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Full Length Research Paper

Bifurcation and oscillation in flow reactor of full mixing

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Experimental results about bifurcation transition of reaction regime from permanent intensified mode to pulsing intensified mode under low temperature oxidation of propane in air are resulted. Reaction is spent in a reactor of full mixing on flow with continuous increase of pressure of reaction environment P = 10 – 160 Torr. Is considered mode of this process as inhibition of process by the excited particles arising at heterogeneous recombination of radicals leading a circuit. It is observed the good consent of experimental and theoretical results (frequency of pulsations).

Keywords: reactor of full mixing in flow, excited particles, pulsation of reaction intensity

INTRODUCTION

Introduce the Problem

The effectiveness of chemical reactors is basic criteria of its use.

Van´t Hoff (Van`t-Hoff, 1936) at first time supposes that the processes of chemical reactions (combustion, oxidation), are the dynamic phenomenon and depending of its organizations can have different efficiently.

That criteria is characterizes intensity of process and is a major factor of efficiency and productivity of a reactor.

In the study of the question of heat and heat transfer in chemical reactors, which has the goal of finding a chain of transition from weak to fire burning in the work of Semenov (Semionov, 1958) and Frank-Kamenetsky (Frank-Kamenetsky, 1948) presenting the results of the possible formation of oscillatory dynamical regimes that are the consequence of exchange reaction with the environment

The further advancement of science about an establishment of a certain dynamic regime in the complex systems of chemical transformations has exhibited on light new singularities of these appearances. Namely dependence of a dynamic regime of chemical process on a variation separately taken of parameter (temperature, mass-exchange, modification of a surface of a reactor, heat exchange with an environment and inside a reactionary medium) describing process. These parameters in many cases can be bifurcation parameters - which small modification can cause a variation mode of a dynamic regime, from stationary to oscillation, from steady to explosive.

Investigation of dynamic appearances important, not only from the point of view of a determination of efficient productivity of reactors, and also for good safety of chemical technologies.

For the first time in works of Yang C. H. (Yang, 1974) and Gray P. (Gray and Yang, 1969) with employees the question on a role of internal energy of particles as factor resulting to oscillating modes in gas phase reaction stems is investigated.

Namely, at oxidation CO with an impurity of hydrogen in isothermal conditions, experimentally observed oscillations in system authors explain as influence on the reaction environment of the excited product of reaction $CO2^*$, intensifying reverse reaction $CO2^* + O \rightarrow CO + O2$.

Ware discovered that the modification of surface on time of reaction can be cause of changing of modes of dynamic regime from damping mode of oscillations to continuously.

Further development of these ideas have in our papers (Sargsyan, 1995; Sargsyan, 2010 and Sargsyan, 2009), which shows that the laws of formation and relaxation of excited particles in the reaction system may be the cause of the pulsation modes and transitions between them in the flow reactors of full mixing.

In given work there are presented the results of experimental investigation of dynamic modes occurring in flow reactor of full mixing, under low temperature oxidation of propane depending on organization of process and treatment of surface of the reaction vessel.

The theoretical model has been developed which explains the observed phenomena, namely inhibitors of reaction formatted on the surface of reaction vessel and penetrating the volume, resulting to bifurcation change in reaction medium and causing oscillation in reactor.

The experimental part is held in the flow reactor of full mixing, which is a more convenient device for modeling of chemical processes with chain character

METHOD

For study of the phenomenon of redistribution of excess internal energy of the particles on the establishment of a dynamic mode in reactors with the process having of the chain nature, one of the universal methods is a technique of flow reactors of full mixing.

Intensive mixing not only provides uniform distribution of temperature and concentration of reactants and reaction products in the reactor, as well as in the initial stages of the process provides a rapid heating of the reaction mixture, which is important in the study of reactions in the flow conditions.

Experimental Set Up

Registration of a luminescence of the reaction mixture is made with a photomultiplier, the range of the recorded waves λ = 4000A ° - 12000A °.

Sounding the oxidation process is performed by detecting the radiation of reaction mixture. Namely in order to obtain information about the rapid changes in the reaction medium (oxidation of hydrocarbons), which in other methods of measurement is not felt by the average picture of the process of registration. The basic innovation of a technique is the organization of process of hitting such manner so as to minimize the IR - background of furnace what allows to register infra-red radiation of a reaction mixture.

In the reactor mixing is carried out by rotation in a reactor of two - petal mixers with a velocity of rotation 1400 rotation / minute.

