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Sonochemical effects on food emulsions

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Abstract. Acoustic cavitation of food emulsions is widely applied as the main processing method to improve the quality of a finished product and its organoleptic characteristics, as well as to increase production performance. To identify the optimal modes of ultrasonic emulsification, we propose a model of emulsion droplet breakup in an acoustic cavitation field, which allows us to determine the dependence of emulsion droplets' diameter on exposure time and intensity of action. The developed models enabled us to pioneer complex research of the dependence of emulsion droplets' diameter on time given the maximum radius of cavitation bubbles and physical properties of liquid phases in the emulsion composition. We carried out the first complex theoretical and practical research of how shapes and positions of absolutely fixed boundaries influence the propagation of oscillations in a activating liquid medium (food emulsion). To verify the adequacy of the obtained theoretical models, we studied the dependence of emulsion droplets' breakup rate (by the example of a model water/oil emulsion) on the exposure time and the intensity of ultrasonic action. The calculation results revealed that the results of a series of experiments and the results obtained with the use of the developed mathematical model are consistent. Based on the theoretical data obtained, we designed an industrial flow- type acoustic cavitation device aimed at acting on food emulsions; it differs from analogous devices in that it has within it a cylindrical wave acting through solid walls of the tunnel for transmitting processed liquid.

Key words: ultrasound, cavitation, model, food emulsion, sonochemistry.

INTRODUCTION

Emulsification processes are one of the most important foundations of the modern food industry (Taylor, 1963; Khmelev, 2012). Acoustic cavitation is one of the most promising means of forming emulsions, since it has a low energy intensity, the possibility of obtaining fine emulsions (up to fractions of 3 μm and less), and high productivity (Álvarez et al., 2007; Khmelev et al., 2014; Krasuly, et al., 2016).

To form a cavitation zone with maximum possible energy effect in liquid media of different properties by means of secondary effects (shock and capillary waves), it is necessary to set certain modes according to the intensity of introduced ultrasonic oscillations, and to ensure certain conditions the volume of a processed medium, the form of a technological volume, the exposure time, etc. (Khmelev, 2007).

The industrial application of ultrasonic devices in modern food production necessitates searching for and providing the most effective (optimal) modes of action on food media (Brotchie et al., 2009; Krasulya, 2013). Setting and maintenance of optimal ultrasonic mode is possible only by knowing the implementation mechanisms of ultrasonic processes and identifying and continuously monitoring the processing media parameters which characterize the change in their properties (Chandrapala, et al., 2012).

Having generalized theoretical and practical results on the research topic, we established that most of the existing theories which describe the process of emulsification under the action of cavitation are aimed at study the behavior of a single cavitation bubble and its interaction with emulsion droplets (Kentish et al., 2008; Patista & Bates, 2008; Krasulya et al., 2014; Shanmugam & Ashokkumar, 2015). However, in real processes involving ultrasonic cavitation of liquid food media, their cavitation zone is generated, as it is practically impossible to obtain a single cavity. Therefore, it is obvious that the efficiency of ultrasonic will be determined by the macroscopic characteristics of the activating medium as a whole (wave impedance, volume content of bubbles or cavitation index, etc.) (Truhaut, 1991).

The purpose of this work is to identify the optimal modes of exposure and the conditions for the propagation of oscillations to create a uniform ultrasonic field throughout a mixture of two mutually insoluble fluids and to obtain emulsions with given dispersion characteristics.

MATERIALS AND METHODS

To study the effects of acoustic cavitation emulsification, we developed a laboratory reactor where the source of ultrasonic treatment is an ultrasonic device, consisting of an electronic generator and a radiator with an immiscible titanium waveguide, which has a mushroom-shaped running end. The device allows for vertical shifting of the working body in order to carry out different modes of exposure.

Since, according to the generalization of the results of theoretical and practical studies, the maximum efficiency of cavitation is ensured at a frequency of 20–25 kHz, we focused special attention on detecting the intensity of ultrasonic oscillations necessary to obtain emulsion droplets of the required diameter in a specific frequency range.

