The Theoretical Study of Ultrasonic Cavitation Intensification of Binary Chemical Reactions "Liquid-Liquid"

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ABSTRACT: *The paper is devoted to proposed phenomenological model of cavitation intensification of chemical reactions in high-intensity ultrasonic field. The model is based statistical approach which is evaluation of volume-averaged chemical reaction rate constant. Averaging is performed over volume that is much more than cavitation bubble volume in which the microscopic value of constant depends on shock wave pressure at cavitation bubbles collapse. The chemical reaction constant dependency on pressure is calculated by using Maxwell distribution of molecules velocities and probability of event that the molecule energy is more than activation energy for given reaction. The numerical analysis of model shown that ultrasonic influence increase of chemical reaction efficiency up to 1.5 times.*

Keywords: – Cavitation, chemical reaction, law of mass action, activation energy, Maxwell distribution

I. INTRODUCTION

Intensification of the rate of chemical reactions in a liquid medium is one of the main tasks of industrial chemistry. Traditionally, this is achieved by increasing the concentration of reagents, increasing temperature or pressure, using expensive catalysts.Ultrasound (US) cavitation effect is one of the most promising ways of accelerating the course of chemical reactions [1-3]. The use of ultrasound not only increases the rate of chemical reaction, but, unlike traditional methods, increases the percentage of reacted substances at final of reaction. When subjected to ultrasonic cavitation treatment of a liquid medium, it is possible to obtain chemical reactions that are impossible in other cases. Starting from the middle of the last century until today, many experimental confirmations of the cavitation acceleration of the chemical reaction of substances have been obtained. However, all the experimental results to date have been obtained only for individual pairs of liquid-liquid substances [1-3] and, as a rule, contain the dependence of the rate of the chemical reaction on the intensity of the oscillations. At the same time, there are no dependencies on the frequency of oscillations, since in view of the resonant properties of ultrasonic working tools, a new ultrasonic device is needed to operate at a different frequency. In addition, there is no unambiguous physical mechanism that explains the acceleration of the chemical reaction. Existing theoretical studies on cavitation acceleration of chemical reactions is devoted only to a qualitative description of these processes and does not allow establishing the numerical dependences of the rate of chemical reaction and the content of reacted substances on the parameters of ultrasonic actionTherefore, it is necessary to create a phenomenological model of the kinetics of the chemical reaction under the action of cavitation.

II. DEVELOPED MODEL OF BINARY CHEMICAL REACTION

The binary chemical reaction represents interaction of molecules of two substances A and B. Result of the considered chemical reactions is two new substances C and D with unit stoichiometric coefficients:

$A + B \rightarrow C + D$.
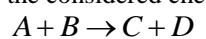
According to law of mass action the kinetic of the reaction on micro level (over local zones less than cavitation bubble) is described by following equation

$$\frac{dA}{dt} = \frac{dB}{dt} = -kAB; \qquad\qquad (1)$$

where A, B are molar concentrations of A and B substances, mol/m^3; k is constant of chemical reaction rate, mol^{-1}·s^{-1}; t is time, s.

Solving of the equation gives the relative content of reaction product (substance C or D):

$$\eta = \frac{kA_0 t}{kA_0 t + 2}.$$ (2)

where A_0 is molar concentration of source substance A at $t = 0$, mol/m^3.

At the cavitation influence the constant of chemical reaction rate is spatially non-uniform due to non-uniformity of pressure in liquid formed by collapsing cavitation bubbles.

Process of pressure changing is random because cavitation bubbles appear in random places. The process has the same characteristics in different places, if ultrasonic field the uniform, because the cavitation bubbles can appear in different places with same probability. That is the random process of pressure changing in mixture of reacting liquid is stationary.

This follows that the changing of concentration (during fixed time Δt which is much more that oscillations period T and much less than typical time for significant changing of $\langle A \rangle_V$, i.e. $T \ll \Delta t \ll \dfrac{\int_V A(\mathbf{r})dV}{\int_V k(\mathbf{r})A^2(\mathbf{r})dV}$) is spatially uniform and satisfies following equation:

$$\frac{\Delta\langle A\rangle}{\Delta t} = -\langle kA^2\rangle;$$ (3)

where the sign $\langle\rangle_V$ is averaging over volume $\langle kA^2\rangle = \dfrac{1}{TV}\int_0^T\int_V k(\mathbf{r},t)A^2(\mathbf{r},t)dVdt$.