The reactor is heated by radiation of heaters of furnace which shielding from a reactor and are continuously blown by a stream of air circulating inside furnace, that represents an opportunity to reduce an infra-red background of furnace and to register IR-radiation of a reactionary mix, in dark area of course of reaction.

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RESULTS

Experimental measurements were makes under the following circuit:

- at first in well pumped out by the for-vacuum pump the reactor provides a portion propane + air in equal quantities;
- at closed conditions at temperature of walls of reactor T = 550 – 600□ K a mixture keeps about five minutes;
- after passage of time of an induction, the valve of pumping opens and simultaneously in system is provides air on medium of active intermediate products of reaction;
- in some seconds (approximately 5 seconds), in system begin submission of propane.

Thus the reaction medium continuously intensively mix's up, that provides uniform distribution of initial substances and a uniform temperature field in the reaction environment.

As is known chemical gas-phase reaction under the relation to the excited particles, products of elementary acts, it is possible to present as no equilibrium process. As almost all products are formed in the excited states, then relax in the basic states, by collisions and radiation. And different products have different times of a relaxation. It is especially shown, when reaction is spent a lot of one of reagents or at use inert after the relation of the reaction environment of the carrier gas.

At low – temperature oxidation of organic connections, it is considered, that reaction is in dark zone as owing to small quantity of the excited particles their radiation visually is not appreciable. However at heats of combustion the luminescence becomes visually observable. Hence, radiation of a reactionary mix unequivocally is a measure of intensity of reaction.

Thus, if at measurement of light-emission of a reactionary mix the intensification or a pulsation is observed, it is meant monotonous or pulsations with an intensification of reaction.

In figure 2. experimental results of oxidation of propane by air are resulted.

Measurements were carried out under the mentioned above circuit. In a reactor at intensive mixing on medium

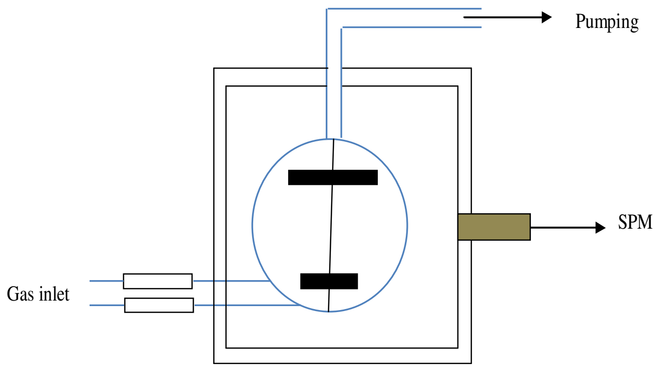

Figure 1 The schema of reaction unit with the furnace of air hitting and a reactor of full mixing on flow. 1 The technique of the reactor with full mixing in the flow, which is used in this work, is described in (Ray, 1977).

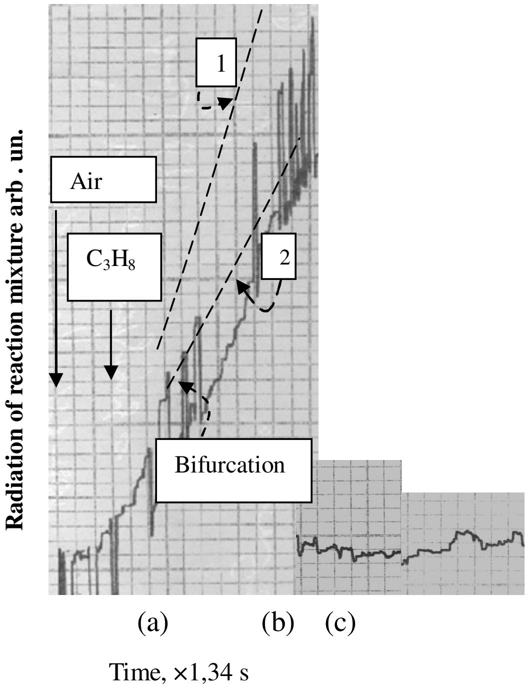

Figure 2 (a) Pulsations of light radiation in a RFMF at oxidation of propane in air. Curve. 1. (Dotted line) - continuation of a course of reaction if has not taken place bifurcation; Curve. 2. (Dotted line) – continuation a course of an intensification after bifurcation in system. (b) – Background of IR radiation from pumping reactor (0.1 - 5 Torr); (c) – Background of IR radiation when in reactor is providing Air from 0.1 Torr to 80 Torr;

