Mathematical Modeling of the Separation Process of Oil-Water Emulsions Using a Demulsifier of Natural Origin

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Abstract. The article presents the results of experimental studies of the separation process of water-in-oil emulsions using demulsifiers of natural origin, consisting of oil ash, table salt and an activating additive - manganese in a nanostructured form. A mathematical model is presented that makes it possible to determine the kinetic characteristics of the process of settling water from an emulsion using a demulsifier containing ash structures and manganese metal.

1. Introduction

In the process of oil extraction for the production of motor fuels, as well as products and semi-products of the chemical industry, it is flooded. Water enters the hydrocarbon feedstock as a result of waterflooding of production wells, which is used to extract it due to the difference in the density of the hydrocarbon feedstock - water media [1-5].

To improve the efficiency of emulsion separation, demulsifiers are widely used, most of which are surfactants. Their use makes it possible to reduce the resistance of the dispersion medium to sticking of small water droplets, which contributes to their enlargement and deposition. [6-8].

2. Experiment, results and discussion

To increase the efficiency of the separation processes of oil-water emulsions, a demulsifier composition based on components of natural origin - table salt ash obtained by burning it in a muffle furnace at a temperature of 1000 °C [9] is proposed.

From consideration of the quantitative values of the binding energy of water with the elements of table salt ash, an element was chosen - Mn in a nanostructured form to increase the efficiency of the demulsifier in the process of oil dehydration [10].

The stability of oil-water emulsions in the presence of a demulsifier based on natural components was assessed using waters of various structures (sea, artesian, their condensates), water concentration from 10 to 70 wt%. Emulsions were obtained by dispersing a weighed portion of water in oil with a paddle mixer.

When using a microscope at a magnification of 400, photographs of emulsions were obtained (Fig. 1-8), allowing to estimate the size of water droplets.
From the data in Fig. 1 and 2, it can be seen that a 10% emulsion contains water droplets ranging in size from 1 to 10 μm, in a 50% emulsion the droplet size is from 1 to 20 μm.

Figures 3 - 4 show photographs of artesian water emulsion samples, from which it can be seen that the 20% emulsion contains droplets of 1 - 12 microns, the “Aktobe oil - artesian water” emulsion with a concentration of 50% has water droplets up to 30 microns.

Figures 5 - 6 show photographs of emulsions containing seawater condensate, from which it can be seen that an emulsion consisting of 80% of the mass. oil and 20% of the mass. condensate contains water droplets with a size of 1 to 10 microns, containing 50% of the mass. condensate - up to 15 microns.
Figures 7 - 8 show photographs of artesian water condensate emulsions.

Figure 7. Oil emulsion with 20% artesian water condensate.

Figure 8. Oil emulsion with 50% artesian water condensate.

From the pictures in Figures 7 - 8 it can be seen that the emulsion containing 20% of artesian water condensate is characterized by the size of water drops from 1 to 10 microns, the emulsion containing 50% of the mass. artesian water, characterized by the size of water droplets up to 15 microns.

The results of evaluating the efficiency of separation of emulsions using the proposed components of the demulsifier are presented in table 1.

| Demulsifier composition | Degree of destruction of emulsion,%, at water content |
|-------------------------|------------------------------------------------------|
|                         | 10% | 20% | 50% | 70% |
| No demulsifier           | 3.0 | 8.4 | 2.2 | 0.5 |
| Ash oil, table salt      | 24.0| 26.3| 14.5| 9.4 |
| Ash of oil, table salt, Mn nanoparticles | 69.0| 55.3| 37.3| 27.3|
| Mn nanoparticles         | 11.0| 7.2 | 6.4 | 5.5 |

To increase the efficiency of the emulsion separation process, 20 wt. solvent - kerosene. The results are shown in Table 2.

| Demulsifier composition | Degree of destruction of emulsion,%, at water content |
|-------------------------|------------------------------------------------------|
|                         | 10% | 20% | 50% | 70% |
| No demulsifier           | 11.0| 8.1 | 4.4 | 2.1 |
| Ash of oil, table salt, Mn nanoparticles | 97.0| 85.5| 76.3| 67.2|

In the process of separating the emulsion "hydrocarbon raw material - water" of water with the introduction of 20% of the mass. from the mass of the emulsion of a low-boiling solvent, which was used as a kerosene fraction, as a demulsifier - a mixture of oil ash, table salt, metal nanoparticles, it is possible to achieve the degree of destruction of the emulsion - 97%.

Using the results of evaluating the structures of water-in-oil emulsions and their stability, a mathematical description was compiled, which makes it possible to determine the kinetic characteristics of the coalescence of water droplets and their deposition.
We consider the process of coalescence of droplets as a second-order reaction from the concentration of adhering droplets. The most likely is the coalescence of droplets that differ as much as possible in size. The constant of its speed with volumes $V_1$ and $V_2$ can be written in the following form:

$$k(V_1, V_2) = \beta \cdot \left(\frac{3 \sqrt{V_1}}{V_2} + \frac{3 \sqrt{V_2}}{V_1}\right)^2$$

(1)

where $k$ is the rate constant of the coalescence of drops, $V_1$ and $V_2$ are the volumes of the drops, $\beta$ is the coefficient, and the tendency of the drops to coalesce.

