$$p = \frac{P}{V_0}; a = \frac{A}{V_0}; y = y - S_{(\tau)} \quad (3.7)$$

If we assume that  $y$  in (3.6) is *very big* ( $y \rightarrow \infty$ ) we shall get an asymptotic form of equation:

$$\frac{d^2T_\infty}{dy^2} + p \frac{dT_\infty}{dy} = 0 \quad (3.8)$$

which is identical to the equation (37) from [5, page 47]. Here:

$$p = \frac{\rho C_p V_0}{\lambda} \quad (3.9)$$

where  $\rho$  is density in the condensed phase,  $C_p$  is the specific heat and  $\lambda$  is the coefficient of heat conductivity.

The conclusion is that without inclusion of the reversible absorption we get an asymptotic solution for the temperatures, which is good only for big  $y$  that is, deep in the polymer fuel.

The equation (3.8) is solved for the limiting conditions:

$$y = 0; \quad T_{\infty} = T_p; \quad y \rightarrow \infty; \quad T_{\infty} \rightarrow T_0 \quad (3.10)$$

A general solution (3.8) is:

$$T_{\infty} = C_1 + C_2 e^{-py} \quad (3.11)$$

Using the limiting conditions we find:

$$C_1 = T_0; \quad C_2 = T_p - T_0 \quad (3.12)$$

so that the solution is:

$$T_{\infty} = T_0 + (T_p - T_0)e^{-py} \quad (3.13)$$

$$p = \frac{\rho C_p V_0}{\lambda}$$

Now we can pass to the solution of a more general equation (3.6).

It is appropriate to introduce the replacement:

$$T = \theta + T_0; \quad dT = d\theta; \quad d^2T = d^2\theta \quad (3.14)$$

and solve the equation:

$$\frac{d^2\theta}{dy^2} + \left( \frac{1}{y} + p \right) \frac{d\theta}{dy} + \frac{p+a}{y} \theta = 0 \quad (3.15)$$

so the condition:

$$y = 0; \quad \theta = T_p - T_0 \quad (3.16)$$

After the replacement:

$$y = \frac{1}{p} x \quad (3.17)$$

the equation (3.15) becomes:

$$\frac{d^2\theta}{dx^2} + \left( 1 + \frac{1}{x} \right) \frac{d\theta}{dx} + \frac{\alpha+1}{x} \theta = 0 \quad (3.18)$$

where:

$$\alpha = \frac{a}{p} \quad (3.19)$$

After replacement of the function:

$$\theta = e^{-x} \psi \quad (3.20)$$

the equation (3.18) becomes a degenerate hypergeometric equation (Kumer's equation):

$$\frac{d^2\psi}{dx^2} + \left( \frac{1}{x} - 1 \right) \frac{d\psi}{dx} + \frac{\alpha}{x} \psi = 0 \quad (3.21)$$

The solution of this equation can be found by means of the potential order:

$$\Psi = \sum_{\nu=0}^{\infty} C_{\nu} x^{\nu} \quad (3.22)$$

and the solutions are Kumer's functions:

$$\Psi = C_0 K_{\alpha}(x) \quad (3.23)$$

where:

$$K_{\alpha}(x) = r(\alpha + 1) \sum_{\nu=0}^{\infty} \frac{(-1)^{\nu}}{(\nu!)^2 r(\alpha + 1 - \nu)} x^{\nu} \quad (3.24)$$

Replacing (3.23) and (3.17) into (3.20) we get:

$$\theta = C_0 e^{-py} K_{\alpha}(py) \quad (3.25)$$

Since  $K_{\alpha}(0) = 1$ , using the limiting condition (3.16) we get that:

$$C_0 = T_p - T_0 \quad (3.26)$$

so that with regard to (3.24), the solution for the temperature:

$$T = T_0 + (T_p - T_0) e^{-py} K_{\alpha}(py) \quad (3.27)$$

where:

$$K_{\alpha}(py) = \Gamma(\alpha + 1) \sum_{\nu=0}^{\infty} \frac{(-1)^{\nu}}{(\nu!)^2 \Gamma(\alpha + 1 - \nu)} (py)^{\nu}$$

and  $\Gamma(x)$ -gamma function:  $\Gamma(x + 1) = x\Gamma(x)$ .

