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Model of ultrasonic cavitation depolymerization of oil for evaluation of optimum modes and conditions providing reducing viscosity at low temperatures

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Abstract. The paper presents the model of ultrasonic cavitation depolymerization which is destruction of oil macromolecules under cavitation. The model allows to evaluate optimum modes and conditions of ultrasonic influence, providing reducing oil viscosity at low temperatures. The model is based on probability approach which allows to simplify the task of cavitation depolymerization calculation in order to solve the system of self-similar equations for macromolecules with different weights concentration. The equations include probability of macromolecules destruction. The probability is determined by cross-section of collision of macromolecules pair and possibility of macromolecule destruction at contact with another molecule. The calculations have shown that the cavitation reduces the modal molecular weight up to 2 times. It causes reducing the oil viscosity up to 4…10 times. This has great actuality for oil transferring at low temperatures.

1. Introduction

The transferring of oil at North, Antarctic (feasibly in future) and tundra conditions represents big problem due to very high viscosity (up to 1 Pa-s). The high viscosity makes oil extraction from bowels of Earth and transferring through pipes impossible. The problem requires preliminary reducing the oil viscosity. One of promising ways for reducing oil viscosity is ultrasonic cavitation depolymerization. The ultrasonic action in the cavitation mode allows us to concentrate the energy of the oscillations propagating in the medium into the energy of cavitation bubbles in which local temperature rises up to 5000 K, and when they explode, shock waves with pressure amplitude up to 1000 MPa occur. This leads to the destruction of molecular bonds, ensures the homogeneity of the structure of a oil, the lower weight of macromolecules, and can reduce the viscosity [1, 2]. Purposeful obtaining of an oil with the necessary viscosity and productivity of ultrasonic treatment of oil for a particular application requires selection of ultrasonic cavitation influence modes and conditions. While the effect of cavitation on the structure of oil macromolecules has not been studied in detail until today. In connection with this, a model of cavitation effect on the molecular structure of a polymer should be developed. The model will make it possible to reveal the dependence of the change in the structure of molecules and the oil viscosity on the modes, conditions and exposition time of cavitation influence.

The developed model is described in following section.
2. The postulates of oil cavitation depolymerization model

Oil is the liquid medium consisting of molecular chains of monomers connected by hydrogen or carbon bonds. Cavitation leads to the destruction of molecular chains (cavitation depolymerization). At the same time, the fractional composition of molecular chains by the concentration of molecules with different amounts of monomeric units determines the rheological properties of the oil. Thus, the proposed model is aimed to determine fractional composition of molecular chains and rheological properties during cavitation depolymerization in dependency on starting viscosity, influence intensity and time. The proposed model of cavitation depolymerization based on following physical mechanism of macromolecules destruction under cavitation. The shock waves generated by cavitation cause increasing the dispersion of velocity of macromolecules, because around cavitation bubble the pressure rises sharply. Due to this the amount of molecules pairs with relative velocity more than the critical one (at the critical velocity one of the molecules is destroyed at collision) increases.

The assumptions used for the model development are as follows:

1. The macromolecule has a linear structure consisting of serially connected monomer units through equal distances $r_e$ (the model of a Gaussian sub chain or “spring beads”).
2. The distribution of macromolecules over the velocities of the centers of mass obeys a Gaussian law (the Maxwell’s distribution).
3. The pairing of collisions of macromolecules (the probability of simultaneous collision of 3 or more macromolecules is negligible).
4. For each elementary act of collision of macromolecules, it is possible to destroy an individual molecule (with the number of monomer units $i$) by only two particles with the numbers of monomer units $M$ and $i-M$.
5. The disruption of the macromolecule occurs only at the point of its contact with another molecule during the collision.
6. The probability of rupture of a macromolecule depends weakly on the position of its point of contact with another molecule, since the number of monomeric units $i >> 1$.
7. The cavitation bubble size is much more than single macromolecule size.