Due to stationarity of random pressure changing process the following condition is true:

$$\frac{\sigma(A^2)}{A^2} \ll \frac{k}{\sigma(k)};$$

where $\sigma(B)$ is root from dispersion of magnitude B; $\sigma(B)$ is defined as $\sigma(B) = \sqrt{\langle(B - \langle B\rangle)^2\rangle}$.

The condition allows to derive following equations (4, 5) from equation (3)

$$\frac{\Delta\langle A\rangle}{\Delta t} = -\langle kA^2\rangle = -\langle(\langle k\rangle + (k - \langle k\rangle))(\langle A^2\rangle + (A^2 - \langle A^2\rangle))\rangle =$$
$$= -(\langle k\rangle\langle A^2\rangle + \langle(k - \langle k\rangle)(A^2 - \langle A^2\rangle)\rangle);$$ (4)

According to the Hölder's inequality

$$\frac{\left|\langle(k - \langle k\rangle)(A^2 - \langle A^2\rangle)\rangle\right|}{\langle k\rangle_V\langle A^2\rangle_V} = \frac{\left|\dfrac{1}{TV}\int_0^T\int_V (k - \langle k\rangle)(A^2 - \langle A^2\rangle)dVdt\right|}{\langle k\rangle\langle A^2\rangle} \leq$$

$$\leq \frac{\dfrac{1}{TV}\sqrt{\int_0^T\int_V (k - \langle k\rangle)^2 dVdt}\sqrt{\int_0^T\int_V (A^2 - \langle A^2\rangle)^2 dVdt}}{\langle k\rangle\langle A^2\rangle} = \frac{\sigma(k)\sigma(A^2)}{\langle k\rangle\langle A^2\rangle};$$

$$\frac{\left|\langle(k - \langle k\rangle)(A^2 - \langle A^2\rangle)\rangle\right|}{\langle k\rangle\langle A^2\rangle} \leq \frac{\sigma(k)\sigma(A^2)}{\langle k\rangle\langle A^2\rangle} \ll 1.$$

$$\frac{\partial \langle A \rangle}{\partial t} = -\langle k \rangle \langle A^2 \rangle$$

(5)

Thus, the molar percent content of reaction product (substance *C* or *D*) at cavitation influence is determined as:

$$\eta = \frac{\langle k \rangle A_0 t}{\langle k \rangle A_0 t + 2} \times 100\%$$

. (6)

The most difficulty for final calculation of η is the calculation $\langle k \rangle$. For the calculation $\langle k \rangle$ it takes into account that k depends on pressure in liquid.

The chemical reaction constant dependency on pressure is calculated by using Maxwell distribution of molecules velocities and energies and probability of event that the molecule energy is more than activation energy for given reaction.

$$f_{umicro}(u_i) = \sqrt{\frac{\alpha(p,T)}{\pi}} e^{-\alpha(p,T)u_i^2} \quad ; \quad f_{smicro}(\varepsilon, p, T) = \left(\frac{2\alpha(p,T)}{m}\right)^{\frac{3}{2}} \frac{2}{\sqrt{\pi}} \sqrt{\varepsilon} e^{-\frac{2\alpha(p,T)}{m}\varepsilon} ;$$

where u_i is the ith component of the molecule velocity, m/s; m is the mass of molecule, kg; p is the pressure in liquids mixture, Pa; T is temperature of mixture, K; ε is molecules kinetic energy, J.