We divide the entire range of droplet sizes into segments based on the volume of a single drop (Fig. 9):

$$\Delta V = V_{i+1} - V_i$$

(2)

![Figure 9](image1.png)

**Figure 9.** Distribution of water droplets over the volume of emulsions.

Then the contribution to the overall rate of coalescence of drops from drops with volumes $V_i$ and $V_j$ will be expressed by the dependence:

$$k(V_i, V_j) \cdot dC(V_i, \tau) \cdot dC(V_j, \tau)$$

(3)

where the number of drops with a volume $V_i \pm \frac{1}{2} \Delta V$ in the emulsion at the time $\tau$ (pcs / m$^3$).

After transforming the structures of water droplets in the emulsion, we obtain expressions for the increase and decrease in the proportion of droplets taking into account (4).

**Growth:**

$$r_+ = 0.5 \cdot \int_0^V k(V_i - V_j) \cdot \rho(V_i - V_j, \tau) C_{all}(\tau) dV_j \cdot \rho(V_j, \tau) C_{all}(\tau) dV_j$$

(4)

where $\rho$ is the density of the continuous medium, kg / m$^3$.

**Decrease:**

$$r_- = \rho(V_i, \tau) C_{all}(\tau) dV_i \cdot \int_0^V k(V_i, V_j) \cdot \rho(V_i, \tau) C_{all}(\tau) dV_j$$

(5)

$$r_- = \rho(V_i, \tau) C_{all}(\tau) dV_i \cdot \int_0^V k(V_i, V_j) \cdot \rho(V_i, \tau) C_{all}(\tau) dV_j$$

(6)

$$r_- = \rho(V_i, \tau) C_{all}(\tau) dV_i \cdot \int_0^V k(V_i, V_j) \cdot \rho(V_i, \tau) C_{all}(\tau) dV_j$$

(7)

The change in the concentration of volume droplets $V_i$ during the time $d\tau$ can be represented as:

$$\frac{dC(V_i, \tau + d\tau)}{d\tau} = C_{all}(\tau + d\tau) \cdot \rho(V_i, \tau + d\tau) \cdot dV_i - C_{all}(\tau) \cdot \rho(V_i, \tau) \cdot dV_i$$

$$\frac{dC(V_i, \tau)}{d\tau} = 0.5 \int_0^V k(V_i - V_j) \cdot C_p(V_i - V_j, \tau) \cdot \rho(V_j, \tau) \cdot dV_j -$$

$$- C_p(V_i, \tau) \int_0^V k(V_i, V_j) \cdot C_p(V_j, \tau) \cdot dV_j$$

(8)
This integro-differential equation will characterize the volumetric distribution of droplets over time without their sources / sinks. The kinetics of the process will be determined by the coefficient $\beta$, which characterizes the tendency of droplets to coalescence, having a dimension of m$^3$ / (pcs s), and the initial droplet size distribution $C_p(V_i, 0)$.

In addition to the coalescence of droplets in the emulsion, delamination is observed during settling. The frequency of collisions of drops will be the greater, the higher the difference in their speed of motion, which explains the increase in the observed coalescence rate with an increase in the difference in the size of the drops [5], since with an increase in their size, the linear rate of their deposition increases as. Among droplets with a radius of up to rmax, a part will reach the interface and pass into a continuous phase.

At the height of the liquid column H at the initial moment, the entire liquid is the initial emulsion; as it settles, it will separate into a phase consisting of the substance of the dispersed phase of the initial emulsion and an emulsion depleted in the substance of the dispersed phase (Fig. 10).

For the section of the emulsion with height dh, we compose the material balance. Obviously, droplets will be added to the material flows (Fig. 1) and (Fig. 2) due to their vertical movement over the volume. The direction of movement of the dispersed phase in this case is from top to bottom.

The flow of droplets with a volume $V_i$ entering the layer dh, pcs / s:

$$j_{\text{mov+}} = S \cdot v_{\text{sedrel}}(V_i, \tau, h) \cdot C_p(V_i, \tau, h)$$

(9)

The flow of droplets leaving the layer dh, pcs / s:

$$j_{\text{mov-}} = S \cdot v_{\text{sedrel}}(V_i, \tau, h + dh) \cdot C_p(V_i, \tau, h + dh)$$

(10)

Where $S$ is the area of the area perpendicular to the direction of the droplets.

Taking into account the size and structure of droplets, we obtain an equation for determining the separation time of emulsions:

$$\frac{\partial C_p(V_i, \tau, h)}{\partial \tau} = 0.5 \int_0^{V_i} k \left( V_i - V_j, V_j \right) \cdot C_p(V_i - V_j, \tau, h) \cdot C_p(V_j, \tau, h) dV_j -$$

$$- C_p(V_i, \tau, h) \int_0^{\infty} k \left( V_i, V_j \right) \cdot C_p(V_j, \tau, h) dV_j -$$

$$- C_p(V_j, \tau, h) \frac{\partial v_{\text{sedrel}}(V_j, \tau, h)}{\partial h} - v_{\text{sedrel}}(V_i, \tau, h) \frac{\partial C_p(V_j, \tau, h)}{\partial h}$$

(11)

3. Conclusions

The composition of a demulsifier based on components of natural origin is proposed to increase the efficiency of the separation process of water-in-oil emulsions, consisting of salt ash, oil ash, and Mn nanoparticles.

A mathematical model of the process of coalescence of water droplets and its settling is proposed, depending on the characteristics of the structure of the emulsion.

4. References

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