The model of periodicity corresponding to secondary multiple cool flames

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

Secondary multiple cool flame which is the periodical reaction having its origin on the surface of oxidized heavy hydrocarbon fuels was interpreted by means of simplified brusselator. The model scheme was analyzed and critical conditions of the appearance of chemical periodicity were put forward. It was also shown that on the basis of proposed model self-ignition diagrams of heavy hydrocarbons may be well understood.

Многократное вторичное холодное пламя, являющееся периодической реакцией, происходящей на поверхности окисленных тяжелых углеводородных топлив, было интерпретировано с помощью упрощенного брусселятора. Модельная схема была проанализирована и были выдвинуты критические условия, в которых может появляться химическая периодичность. Было также показано, что на основании предложенной модели могут быть хорошо объяснены диаграммы самовоспламенения тяжелых углеводородов.

When compared to multiple cool flames which are commonly observed in nonisothermal oxidation of organic gases and belong to the group of the so-called thermokinetic oscillations, fuels such as polypropylene, linear paraffins, squalene, stearic acid, *etc.* under conditions of their cool flame combustion perform periodical reaction which has clearly its origin on the surface of the oxidized liquid [1—7]. The careful measurements of the temperature of the surface layer [8] revealed that it decreases synchronically with the corresponding periodic increase of the temperature in the gaseous phase. The scale of the temperature drops on the surface is, however, of the extent 0.2 °C in maximum so the process may be treated as an isothermal one. The remarkable oscillatory changes of the temperature, luminescence and pressure above the surface of the fuel are due to the repeating

release of oxygen-rich products from the liquid and are, therefore, of secondary nature. Accordingly, the phenomenon was given the name, secondary multiple cool flame (SMCF).

Stabilization of this oscillation reaction by means of tubular reactor [5] with retrodiffusion of oxidizing gases (mixture of oxygen and nitrogen) made possible to establish the dependence of the most important parameters of the reaction such as period τ and amplitude y_{max} expressed in relative units on experimental conditions, *i.e.* on the temperature T of the reactor, the flow of oxidizing gas ϕ, the concentration of oxygen $c(O)$ above the fuel surface and on the geometry of the experiment [8], respectively.

The interpretation was presented which postulates the oscillating process as a consequence of the kinetic element of instability of the surface [8, 9]. The latter may appear in the liquid heated from the top provided that the gaseous products are formed according to the formal kinetic scheme of the order higher than 1.

In the present paper we have proposed the simple model of oscillation reaction which corresponds to SMCF and involves the kinetic element of instability of the surface. In paper [8] the concentration of oxygen in the gas mixture introduced to the surface was implicitly included into proportionality constants of the kinetic element of instability. Here we consider it as time-dependent and *via* the proportionality constants of kinetic element of instability it moderates the stability conditions for the surface. The proposed model which is, in fact, the simplified brusselator was subjected to the analysis and the dependences of the period τ and amplitude of oscillations y_{max} on its individual parameters were determined numerically. The critical conditions of the appearance of SMCF which follow from the model were put forward and possible correspondence with self-ignition diagrams [7] determined under static conditions was outlined.

Experimental and computation procedures

SMCF may be investigated by different experimental methods. The most simple is *e.g.* the registration of changes of chemiluminescence intensity or temperature above the fuel surface in experimental arrangement described in previous papers [5—7]. The representative record of SMCF (Fig. 1) shows that the latter is of fully relaxation character, *i.e.* that "microexplosion" like part is followed by a continuous decrease to a given steady value.
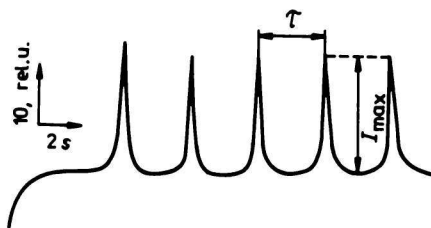

Fig. 1. The initial part of the record of chemiluminescence intensity I above the melt of polypropylene at 300 °C. The flow of gases supplied to the surface from the distance 5 cm was $\phi = 4$ dm³ h⁻¹, volume fraction of oxygen $\varphi = 40$ %.

The computation of theoretical courses was performed by a numerical solution of corresponding set of differential equations on small calculator Texas-Instrument TI-59 according to the procedure described elsewhere [10]. (The maximum length of the time step was 0.01 rel. u.)