We used 'vegetable oil/water' food emulsions as objects for the research. Sunflower-seed oil (deodorized, refined with a 99.9% fat content) was used as vegetable oil. The vegetable oil used had the following chemical and physical characteristics of crude vegetable oil: Relative density (at 20 °C) – 0.9 ± 0.02 C/water, Refractive index – 1.464 ± 0.002 (ND 40 °C), Saponification Value – 191 ± 0.5 mg KOH g^{-1} oil, Iodine value – 119 ± 0.5. The tap water used had the following quantitative characteristics: hydrogen index 6.5, total hardness – 6.8 mg L^{-1}, phenol index – 0.20 mg L^{-1}. To conduct the experiment, we used food emulsions with a different ratio of ingredients:

- the first option – 30% vegetable oil + 70% water;
- the second option – 50% vegetable oil + 50% water;
- the third option – 5% vegetable oil + 95% water;

– the fourth option – 30% vegetable oil + 70% water.

For the preparation of reference samples, we used technological device an RKU-type with a piezoceramic radiator (Russia). Ultrasound details: frequency mechanical oscillations – 22 ± 1.5 kHz, the maximum power consumption – 1,000 W. The time of ultrasound exposure varied from 20 to 40 minutes, and the power of sonication varied from 500 W to 1,000 W:

– mode №1 – 20 min, 700 W;
– mode №2 – 20 min, 1,000 W;
– mode №3 – 20 min, 500 W;
– mode №4 – 40 min, 500 W.

The temperature of the food emulsion before its exposure to ultrasound was 15 °C.

The distribution of fat globules in food emulsion according to its concentration and processing time was photographed with the help of an optical microscope.

The software package Altami Studio was used to process the obtained fat globule images.

Mathematical measurement processing was carried out by conventional statistics methods and expressed as the arithmetic mean (M) and it's standard error (m). We used the Mann – Whitney test (U) to determine the statistically significant differences between the test and reference groups. Differences were considered significant at $P < 0.05$. Statistical interrelations were studied using nonparametric correlation analysis by calculating the Spearman correlation coefficients (Rs). Results were obtained using generally accepted methods of statistical analysis and expressed as an arithmetical average and its standard deviation. Differences were deemed significant where $P < 0.05$.

RESULTS AND DISCUSSION

To identify the optimal ultrasonic emulsification modes, we developed a model of emulsion droplet breakup in an acoustic cavitation field. The model is based on droplet deformation Eq. (1) proposed by foreign researchers:

$$mx = F - kx - dx \quad (1)$$

where m is the mass of the droplet, kg; F is the external force acting on the droplet from the direction of fluid flow, N; k is the coefficient of elasticity of the droplet, N m^{-1}; and d is the damping ratio of the droplet, kg s^{-1} (Taylor, 1963).

According to this equation, the droplet wall is regarded as a load of mass m on a spring (equivalent to the surface tension forces) with a damper (equivalent to the viscosity of a disperse phase).

The coefficient of elasticity of a droplet is determined by formula 2:

$$\frac{d}{m} = C_d \frac{\sigma}{\rho_d R^3} \quad (2)$$

where C_d is the coefficient of proportionality, which depends on the droplet deformation mode; σ is the surface tension in the interface between the carrier phase and the dispersed phase, N m^{-1}; and ρ_d is the density of the dispersed phase, kg m^{-3}.

The damping ratio of a droplet is determined by formula 3:

$$\frac{d}{m} = C_d \frac{\mu_d}{\rho_d R^2} \tag{3}$$

where C_d is the coefficient of proportionality, which depends on the mode of droplet deformation and μ_d is the viscosity of the dispersed phase, Pa·s.

The external force F under acoustic cavitation is proportional to the amplitude of the shock wave pressure in its front when a cavitation bubble collapses.

The solution of differential Eq. (1) enables us to find the maximum value of droplet deformation and determine the possibility of its breakup. According to Taylor (1963), if the maximum droplet deformation is greater than a quarter of its diameter d, the droplet breaks up into 2 identical droplets of the diameter $\frac{d}{\sqrt[3]{2}}$.

Therefore, the dependence of the droplet diameter on time is defined by differential Eq. 4:

$$\frac{\partial d}{\partial t} = dt_{bu}(d) \ln \frac{1}{\sqrt[3]{2}} \tag{4}$$

where $t_{bu}(d)$ is the dependence of the breakup time of a single droplet on its diameter.