The model is based on the presented assumptions. The model has four stages presented as follows:

1. The determination of characteristic of cavitation area depending on modes and conditions of ultrasonic influence. Results of the stage are $n_{sub}$ (concentration of cavitation bubbles, m$^{-3}$), $R(t)$ (bubble radius, m), $P(t)$ (shock wave pressure near the bubble, Pa).
2. The determination of probability of macromolecules breakup $\beta_{ij}$ at collision of macromolecules pair with number of monomeric units $i$ and $j$ respectively.
3. Calculation of evolution of fraction composition of molecules $c_i$ ($c_i$ is the numeric concentration of molecules with number of monomeric units $i$).
4. The calculation of oil viscosity dependent on fraction composition of molecules.

Each stage allow to obtain own results which is input data for next stage. The first stage is for determination of characteristic of cavitation area dependent on US oscillations intensity and polymer viscosity at the current time moment. The last stage allows to determine the polymer viscosity of fraction composition of molecules and finally to determine the polymer viscosity dependency on time and intensity influence.

For the 1st stage (determining of characteristic of cavitation area) the sub model of cavitation bubbles formation was presented in [1, 3].

The sub model is based on Gilmor’s equation of cavitation bubble dynamics [3] and the probability models of cavitation bubbles coalescence and breakup which allow determining cavitation bubbles concentration according to the expression

$$ n_{sub} = \frac{2(j - 1)}{25\pi R_{MAX}^2 i [d_{12} (T) - d_{12} (0)]}, \tag{1} $$

$j$ is the number of cavitation nuclei formed after single bubble collapse [3]; $R_{MAX}$ is the maximal cavitation bubble radius, m; $i$ is number of periods of oscillations required for single expansion-
collapse of bubble cycle; $T$ is period of US oscillations, s; $d_{12}$ is the vector of distance between centers of bubble pair, m.

The forms and locations of advanced cavitation area (green zones in Fig. 1) are determined by modified wave equation taking into account influence of cavitation bubbles on acoustic properties of liquid [1]:

$$
\Delta \left( \sqrt{2 \rho c I(x) e^{i\varphi(x)}} \right) + \frac{\omega^2}{c_0^2} \left( 1 - \frac{\rho_0 c_0^2}{c^2} \delta \left( \sqrt{2 \rho c I(x) e^{i\varphi(x)}} \right) \right) \sqrt{2 \rho c I(x) e^{i\varphi(x)}} = 0 ,
$$

(2)

$I$ is the intensity of ultrasonic vibrations, W/m$^2$; $\varphi$ is the phase shift of vibrations of acoustic pressure in liquid; $\omega$ is the circular frequency of the initial ultrasonic field, s$^{-1}$; $c_0$ is the acoustic speed in a continuous liquid, m/s; $\rho_0$ is the steady-state density of continuous liquid, kg/m$^3$; $\rho$ is the density of cavitating liquid, kg/m$^3$; $c$ is the acoustic speed in cavitating liquid, m/s; $c$ is the acoustic speed in cavitating liquid, m/s; $\delta \left( \sqrt{2 \rho c I(x) e^{i\varphi(r)}} \right)$ is the complex amplitude of the change of volume content of the cavitation bubbles relative to mean value, $x$ is the radius-vector of liquid, m.

The color distributions of cavitation zones at different conditions are presented in Fig. 1.

![a) distributions of cavitation zones in cylindrical volume without reflectors](image1)

![b) distributions of cavitation zones in cylindrical volume with reflectors (the oil flow is perpendicular to cylinder axis)](image2)

Figure 1. Color distributions of cavitation zones.

As follows from the Fig. 1, the cavitation zones distribution at circular plate reflectors is more uniform than without reflectors.

Thus, the optimum conditions of ultrasonic influence are presence of circular plate reflectors because these provide uniformly oil viscosity reducing.

The sub model allowing to determine radius of bubble, concentration of bubbles and shock wave pressure. Founded values are used for determination of macromolecules breakup probability and fraction composition evolution. The sub model for determining fraction composition evolution is described in following section.