of slowed connected intermediate products, staying in reactor after passage of the period of an induction oxidation of propane with air (T = 600K, P = 3 - 5 Torr), air provided air. In figure it is visible, that it was observed increase in intensity of radiation. After a while approximately (approximately 5 seconds), has joined inlet of propane. Growth of intensity of radiation from a reactionary zone became sharper (an approximation line 1). However in approximately 2 seconds in system has taken place the bifurcation then growth of intensity of radiation has appreciably decreased (an approximation line 2), but simultaneously in system pulsations of intensity of radiation have appeared.

3.2 The theoretical modeling and discussion

In the given concrete case on our opinion the bifurcation parameter is the probability of breakage

(β =1 / ν, where ν - number having ringed of chain before breakage).

It is known [2] that at chain development rate of reaction depend on describing parameters as:

$$W = \frac{n}{t} = \frac{n_0}{\beta-\delta}\left(1 - e^{-\frac{\beta-\delta}{\tau}t}\right) \qquad (1)$$

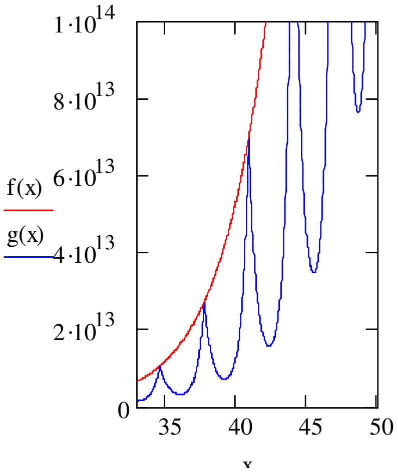

Figure 3 Dependence of rate of the chain branching reaction on time at different values of probability of a branching and probabilities of continuation of chain.
f(x) – the profile of concentration of active particle when β is constant - formula (1): g(x) – when β have oscillating character - formula (2).

Where β - probability of breakage; δ -probability of a branching of chain; τ- average time of development of one chain.

Then occurrence in system of inhibitor formed on a surface owing to heterogeneous recombination of radical's feedback introducing in system and bringing to oscillations, it is possible to present in the qualitative image as oscillations so-called parameter describing breakage of chair β.

In the simply case we will present these oscillations as sine wave function β □ sin (t).

Then the equation (1) will look like:

$$W = \frac{n}{\tau} = \frac{n_0}{\beta(1+\sin(t))-\delta}\left(1 - e^{-\frac{\beta(1+\sin(t))-\delta}{\tau}t}\right) \qquad (2)$$

The calculation of these two functions of program MATHCAD received at use is resulted on figure 3.

If to take into account, which the inhibition of process by the excited particle can lead to oscillating nearly surface layer, initiating occurrences of sharp pulsations of intensity in volume (Sargsyan, 1995) it is easy to explain occurrence of dependences (1) and (2). As shown in work (Yang, 1974) oscillating nearly surface layer causes flashes in the center of a reactor, as is observed as sharp peaks in space between curves (1) and (2) Figure 2.

The pulsation phenomena's observable in our experiments at low temperature oxidation of organic connections by the example of oxidation of propane by air we are inclined to explain within the limits of performances developed by us recently, namely amplification of reaction owing to increase of pressure in system and simultaneously inhibition of process by the excited intermediate product of reaction formed at heterogeneous recombination of radicals.

Such performance correctly characterizes process and can to describe at various values of describing parameters pulsation oxidation in flow reactors.

Known particles in metastable levels which are formed at reactions of oxidation of organic connections, it basically O3, O2 (1Δg), CH2O*, and also highly-vibrationally-excited molecules of H2 (v ≥ 5), O2 (v ≥ 5) which being formed at heterogeneous recombination and getting in volume can to break in the observable image established a mode of chain process. As have shown results of works (Yang, 1974; Sargsyan, 1995 and Ray, 1977) and our theoretical researches, a heterogeneous origin of these particles is the reason of occurrence of bifurcation in systems with the chain mechanism (owing to modification of a surface) if the composition of a mixture not strongly changes in a course of reaction.