According to the distributions the obtained expression of $k(p)$ is

$$k(p) = N_A \pi d^2 \left(\frac{4}{\pi \alpha(p,T)}\right)^{\frac{1}{2}} e^{-\frac{2\alpha(p,T)E_{AC}}{m}} ;$$

where N_A is Avogadro's number, mol[-1]; E_{AC} is the molecule activation energy

The average value for the coefficient is

$$\langle k \rangle = \frac{4\pi n_{bub}}{\tau} \int_0^\tau \int_{R(t)}^{R_{crit}(t)} r^2 \left(k(p(r,t)) - k(p_0)\right) dr dt + k(p_0);$$

(7)

where $R_{crit}(t)$ is the distance from cavitation bubble at which the minimum pressure necessary for chemical reaction acceleration is achieved, m; τ is period of ultrasonic oscillations, s; n_{bub} is concentration of cavitation bubbles determined by models from [4-7], m[-3]; $R(t)$ is radius of cavitation bubble (determined by models from [4-7]), m; $p(r,t)$ is shock wave pressure (determined by models from [4-7]) at distance r from bubble and time t, Pa.

The substitution of the expression (5) into the general expression for percent content of reaction product allows to numerically calculate dependences of content of product of chemical reaction on intensity and frequency of ultrasonic oscillations.

The obtained dependences are presented in the next section.

III.   OBTAINED RESULTS

In the Fig. 1-3 the dependences of content of product of chemical reaction on US intensity at different viscosities of reacting liquids mixture and frequencies are presented.
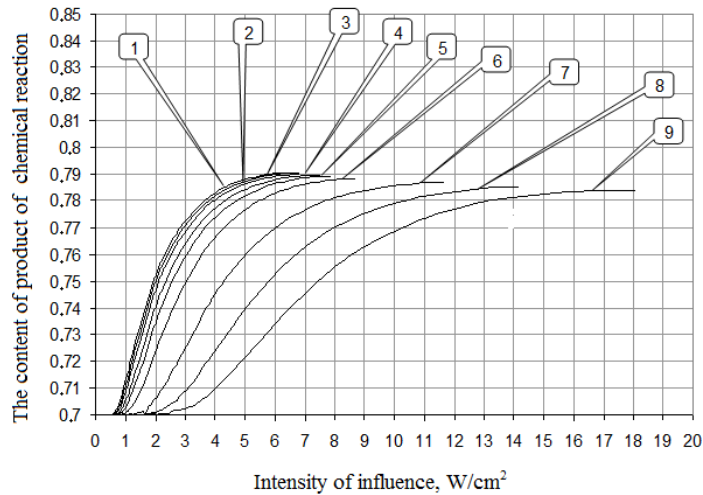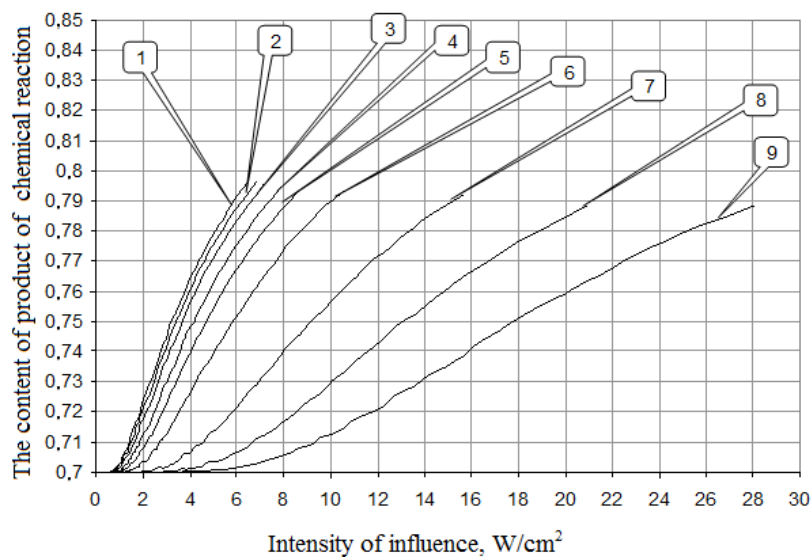
1 – viscosity 1 mPa·s; 2 – 5 mPa·s; 3 – 10 mPa·s; 4 – 20 mPa·s; 5 – 30 mPa·s; 6 – 50 mPa·s; 7 – 100 mPa·s; 8 – 150 mPa·s; 9 – 200 mPa·s

