OZONE DECAY IN CHEMICAL REACTOR
FOR OZONE-DYNAMICAL DISINTEGRATION OF USED TYRES

V.I. Golota, O.V. Manuilenko*, G.V. Taran, Yu.V. Dotsenko, A.S. Pismenetskii, A.A. Zamuriev, V.A. Benitskaja

National Science Centre "Kharkov Institute of Physics and Technology", Kharkov, Ukraine
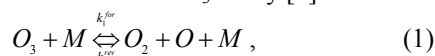*E-mail: ovm@kipt.kharkov.ua

The ozone decay kinetics in the chemical reactor intended for used tyres disintegration is investigated experimentally and theoretically. Ozone was synthesized in barrierless ozonizers based on the streamer discharge. The chemical reactor for tyres disintegration in the ozone-air environment represents the cylindrical chamber, which feeds from the ozonizer by ozone-air mixture with the specified rate of volume flow, and with known ozone concentration. The output of the used mixture, which rate of volume flow is also known, is carried out through the ozone destructor. As a result of ozone decay in the volume and on the reactor walls, and output of the used mixture from the reactor, the ozone concentration in the reactor depends from time. In the paper the analytical expressions for dependence of ozone concentration in the reactor from time and from the parameters of a problem such as the volumetric feed rate, ozone concentration on the input in the reactor, volume flow rate of the used mixture, the volume of the reactor and the area of its internal surface is obtained. It is shown that experimental results coincide with good accuracy with analytical ones.
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1. INTRODUCTION

The ozone decay in the chemical reactor developed for used tyres disintegration is investigated in the paper. Ozone was synthesized in barrierless ozonizers, which are based on the atmospheric pressure streamer discharge [1, 2]. Working gas is oxygen, or drained air.

2. THEORY

The conventional mechanism of O_3 decay [3] is:

$$O_3 + M \underset{k_1^{rev}}{\overset{k_1^{for}}{\Leftrightarrow}} O_2 + O + M , \qquad (1)$$

$$O_3 + O \overset{k_2^{for}}{\Rightarrow} 2O_2 , \qquad (2)$$

where M = {O_3, O_2, N_2, H_2O}, k_1^{for}, k_1^{rev} denote the forward and reverse rate constants for (1), k_2^{for} is the forward rate constant for (2). The constants k_1^{for} and k_1^{rev} for different gases-thinners are different. It is convenient to introduce efficiency ξ of gas-thinners by means of a factor which enters into the rate constants [3]. Efficiency ξ shows, in how many times the appropriate constant changes, if one gas-thinner to replace with another with other conditions being equal. In [3,4] the following values for effectiveness are presented: ξ = 1,0(O_3), 0,44(O_2), 0,41(N_2), 3,9(H_2O).

It is easy to obtain from (1)-(2) the equation for O_3 concentration $[O_3]$:

$$\frac{d}{dt}[O_3] = -\frac{2k_1^{for}k_2^{for}M}{k_1^{rev}M[O_2] + k_2^{for}[O_3]}[O_3]^2 , \qquad (3)$$

As follows from (3), the O_3 decay is described by kinetics of variable order from the first to the second kind, depending on the experiment parameters. If $k_2^{for}[O_3] \gg k_1^{rev}M[O_2]$, then the reaction of O_3 decay becomes the reaction of first order with the reaction rate $k_V^{(1)} = 2k_1^{for}M$. Otherwise, if $k_2^{for}[O_3] \ll k_1^{rev}M[O_2]$, the reaction of O_3 decay is the reaction of second order with the reaction rate $k_V^{(2)} = 2k_1^{for}k_2^{for}/k_1^{rev}[O_2]$.

The chemical reactor for tyres decomposition by means of ozone-air environment represents the cylindrical chamber from stainless steel, volume V=0.3 m^3, which is feeded by the ozone-air mix with O_3 concentration C^{in} from the ozonizer [2] with the rate of volume flow U^{in}. The output of the used mix is carried out with the rate of volume flow U^{out} into surrounding space. As a result of O_3 decay in the volume, on the walls of the chamber and output of the ozone-air mix from the reactor, the time-dependent O_3 concentration C is got in the reactor.