At strong change of composition of a mixture in a course of reaction owing to what rate of relaxation of the excited particles can is appreciable will change, it also can become of bifurcation parameter (Yang, 1974; Gray and Yang, 1969)

The basic philosophy of a question - that redistribution of energy of reaction results to oscillations is not broken, that speaks well the new approach advanced by us. Namely, pulsation oxidation can be caused by redistribution of energy of reaction (energy of the excited particles) in the reactionary environment accompanying with change of structure of active particles owing to what the way of achievement of system to balance varies.

Slow subsystem in feedback is surplus of internal energy of metastable particles or a step relaxation of highly-vibrationally-excited molecules as, it is known, that for education of nonlinear connection resulting to oscillations in reaction environment in reasonable values of frequency of pulsations (about a second and more), the slow subsystem (the external factor) is necessary.

For concrete mathematical registration of the above-stated performances, namely the proof, that surplus of internal energy can become the reason of occurrence of pulsing combustion, we offer model including all basic stages in processes of low temperature oxidations of organic connections, both in volume, and on a surface of a reactionary vessel, and also a stage of a birth and a relaxation of the excited particles.

a)The basic elementary states under low temperature oxidation of organic compounds resulting to appearance of pulsation phenomemenon in reaction system:

Z + A → X + C	k1
X + B → Z + L	k2
L + S → X'S + Y	k3
Y + B → Z + D	k4
X + S → XS	k5
XS + X'S → In* + 2S	k6
In* + X → Prod.	k7
In* → Stab.	k8,

Where A, B - initial substances; X, Y, Z - active particles; S - the surface active center; XS, X'S - adsorbed on a walls surface active particles; L - a unstable intermediate product; C, D - products; In* - the excited particle, an intermediate product, reactions a transforming radical leading a circuit in radical poorly reacting with initial substance which by volumetric square-law recombination turns to the substance withdrawn from system.

For example (a) - HS + HS → H2(v >> 1) + 2S;

(б)- H2(v >> 1) + RO2(RCO3) → (H2•RO2)* →
RH + HO2
or (H2•RCO3)* → RH + HO2 + CO;

(c) - 2HO2 → H2O2 + O2,

where (H2•RO2)* и (H2•RCO3)* - transitive complexes. Energy of excitation of hydrogen in this case Ev> 4 ≥ 2.8 эВ, allows process (6) to carried out.

Thus internal energy of excitation of one of participants of the elementary act can lead to formation of initial substances and by that to inhibiting of the process.

Other example: + CH3OS → CH2O* + H2OS;

CH2O* + RCO3 → CH2O + RO + CO2, that also results in inhibition of process of oxidation of acetaldehyde (Sargsyan, 2009). In this case molecules of the excited formaldehyde in a metastable status are inhibited the processes process.

In model is accepted, that particle L - an unstable intermediate product of reaction (2) breaks up to surfaces of a wall with an output in volume of a radical (3). Active particles adsorbed on a walls surface, owing to heterogeneous recombination (6), generate the excited particle which in volume on a complex circuit of reactions transforms an active particle X into a product of reaction (7).

The purpose of studying of the suggested model was most the general and universal research of an opportunity offered by us before idea about a role of the excited and other active particles generated in nearly surface layer of a reactor, in an establishment of dynamic reactionary systems (Yang, 1974). The offered model, takes into account the basic directions of influence of surface processes on volumetric. In particular, an output from a surface in volume of the active particle formed at surface dissociation of an intermediate product of reaction (3), and also the excited particle formed owing to heterogeneous recombination of radicals (6).

As in flowing systems when initial substances continuously move in system, and products are withdrawn from it, the reaction system quickly reaches an equilibrium status for the description of system, differentials of concentration of active particles and intermediate products

$XS + X' = QS$

as a rule, are equated to zero, and concentration of initial substances are accepted by constants, except for concentration of those particles which participate in nonlinear reactions (Semionov, 1958; Frank-Kamenetsky, 1948). Besides in order to prevent unnecessary mathematical complexities is accepted, that quantities of active particles XS adsorbed on a surface and X'S are equal among themselves, and one total equation describing change of total of adsorbed active particles (S0) in due course where QS - the total of adsorbed active particles, heterogeneous recombination which results in education excited inhibitor is written as $[XS] + [XS'] = [QS]$.