If  $\alpha$  is whole number, that is,  $\alpha = n$ , Kumer's functions become polynomials of the power  $n$ , that is:

$$K_n(x) = n! \sum_{\nu=0}^n \frac{(-1)^{\nu}}{(\nu!)^2 (n - \nu)!} x^{\nu} = \frac{1}{n!} \frac{d^n}{d_x^n} (x^n e^{-x}) \quad (3.28)$$

These polynomials are called Lager's polynomials

In general, characteristics of Kumer's functions are as follows:  $K_{\alpha}(0) = 1$ ;  $\lim_{x \rightarrow 0} K_{\alpha}(x) = 0$ . In addition, Kumer's functions have the finite number of zeros; as a rule,

if  $m - 1 < \alpha \leq m$  Kumer's function has  $m$  zeros.

On the basis of these characteristics of Kumer's functions it can be concluded that the curve (3.27) crosses the line  $T = T_0$  at least once and it gravitates toward  $T_0$  when  $y \rightarrow \infty$ .

#### 4. CONCLUSION

It should immediately be emphasized that  $a$ , and  $\alpha$  as well, are phenomenological parameters; therefore, it is not possible to know precisely how many times  $T_{(y)}$  crosses the line  $T = T_0$ .

Assuming that  $0 < \alpha < 1$  we shall draw a standard temperature curve in the condensed phase  $T_\infty$  and the curve  $T$  given by formula (3. 27) for  $0 < \alpha < 1$  (Figure 2.).

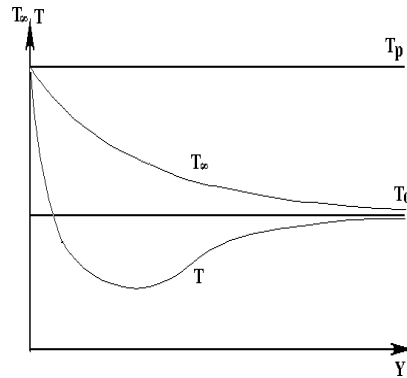


Fig. 2. The temperature curve in the condensed phase  
 $T_0$  - asymptotic value of the temperatures  $T_\infty$  and  $T$  when  $y \rightarrow \infty$ .

It can be seen that due to the reversible absorption the temperature is dropping faster near the border  $gg'$  (fuel) and then is gravitating toward the same value just as  $T_\infty$  when  $y \rightarrow \infty$ . This case should be certainly tested experimentally.

In experimental analyses the absorption frequency  $A$  is very small, of  $10^{-4}$  Hz [7] order, so that the corrected temperature curve shall cross the temperature border.  $T_0$  in the depth of several tens of meters. Since there are no such fuel layers, the section cannot be recorded. This practically means that the corrected temperature introduced in this paper is only lower than the standard predicted temperature. On the other hand, it means that the fuel layer is heated poorer than predicted by the standard approach. In practice, it means longer combustion and longer fire.

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## **ANALIZA POJAVA U KONDENZOVANOJ FAZI POLIMERNOG GORIVA**

**Ratko Vujović**

*Ispitivana je prostorna raspodela temperature u kondenzovanoj fazi polimernog goriva. Za razliku od standardnog prilaza gde se pretpostavlja da polimerno gorivo ireverzibilno apsorbuje masu i energiju iz oblasti produkata razgradnje u ovom radu se pretpostavlja da pored ireverzibilne postoji i reverzibilna apsorpcija što je u svakom slučaju realističnija procena pojava u kondenzovanoj fazi. Na osnovu ove opštije pretpostavke nađena je zavisnost temperature od dubine sloja goriva. Pokazano je da uključivanje procesa reverzibilne apsorpcije daje niže temperature od onih koje predviđa standardna teorija. To u praksi znači da se gorivo sporije zagreva nego što se misli i da je trajanje požara duže.*

**Ključne reči:** *polimerno gorivo, sagorevanje, toplota, požar, kondenzovana faza, reverzibilna i ireverzibilna apsorpcija.*