3. The postulates of the oil cavitation depolymerization model

The sub model for determining oil macromolecules fraction composition evolution is based on probability approach. According to the approach the intensity of molecules breakup is characterized by breakup probability $\beta_{ij,k,M}$ at unity concentration of molecules with weights (numbers of monomer units) $i$ and $j$ per unit of time. $\beta_{ij,k,M}$ is the probability of breakup of molecule with weight $i$ ($i$-weight molecule) on two molecules having weights $k$ and $i$–$k$. The breakup occurs at collision between $i$-weight and $j$-weight molecules on points separating $i$-weight molecule on $k$-weight and $(i$–$k$)-weight molecule, $j$-weight molecule on $M$ and $(j$–$M)$ molecule.

The obtained concentrations evolution equation (3) including the probability is
\[
\frac{\partial c_i}{\partial t} = \frac{1}{2} \sum_{j>i, k>i} \left( \sum_{M_2=1}^{k-1} \beta_{jk,ij,M_2} + \sum_{M_2=1}^{k-1} \beta_{jk,j-i,M_2} + \sum_{M_1=1}^{i-1} \beta_{ij,ij,M_1} + \sum_{M_1=1}^{i-1} \beta_{ij,k-i,M_1} \right) c_j c_k + \\
+ \sum_{j>i, k<i} \left( \sum_{M_2=1}^{k-1} \beta_{jk,ij,M_2} + \sum_{M_2=1}^{k-1} \beta_{jk,j-i,M_2} \right) c_j c_k - \sum_{i,M_1=1,...,i-M_1=1,...,i-l=1}^{i-1} \beta_{ij,ij,M_1} c_i c_j,
\]

where \(c_i\) is number concentration of \(i\)-weight molecule, mol/m\(^3\).

At the large average molecular weight (much more than 1) the \(\beta_{ij,k,M}\) is independent on \(k\) and \(M\) (assumption 6 in section 2) and equals to \(\beta_{ij}\). According to it the equation (3) is reduces to (4) which likes a Smoluchovski equation [4]:

\[
\frac{\partial c_i}{\partial t} = \sum_{j>i, k>i} (k + j - 2) \beta_{jk} c_j c_k + 2 \sum_{j>i, k<i} (k - 1) \beta_{jk} c_j c_k - \sum_{i,l} (i-1)(l-1) \beta_{ij} c_i c_j.
\]

The probability included in equation (4) is determined by the analysis of pair molecules collision, presented in following section.

4. The determining of probability of macromolecules destruction

The molecules breakup occurs after the molecules collision when the relative molecules speed exceed critical value \(v_{min}\). The process is schematically presented in Fig. 2.

Each macromolecule participating in collision characterized by velocity \(v_{ij}\), number of monomeric units \(i, j\) and orientation vector \(\mathbf{n}_{ij}\).

The determining of probability of macromolecules destruction is proportional to intersection during relative motion of macromolecules probability and to \(i\)-weight macromolecule breakup at collision. According to the accepted linear model of macromolecule (“spring-beads”), the macromolecules collision cross-section is like a parallelogram (Fig. 2a).

The square of collision cross-section (5) is

\[
S = \frac{1}{2} N_i N_j r_e^2 \left( \mathbf{n}_i - \frac{(\mathbf{n}_j \cdot \mathbf{v}_j)}{||\mathbf{v}_j||^2} \mathbf{v}_j \right) \times \left( \mathbf{n}_j - \frac{(\mathbf{n}_i \cdot \mathbf{v}_i)}{||\mathbf{v}_i||^2} \mathbf{v}_i \right),
\]

where \(\mathbf{n}_i\) is orientation vector of \(i\)-th molecule; \(\mathbf{n}_j\) is orientation vector of \(j\)-th molecule; \(N_i\) is number of monomeric units in \(i\)-th molecule; \(N_j\) is number of monomeric units in \(j\)-th molecule; \(r_e\) is equilibrium distance between monomeric units, m.