In view of this approach, and also accepting, that[S]=[S^0]-[QS] where - [S0] the maximal number of the active centers on unit of a surface of a wall, is possible to receive three differential equations, describing process:

$$\frac{dy_0(t)}{dt} = k_2[B]y_0(t) - k_5[X_e]\big(S_r - y_2(t)\big)y_0(t) - k_7[X_e]y_1(t)y_0(t)$$

$$\frac{dy_1(t)}{dt} = k_6[X_e]y_2^2(t) - k_7[X_e]y_1(t)y_0(t) - k_2y_8(t)$$

$$\frac{dy_2(t)}{dt} = k_2[B]y_0(t) + k_5[X_e]\big(S_r - y_2(t)\big)y_0(t) - \frac{k_6[X_e]y_2^2(t)}{2}$$

For simplification of the decision of system of the equations we shall enter more convenient variables:

$$y_0(t) \equiv \frac{[X]}{[X_e]}, y_1(t) \equiv \frac{[In*]}{[X_e]}, y_2(t) \equiv \frac{[QS]}{[X_e]}, S_r \equiv \frac{S^0}{[X_e]}$$

where [Xe] and S_r-the equilibrium concentration of an active particle X, and quantity of free active centre in unit square of surface;

It was represented interesting to find the decision of system in the conditions close in really observable at low temperature oxidation of organic connections. Values of describing parameters are resulted in the table.

Solution the above-stated system with use of the program "MATCAD" a method of the decision of system of the differential equations with the help of functions "Rkadapt" at entry conditions (Table 1.), are resulted on fig. 4 - 5.

Table 1 Values of describing reaction systems at lower temperature oxidation of the organic compounds, the models used at calculation.

	S_r	$k_2[B]$	$k_5[X_e]$	$k_6[Xe]$	$k_7[X_e]$	K_8	X_e,
I	100	10^3	0.01	120	15	1	$10^{11÷12}$
II	1200	10^3	0.125	1	250	10^3	$10^{11÷12}$

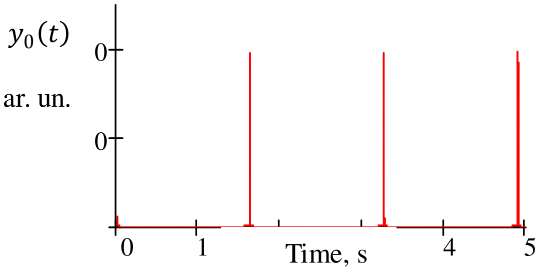

Figure 4 Dependences of concentration of active particles $y_0(t)$ from time in a case (I) (tab).

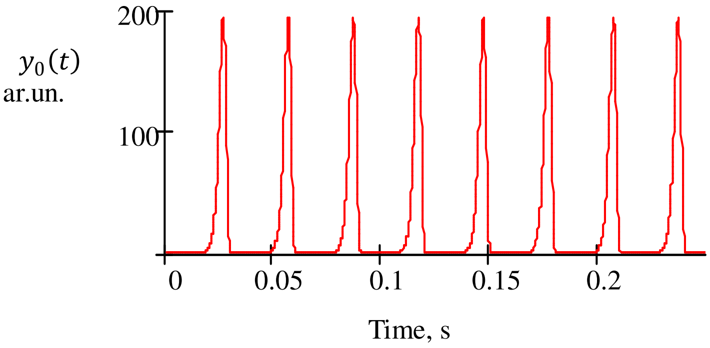

Figure 5 Dependences of concentration of active particles $y_0(t)$ from time in a case (II) (tab).

CONCLUSIONS

In the submitted work by experimental way is observed the intensification of reaction due submission of gas on medium of weak reaction, and appearance of bifurcation owing to inhibition of reaction by products heterogeneous recombination, bringing system on less intensive growth with oscillation intensity of course.

It is possible to conclude, that process is intensified owing to increase of concentration of gas reagent, and oscillations are arising because of inhibition of process by the excited products of surface reactions.

Theoretical modeling has shown that such performance is reasonable, as at reasonable values of describing parameters, the model really supposes occurrence of oscillations in the system.

Sources of radiation of the reactionary environment are the excited particles formed as owing to heterogeneous recombination active particles on a surface of a reaction vessel, and born in volumetric processes. As is known for maintenance of balance on forward and internal degrees of freedom of reagents of reaction or a lot of one of reagents often are spent or at the presence of gas of a thinner. As a result of it are formed a plenty of particles in electronically excited or basically electronic but highly-vibrationally-excited states, in quantity considerably exceeding equilibrium value at the given temperature. In result in system there is a radiation which can be registered (Sargsyan, 2009).

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