Fig. 1: The final content of product of chemical reaction dependences on US intensity at different viscosities of reacting liquids mixture (frequency is 22 kHz)
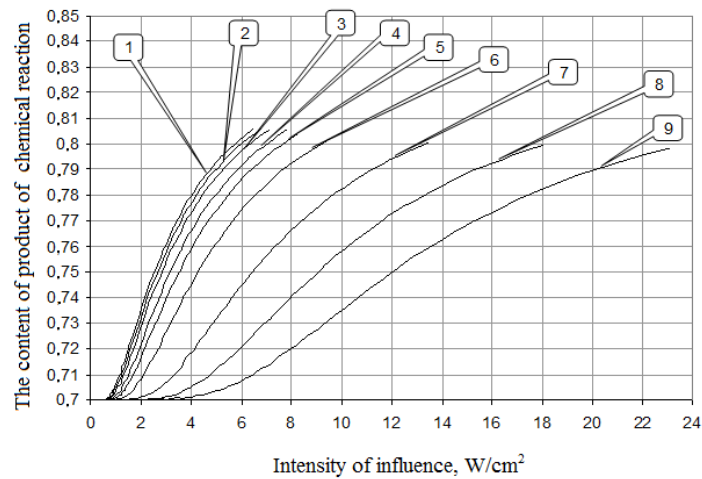
1 – viscosity 1 mPa·s; 2 – 5 mPa·s; 3 – 10 mPa·s; 4 – 20 mPa·s; 5 – 30 mPa·s; 6 – 50 mPa·s; 7 – 100 mPa·s; 8 – 150 mPa·s; 9 – 200 mPa·s

Fig. 2: The final content of product of chemical reaction dependences on US intensity at different viscosities of reacting liquids mixture (frequency is 33 kHz)

1 – viscosity 1 mPa·s; 2 – 5 mPa·s; 3 – 10 mPa·s; 4 – 20 mPa·s; 5 – 30 mPa·s; 6 – 50 mPa·s; 7 – 100 mPa·s; 8 – 150 mPa·s; 9 – 200 mPa·s

Fig. 3: The final content of product of chemical reaction dependences on US intensity at different viscosities of reacting liquids mixture (frequency is 44 kHz)

As follows from the dependences, ultrasonic influence allows to increase content of reaction product from 70 to 80% (content of unreacted liquids reduced up to 1.5 times). Dependences have a break corresponding to the no bubble collapse and transition to the degenerated cavitation mode, when large bubbles exist for a long time without the formation of shock waves.According to the dependencies, it is evaluated that the maximum content of reaction product is achieved at intensities of impact close to the break in the graphs (the regime of degenerated cavitation), due to a monotonous increasing of content. The intensities providing maximum content is optimum intensities.At the same time, the optimum intensity increases with increasing viscosity of the mixture of reactants, because the viscosity prevents the expansion of the cavitation bubble.For example, at a frequency of 22 kHz and a viscosity of reacting liquids mixture of 1 mPa·s, the optimum intensity is 6.5 W/cm^2, and at a viscosity of 200 mPa·s, the optimum intensity is 18 W/cm^2.The study of frequency influence was shown that frequency affects on content of product weakly. However the optimum frequency providing maximum content of product exists. According to the presented data the optimum frequency is about 33 kHz.

IV.　OBTAINED RESULTS

Thus the model of ultrasonic intensification of chemical reaction was developed. The model is based on statistical approach for calculation of average chemical reaction rate constant by physical kinetics methods.The numerical analysis of model shown that ultrasonic influence can reduce content of unreacted liquids up to 1.5 times, the optimum intensities providing maximum reaction efficiency exist and depend on source liquids mixture. For example, at a frequency of 22 kHz and a viscosity of reacting liquids mixture of 1 mPa·s, the optimum intensity is 6.5 W/cm^2, and at a viscosity of 200 mPa·s, the optimum intensity is 18 W/cm^2.The study of frequency influence was shown that frequency affects on content of product weakly. However the optimum frequency providing maximum content of product exists. The optimum frequency is about 33 kHz.The obtained data can be used for selection of operating modes of ultrasonic equipment for chemical reaction intensification.

ACKNOWLEDGEMENTS

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