According to the Sommerfeld model [5-7] and due to the expression for collision cross-section square the expression for macromolecules breakup probability is as follows:
\[
\begin{align*}
P(C_{v_i,n_i},C_{v_j,n_j},\Delta V,\Delta t) &= P\left(C_{v_i,n_i},C_{v_j,n_j},\Delta V,\Delta t\right) \\
&= H\left(\left|v - v\right| - v_{\text{min}}(n_i,n_j)\right) C_{v_i,n_i} C_{v_j,n_j} \times \\
&\quad \times \Delta V \Delta t |v - v| Sdv, dv_j d\Omega(n_j) d\Omega(n_j),
\end{align*}
\]  

(6)

\(P\) is number of molecules pairs destructed in volume \(\Delta V\) during time \(\Delta t\); \(C_{v_i,n_i,\Delta V,\Delta v} d\Omega(n)\) is number of macromolecules in volume \(\Delta V\) having velocities from range \([v_x,v_x + dv_x]\times[v_y,v_y + dv_y]\times[v_z,v_z + dv_z]\), orientations with the solid angle \(d\Omega(n)\) and number of monomeric units \(N_i\); \(H(v)\) is Heaviside’s function which equals 1, if \(v \geq 0\), and 0 if another case; \(n_i\) is i-th macromolecule orientation vector; \(n_j\) is j-th macromolecule orientation vector; \(N_i\) is number of monomeric units in i-th macromolecule; \(N_j\) is number of monomeric units in j-th macromolecule; \(v_{\text{min}}(n_i,n_j,n_i,n_j)\) is minimal (critical) velocity necessary for breakup of i-th macromolecule when it collides with j-th macromolecule, m/s.

According to the made assumptions, the distribution by velocities of centers of molecules masses obeys Maxwell’s law and the distribution by macromolecules orientation is uniform (it is assumed, that oil is isotropic liquid). Therefore the probability of molecules collision and breakup was integrated by each velocities components and orientations.

\[
\beta_{\text{micro}} e_i e_j \Delta V \Delta t = \frac{N_A}{64\pi^2} \Delta V \Delta t \int |v - | v| \int P dv, dv_j d\Omega(n_j) d\Omega(n_i),
\]  

(7)

where \(i, j\) are weights of considered macromolecules ensembles; \(v_i\) is macromolecules velocity with weight \(i\), m/s; \(v_j\) is macromolecules velocity with weight \(j\), m/s; \(n_i\) is orientation vector of macromolecule with weight \(i\), m/s; \(n_j\) – is orientation vector of macromolecule with weight \(j\), m/s; \(N_A\) is Avogadro number, \(6.02 \times 10^{23} \text{ mol}^{-1}\).

Because the during cavitation ensemble pressure field \(p(t,r)\) in oil is non-uniform and non-constant, the probability is averaged by ultrasonic oscillations period \(T\) and local volume \(\Delta V\) with size much more than cavitation bubble diameter but much less than ultrasonic wave length:

\[
\beta_y = \left< \beta_{\text{micro}} \right> = \frac{1}{T \Delta V} \int_0^T \int_0^{\Delta V} \beta_{\text{micro}} p(t+i+r) dV dt.
\]  

(8)

The expression (8) gives the specific probability of macromolecules collision and breakup included in equation (4).