Results and discussion

The oscillating model for SMCF

From the balance of the heat in the surface layer of oxidized fuel we have shown [8] that the concentration x of product X of fuel degradation on the surface may be described by differential equation

$$-\frac{dx}{dt} = ax^2 - bx + c \tag{1}$$

where a, b, and c are for given conditions constants depending on both the concentration of oxygen and the temperature. More explicitly it was pointed out that the constant c is proportional to the temperature gradient from the gas to the surface. Provided that the value of discriminant of quadratic term on the right side of expression (1) is negative, the solution of eqn (1) proceeds periodically through singularities with time and eqn (1) may thus be considered as element of system instability.

For the concentration y of particles Y in gaseous phase (according to [11] Y are the most probably low-molecular hydrogen peroxides) released from the surface it may be deduced similarly that

$$\frac{dy}{dt} = \alpha y^2 - \beta y + \gamma \tag{2}$$

where coefficients α, β, and γ are functions of coefficients a, b, and c. In correspondence with our previous results we assume that α depends on concentration of oxygen $c(O)$ so that

$$\alpha = \alpha' \cdot c(O) \ (\alpha' \text{ is coefficient}) \tag{3}$$

The model of oscillation process may be received from eqn (2) considering time changes of some other variable modifying the value of parameters α, β, and γ. At insignificant changes of the surface temperature during the oscillatory reaction we have supposed that this variable is the concentration of oxygen $c(O)$. Taking into account eqn (2) the balance of oxygen in the close proximity of surface may be written simply as

$$\frac{dc(O)}{dt} = s - \alpha' c(O) \ y^2 \tag{4}$$

where s denotes the flow of oxygen to the surface defined as

$$s = \phi \cdot c_O \tag{5}$$

where c_O is the concentration of oxygen in the gases of the flow ϕ introduced to the surface.

The analysis of the model

The solution of eqns (2) and (4) for y and $c(O)$ and the values of parameters $\alpha' = 5$, $\beta = 10$, $\gamma = 1$, and $s = 9$ is shown in Fig. 2. It may be seen that the theoretical course represented by sustained oscillations is fully of the relaxation character. The sharp pulse of Y in the gaseous phase is preceded by the increase of concentration of oxygen in the neighbourhood of the surface. The latter, however, starts to decrease earlier than y reaches its maximum.
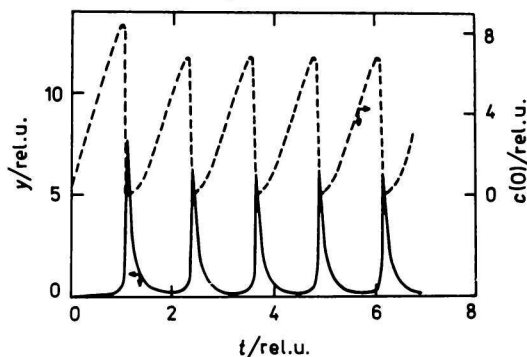

Fig. 2. The course of y and $c(O)$ with time for eqns (2) and (4); $\alpha' = 5, \beta = 10, \gamma = 1, s = 9$.

The values of induction period t_{ind}, period τ, and maximum and minimum concentrations of y and O_2 are for some chosen parameters α', β, γ, and s given in Table 1. The development of the theoretical curves with variation of e.g. parameter β of eqns (2) and (4) is in Fig. 3. It may be seen that for the given set of three constant parameters there exist some limit values of the fourth parameter within which the system shows sustained oscillations.

In oscillatory region the decreasing value of α' leads to the increase of period and amplitude of oscillations; the same tendency may be observed when γ decreases or β increases (Table 1).

The parameters approaching the critical limiting value bring about the damping of oscillatory course whereas those beyond the critical conditions give the monotonous course of either y or $c(O)$ with time.

We may observe two types of nonoscillating courses:

1. y monotonously increases with time until a new higher stationary level

Table 1

Induction period t_{ind} of the appearance of the first oscillation, period τ of oscillations and the values of maximum amplitudes $y_{1, max}$, $y_{i, max}$ ($i = 2, 3 \ldots n$), $c(O)_{1, max}$ and $c(O)_{i, max}$ obtained from the solution of eqns (2) and (4) for some values of parameters α', β, γ, and s (all values are dimensionless)