The dependence of the breakup time of a single droplet on its diameter is determined as follows. According to Eq. (1), the maximum value of droplet deformation is proportional to the external force acting on the droplet from the direction of fluid flow. This force is proportional to the amplitude of the shock wave pressure as it reaches the droplet walls. Since a droplet breaks up if and only if its maximum deformation exceeds half the radius, accordingly, the breakup will occur when the amplitude of the shock wave pressure near the droplet walls exceeds a certain threshold value.

This means that a droplet will break up by force of the action of cavitation bubbles formed in its neighborhood due to shock wave scattering.

Based on this information, the droplet breakup time is determined by the interval when at least one cavitation bubble forms in the zone V_b.

The time interval for the formation of bubbles leading to the droplet breakup is determined on the basis of the probabilistic approach in accordance with obtained expression 5:

$$t \approx \frac{T}{nV_b} \tag{5}$$

where n is the concentration of cavitation bubbles determined according to (Khmelev et al., 2014), m^{-3}; T is the period of bubble collapse, s; and V_b is the volume of the zone of bubble collapse leading to the droplet breakup, m^3.

We obtained the dependences of the droplet breakup time, represented by a graph and shown in Fig. 1.

As follows from the dependences obtained (Fig. 1), the greatest breakup time is required for droplets of small diameter (the breakup time of 20 μm droplets three times exceeds the breakup time of 100 μm droplets). The reason for this is the small volume of the neighborhood of a droplet, where collapsing bubbles lead to droplet breakup. Therefore, in order to effectively carry out the process of obtaining an emulsion with dispersed phase particles of a small diameter, it is necessary to increase the radius of cavitation bubbles, and, consequently, to increase the intensity of ultrasound.