The final expression of the probability is following:

\[
\beta_y = N_A \frac{n_{\text{bulk}}}{T} \int_0^T \int_0^{\Delta V} 8r^2 r^2 \sin^2 \theta_i \sin^2 \theta_j \times
\]

\[
\sqrt{2\delta_i^2 + 2\delta_j^2} e^{-\frac{v_{\text{min}}^2(i,j,\theta_i,\theta_j,\alpha)}{2\delta_i^2 + 2\delta_j^2}} \left[\frac{v_{\text{min}}^2(i,j,\theta_i,\theta_j,\alpha)}{2\delta_i^2 + 2\delta_j^2} + 1\right]^{\frac{1}{\sqrt{\pi}}} \partial \theta_i \partial \theta_j \partial \alpha \partial r \partial t,
\]  

(9)

\(\alpha = \cos(\phi_i - \phi_j)\), \(\delta_i = C_i p(r)\),

where \(C_i\) is proportionality coefficient determined by thermodynamically conditions in the polymer liquid, m/s; \(r_e\) is equilibrium distance between monomer units, m; \(N_A\) is number of Avogadro, mol\(^{-1}\).
$n_{hub}$ is cavitation bubbles concentration, m$^{-3}$; $v_{min}$ is minimal relative macromolecules pair velocity necessary for macromolecules breakup, m/s; $P(t)$ is the shock wave pressure, Pa; $R(t)$ is the radius, m.

The minimal relative macromolecules pair velocity $v_{min}$ obeys energy conservation law (sum of molecules kinetic energy and hydrogen bonds potential energy is constant) and can be determined empirically by indirect methods (approximation of viscosity dependence of time at fixed cavitation energy). In the energy conservation laws the Morse potential function of monomeric unit interaction

$$V(r) = D_n \left[1 - e^{-\alpha(r-r_0)}\right]^2$$

is used [8].

The substitution of probability (9) in equation (8) allows to calculate macromolecules fraction composition evolution. Results of calculation are presented in the next section.

5. The calculating of macromolecules fraction composition evolution

The calculated mass fractions of oil molecules with different monomer units are presented in Fig. 3, 4. In each Figure the model oscillations frequency is 22 kHz.

![Figure 3](image1.png)

Figure 3. Macromolecules dispersed composition at different times (intensity of ultrasonic influence 25 W/cm$^2$).

According to the presented histograms, at the intensity 10 W/cm$^2$ the modal number of monomer units is reduces up to 40%. It is enough to reduce viscosity up to more than 3.5 times.

![Figure 4](image2.png)

Figure 4. Macromolecules dispersed composition at different times (intensity of ultrasonic influence 25 W/cm$^2$).

According to the distributions presented in Fig. 4, higher intensity causes the faster maximum shift. For example, through 300 s, the modal number of monomer units reduces up to more than 2 times. It causes viscosity reducing up to more than 10 times. In the following section the results of calculation of oil viscosity changing were presented.

6. The calculating of oil viscosity evolution

The oil like a polymeric liquid, because viscosity is calculated by empirical law, obtained by Rouse P.E., Khokhlov A.R., Pyshnograi G.V. [9–10]:

$$\eta(t) = \eta(0) \sum_{i=1}^{N} C_i 2^{\delta+1} (i) i^{3\delta+2}$$

$$\sum_{i=1}^{N} C_i 2^{\delta+1} (0) i^{3\delta+2}$$

$t$ is time, s; $\delta$ is empirical parameters which equals to 2.4 for most part of polymers.
According to expression (9) and equation (6) for concentrations $c_i$, the dependences for viscosity on time were obtained (Fig. 5).

**Figure 5.** Macromolecules dispersed composition at different times (intensity of ultrasonic influence 10 W/cm$^2$).

According to the dependences, the ultrasonic with intensity 25 W/cm$^2$ reduces the viscosity up to 10 times and more (for polymer with starting viscosity 0.4 Pa·s). As well as, the possibility of ultrasonic cavitation depolymerization of high viscous oils at low temperatures (0.8 Pa·s) was shown. Ultrasonic cavitation influence can reduce viscosity up to 3.5 times during 1000 s at starting viscosity 0.8 Pa·s (US oscillations intensity is 160 W/cm$^2$).

For ultrasonic depolymerization of high viscous oil at low temperatures the larger intensities is required due to viscosity prevents cavitation.

Obtained results can be used for choose the operating modes and conditions of industrial ultrasonic equipment for cavitation depolymerization of oil for its transferring at low temperatures.

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