If the O_3 decay in the volume is described by the first order kinetics with the reaction rate $k_V^{(1)}$, then the equation for O_3 concentration change is following [5]:

$$\frac{dC}{dt} = a - bC - k_V^{(1)}C , \qquad (4)$$

where $a = U^{in}C^{in}/V$, $b = (U^{out} + \vartheta S)/V$. The second item in the expression for b considers the O_3 disintegration on the reactor wall [5], S is the area of the reactor internal surface, ϑ is the coefficient considering probability of O_3 decay on a wall. Assuming, that the initial O_3 concentration is C_*, we will obtain:

$$C(t) = C^{ss}\left\{1 - \frac{a - \lambda^{(1)}C_*}{a}\exp[-\lambda^{(1)}t]\right\} , \qquad (5)$$

where $\lambda^{(1)} = b + k_V^{(1)}$, $C^{ss} = a/\lambda^{(1)}$ is the steady state O_3 concentration in the reactor. If C^{ss} is known from the experiment, neglecting O_3 decay on the chamber walls, it is possible to estimate $k_V^{(1)}$: $k_V^{(1)} = (U^{in}C^{in}/C^{ss} - U^{out})/V$.

If the O_3 decay in the volume is described by the second order kinetics with the reaction rate $k_V^{(2)}$, then the equation for O_3 concentration change is following:

$$\frac{dC}{dt} = a - bC - k_V^{(2)}C^2 , \qquad (6)$$

which solution is:

$$C(t) = C^{ss}\left\{1 - \frac{2\lambda^{(2)}\Lambda\exp[-\lambda^{(2)}t]}{(\lambda^{(2)} - b)(1 + \Lambda\exp[-\lambda^{(2)}t])}\right\} , \qquad (7)$$

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where $C^{ss} = (\lambda^{(2)} - b)/2k_V^{(2)}$ is the stationary O_3 concentration in the reactor, $\lambda^{(2)} = b\sqrt{1 + 4ak_V^{(2)}/b^2}$, $\Lambda = (\lambda^{(2)} - 2k_V^{(2)}C_* - b)/(\lambda^{(2)} + 2k_V^{(2)}C_* + b)$. If, in this case, C^{ss} is known from the experiment, neglecting O_3 decay on the chamber walls, it is possible to estimate $k_V^{(2)}$:
$k_V^{(2)} = (U^{in}C^{in}/C^{SS} - U^{out})/VC^{SS}$.

Fig. 1 shows the time dependence of O_3 concentration in the reactor at $C_* = 0$ g/m³, $U^{in} = U^{out} \equiv U = 0.6$ m³/h, $C^{in} = 20$ g/m³. Curve C1 is obtained in the assumption that the O_3 decay kinetics is the kinetics of the first order – expression (5), curve C2 is obtained in the assumption that the decay kinetics is the kinetics of the second order – expression (7), Δ = C1 - C2. $k_V^{(1)}$, $k_V^{(2)}$ are estimated from the experiment (Fig. 3,a). Fig. 1 shows that the difference is insignificant.
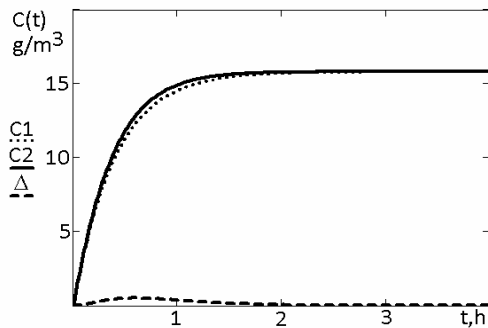

Fig. 1. O_3 concentration (g/m³) in the reactor vs time (hours). C1 – expression (5), C2 – expression (7), Δ = C1 - C2. U = 0.60 m³/h

3. EXPERIMENT

For our experiments $U^{in} \approx U^{out} \equiv U$. In this case, as follows from expressions for C^{ss}, both in the case of the O_3 decay kinetics of the first order, and in the case of the O_3 decay kinetics of the second order, at the same volume flow rate U, with the growth of the O_3 concentration at the input C^{in}, the value of stationary concentration C^{ss} in the reactor grows, remaining always less than C^{in}. Besides, the C^{ss} grow with the growth of the U at C^{in} = const, remaining always less than C^{in}.