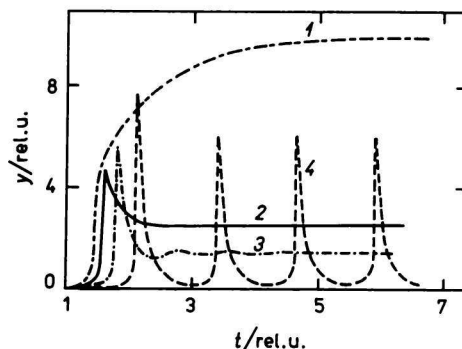| α'	β	γ	s	t_{ind}	τ	$y_{1, max}$	$y_{i, max}$	$c(O)_{1, max}$	$c(O)_{i, max}$
5	10	1	9	1.11	1.28	7.71	6.00	8.37	6.78
5	10	1	7	1.34	1.58	6.79	6.67	7.75	7.56
5	10	1	5	1.76	1.96	5.91	5.91	7.04	7.06
5	10	1	3	2.73	2.89	4.632	4.59	6.30	6.30
1	10	1	9	3.84	4.10	29.84	29.47	31.68	31.68
3	10	1	9	1.61	1.85	11.15	11.40	12.52	12.41
5	10	0.2	9	3.75	4.18	29.73	30.46	32.82	32.82
7	10	1	9	0.89	0.81	5.97	2.35	6.51	2.73
5	15	1	9	1.85	2.03	13.62	12.89	15.03	15.03

Fig. 3. The course of y with time for eqns (2) and (4) for $\alpha' = 5$, $\gamma = 1$, $s = 9$, and $\beta = 1$ (1), 4 (2), 7 (3), and 10 (4).

corresponding to a stabilized cool flame in the gaseous phase is attained (Fig. 3, curve 1);

2. y overshoots some steady level which is then approached by a monotonous decrease (Fig. 3, curve 2).

Sometimes higher value of the first pulse which was also observed experimentally corresponds to the marked difference between initial conditions and conditions corresponding to a steady value of y. The existence of limit cycle and oscillatory behaviour of the system may be expected when the corresponding steady state is unstable [11]. This should be fulfilled provided that the real part of the roots of characteristic equation represented by the sum of partial derivatives of right sides of given differential equations (2) and (4) according to y and $c(O)$ is for steady conditions positive, *i.e.*

$$\frac{\partial}{\partial y}\left(\frac{dy}{dt}\right)_{c(O)} + \frac{\partial}{\partial c(O)}\left(\frac{dc(O)}{dt}\right)_{y} > 0 \qquad (6)$$

At the same time, the product of partial derivatives

$$\frac{\partial}{\partial c(O)}\left(\frac{dy}{dt}\right)_{y} \cdot \frac{\partial}{\partial y}\left(\frac{dc(O)}{dt}\right)_{c(O)}$$

should have the negative sign. In our case, this last condition is valid for all values of y and $c(O)$.

Since steady concentrations of y and O_2 are

$$y = \frac{s+\gamma}{\beta} \quad \text{and} \quad c(O) = \frac{\beta^2 s}{(s+\gamma)^2} \qquad (7)$$

after the determination of corresponding partial derivatives, the inequality (6) may also be written as

$$\frac{2\beta s}{\beta+\gamma} - \beta - \alpha' \frac{(s+\gamma)^2}{\beta^2} > 0 \qquad (8)$$

giving thus the boundaries of the expected oscillation region. In Fig. 4, the expression (8) is graphically illustrated as dependence of s on one of the parameters α', β, and γ.
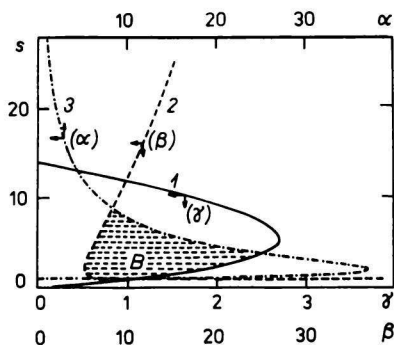

Fig. 4. Dependence of boundary values of s on individual parameters α', β, γ.
1. s on γ ($\alpha' = 5$, $\beta = 10$)
2. s on β ($\alpha' = 5$, $\gamma = 1$)
3. s on α' ($\beta = 10$, $\gamma = 1$)
The dashed zone corresponds to the region of the existence of oscillatory solution of eqns (2) and (4).

Composing the individual lines *1*, *2*, and *3* of Fig. 4 we may, thus, construct the theoretical diagrams of the existence of the oscillating course for the model of SMCF.

From the shape of individual lines we may see that the resulting pictures are in a good qualitative agreement with the so-called self-ignition diagrams of individual heavy fuels which were under static conditions determined experimentally [12].

Differential equations (2) and (4) may, thus, be taken as a good approximation

of the SMCF. It is worth noticing, however, that eqn (2) was obtained from the heat balance of the surface layer and not from the kinetic scheme [13]. It justifies thus the apparent trimolecularity in eqn (2) which is the most frequent objection against the reality of brusselator [11].

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