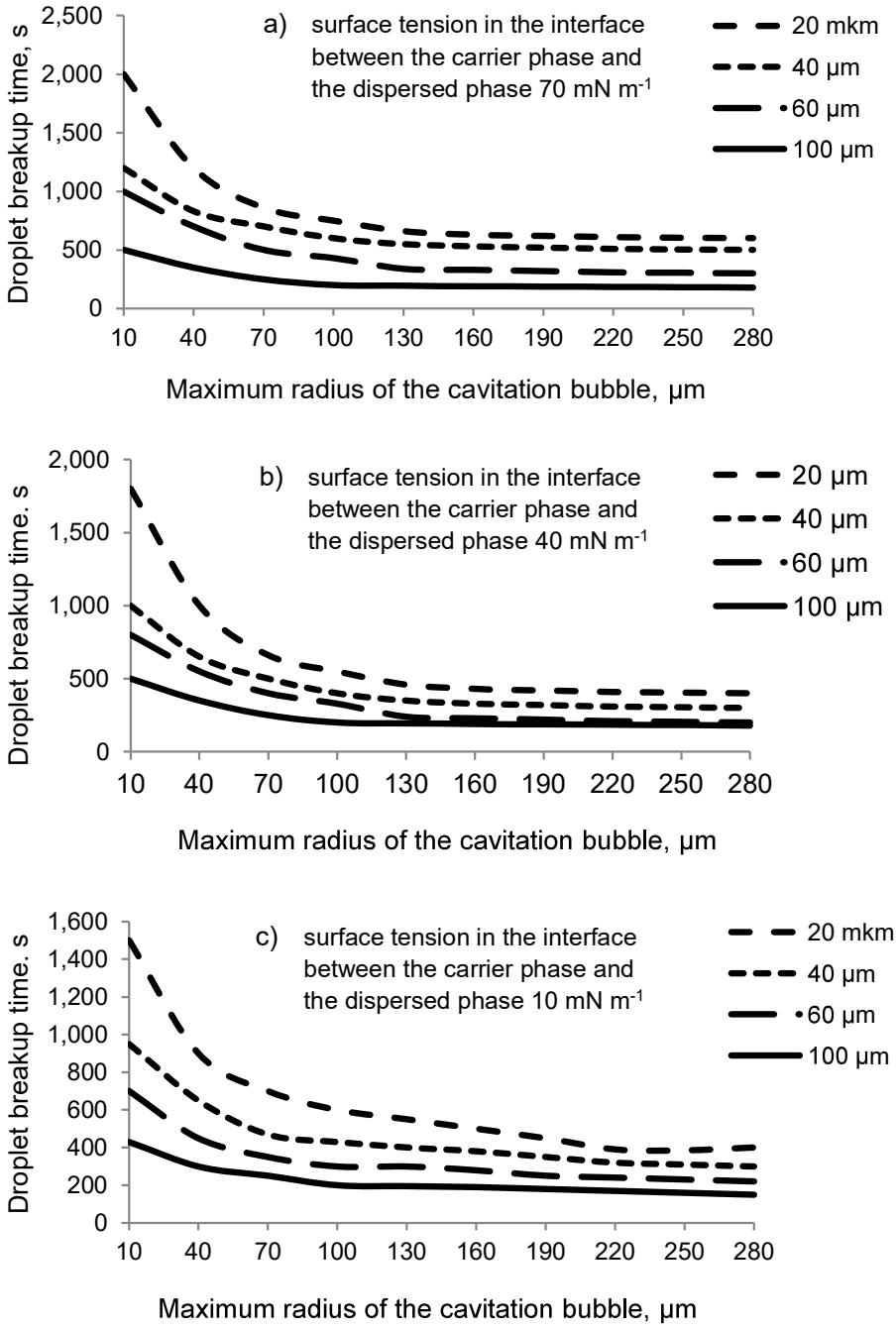

Figure 1. Dependences of the droplet breakup time on the maximum radius of the cavitation bubble depending on its various diameters and surface tensions in the interface between the carrier phase and the dispersed phase.

There is a certain threshold radius for each droplet size, from which decrease in the breakup time of the droplet ceases. For example, the minimum breakup time of 20 μm droplets is achieved when the radius of cavitation bubbles is 250 μm. And for the breakup

of 100 μm droplets, the bubble radius should be 130 μm. Exceeding the threshold radius of cavitation bubbles will not lead to an increase in the efficiency of emulsification; moreover, if the bubble radius exceeds 300 μm, according to (Khmelev, 2012), a degenerate cavitation will form, and the emulsification process might stop.

The obtained droplet breakup time allows us to find the dependence of the droplet diameter on time (Fig. 2) when emulsifying sunflower oil in water.

As follows from the presented dependence, under the action with the intensity of 1.5 W cm^{-2}, even after a 20-minute exposure, the droplet diameter still exceeds 20 μm, which is insufficient for a number of technological processes.

Action with the intensity of 3 W cm^{-2} allows for emulsions with a droplet diameter of 15 μm within 20 minutes, while action with the intensity of 9 W cm^{-2} and more allows obtaining emulsion droplets with a diameter of less than 7–10 μm within just 20 minutes of exposure time.

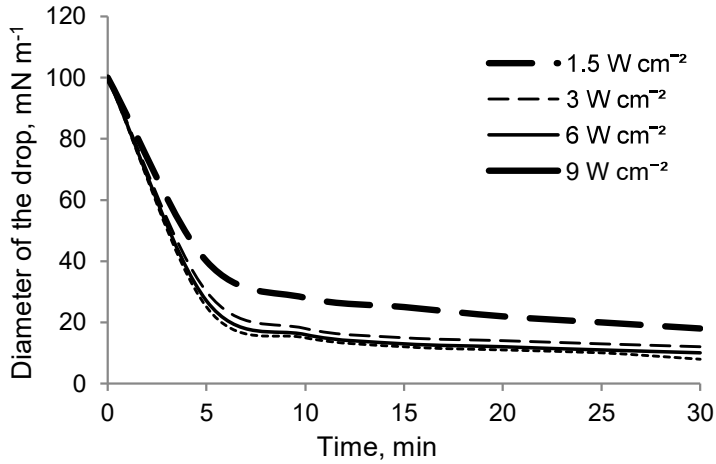

Figure 2. Dependence of emulsion droplets' diameter on time under the action of different intensity.

To verify the adequacy of the obtained theoretical models, we studied the dependences of the breakup rate of emulsion droplets (by the example of a model emulsion of water/oil type) on time and intensity of ultrasound (Fig. 3).