Figs. 2;a, 3,a show the measured time dependence of O_3 concentration $C(t)$ in the reactor, and Figs. 2,b; 3,b show the theoretical estimations (7), corresponding to them, at O_3 concentrations at the input C^{in} = {5, 10, 15, 20} g/m³ and the volume flow rate U = 0.3 m³/h (see Fig. 2), and U = 0.6 m³/h (see Fig. 3). It is clear that experimental curves with good accuracy coincide with the theoretical ones.

The residence times ($\tau = V/U$) are τ = 1 hour (at U = 0.30 m³/h, see Fig. 2), and τ =0.5 hour (at U = 0.6 m³/h, see Fig. 3). As Figs. 2, 3 show at $t \sim (2-3)\tau$ the O_3 concentration in the reactor comes close to its stationary value $C(t) \approx C^{ss}$. Besides, at U = const, with the growth of C^{in}, the value C^{ss} grows, remaining always less than

C^{in}. As Figs. 2,3 show, the stationary concentrations C^{ss} grow with the growth of the volume flow rate U at C^{in} = const, what coincides with theory conclusions.
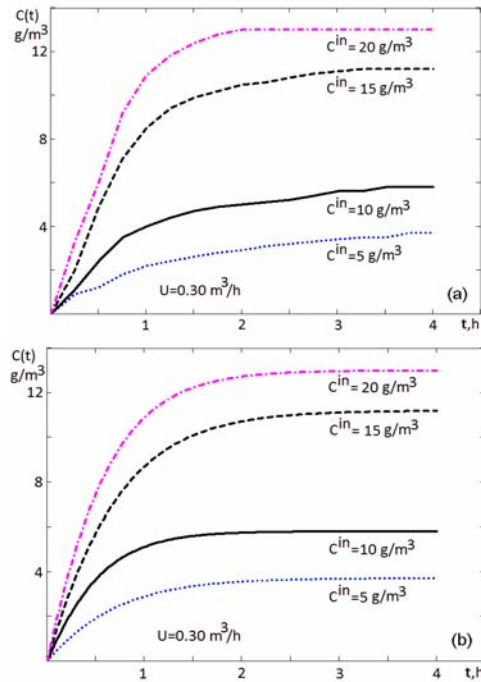

Fig. 2. O_3 concentration (g/m³) in the reactor vs time (hours) at O_3 concentration at the input 5 g/m³, 10 g/m³, 15 g/m³, 20 g/m³: experiment (a), theory (b), U=0.3 m³/h

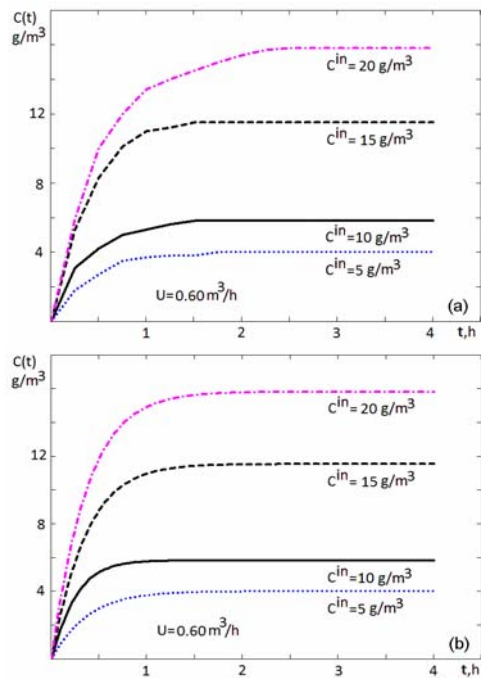*Fig. 3. O_3 concentration (g/m³) in the reactor vs time (hours) at O_3 concentration at the input 5 g/m³, 10 g/m³, 15 g/m³, 20 g/m³: experiment (a), theory (b), U=0.6 m³/h*

4. CONCLUSIONS

The results of theoretical and experimental investigation of ozone decay in the reactor intended for used tyres disintegration in the ozone-air environment are presented. The analytical expression for dependence of

ozone concentration in the reactor from time and from parameters of a problem, such as the volume flow rate, the ozone concentration at the input of the reactor, volume flow rate of the used mix output, reactor volume, the area of its internal surface are obtained. It is shown that at the same input volume flow rate, with the growth of ozone concentration at the input, the value of stationary ozone concentration grows in the reactor, remaining always less than the concentration at the input. Also it is shown that at the same ozone concentration at the input, with the growth of the input volume flow rate, value of stationary concentration of ozone in the reactor also grows, remaining always less than the concentration of ozone at the input. The ozone decay in the reactor at various input volume flow rates (0.3, 0.6 m^3/h) and various ozone concentrations at the input (5, 10, 15, 20 g/m^3) are studied experimentally. It is shown that experimental results with good accuracy coincide with the theoretical ones.

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РАСПАД ОЗОНА В ХИМИЧЕСКОМ РЕАКТОРЕ ДЛЯ ОЗОНО-ДИНАМИЧЕСКОГО РАЗЛОЖЕНИЯ ИЗНОШЕННЫХ ШИН

В.И. Голота, О.В. Мануйленко, Г.В. Таран, Ю.В. Доценко, А.С. Письменецкий, А.А. Замуриев, В.А. Беницкая

Экспериментально и теоретически исследована кинетика распада озона в химическом реакторе, предназначенном для дезинтеграции изношенных шин. Озон синтезировался в безбарьерных озонаторах на стримерном разряде. Химический реактор для разложения шин в озоно-воздушной среде представляет собой цилиндрическую камеру, в которую от озонатора с определенной объемной скоростью подается озоно-воздушная смесь с известной концентрацией озона. Вывод отработанной смеси, объемная скорость которой известна, осуществляется через деструктор озона. В результате распада озона в объеме, на стенках реактора и вывода озоно-воздушной смеси, концентрация озона в реакторе зависит от времени. Получены аналитические выражения для зависимости концентрации озона в реакторе от времени и от параметров задачи, таких как: объемная скорость подачи озоно-воздушной смеси на вход реактора, концентрация озона на входе, объемная скорость вывода отработанной смеси, объем реактора и площадь его внутренней поверхности. Показано, что экспериментальные результаты с хорошей точностью совпадают с аналитическими.

РОЗПАД ОЗОНУ У ХІМІЧНОМУ РЕАКТОРІ ДЛЯ ОЗОНО-ДИНАМІЧНОГО РОЗКЛАДАННЯ ЗНОШЕНИХ ШИН

В.І. Голота, О.В. Мануйленко, Г.В. Таран, Ю.В. Доценко, А.С. Письменецький, А.А. Замурієв, В.А. Беницька

Експериментально і теоретично досліджено кінетику розпаду озону в хімічному реакторі, який було розроблено для розкладання зношених шин. Озон синтезувався у безбар'єрних озонаторах на стримерному розряді. Хімічний реактор для розкладання шин у озоно-повітряному середовищі є циліндричною камерою, в яку від озонатора з певною об'ємною швидкістю подається озоно-повітряна суміш з відомою концентрацією озону. Виведення відпрацьованої суміші, об'ємна швидкість якої відома, здійснюється через деструктор озону. В результаті розпаду озону в об'ємі, на стінках реактора і виведення озоно-повітряної суміші, концентрація озону в реакторі залежить від часу. Одержано аналітичні вирази для залежності концентрації озону у реакторі від часу і від параметрів задачі, таких як: об'ємна швидкість подачі озоно-повітряної суміші на вхід реактора, концентрація озону на вході, об'ємна швидкість виведення відпрацьованої суміші, об'єм реактора і площа його внутрішньої поверхні. Показано, що експериментальні результати з хорошою точністю співпадають з аналітичними.