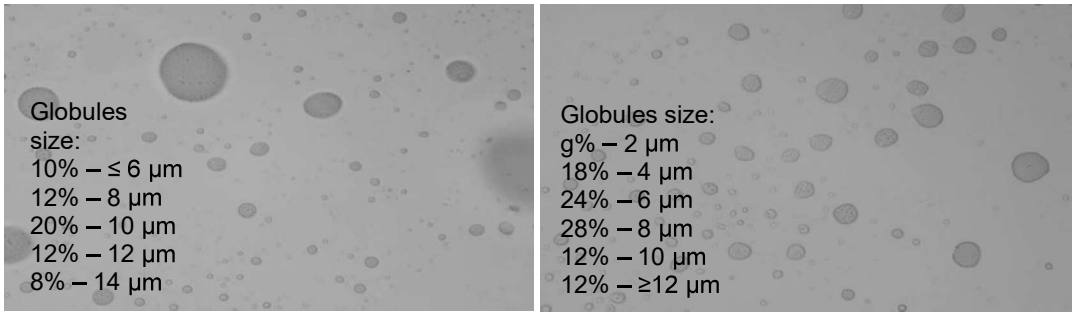

Figure 3. Photos of the model emulsion (magnification × 1,600): left – before the processing, right – after the processing (US 700 W, 20 min).

The resulting images were processed with the use of software, and the hexograms of the distribution of fat globule sizes at different modes of sonochemical action were plotted based on the obtained results (Fig. 4).

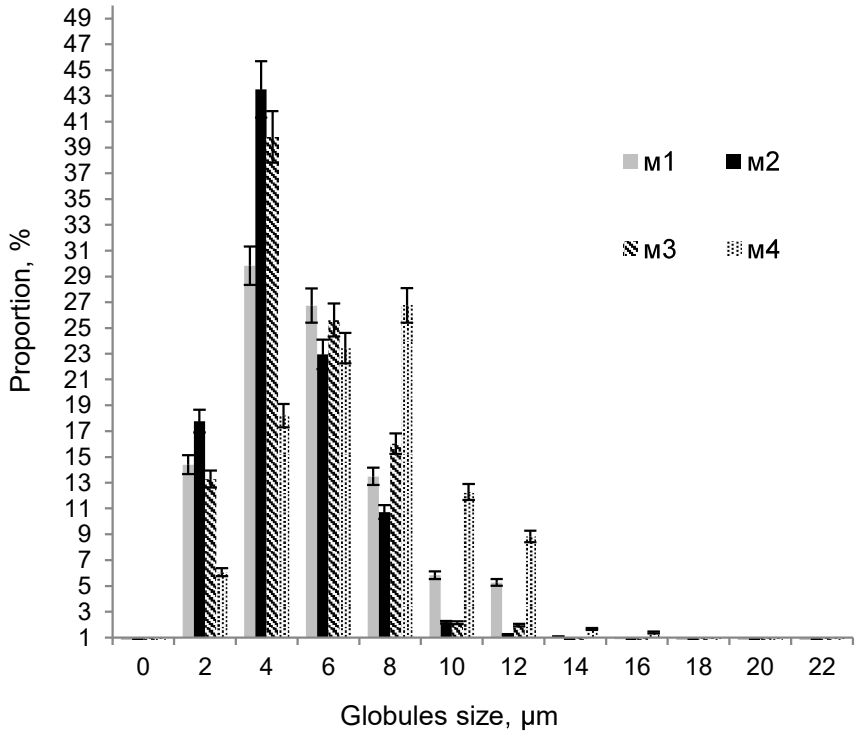

Figure 4. Hexagram of the distribution of fat globules at the different processing modes: M1: 30% vegetable oil + 70% water; US 20 min, 700 W; M2: 50% vegetable oil + 50% water; US 20 min, 1,000 W; M3: 5% vegetable oil + 95% water; US 20 min, 500 W; M4: 30% vegetable oil + 70% water; US 40 min, 500 W.

Based on the results of droplet size calculations, we found that the results of a series of experiments and the results, obtained with the help of the mathematical model, are consistent. We established that the optimal concentration of emulsion is 30% – vegetable oil and 70% – water, and the optimal processing time is 40 minutes with an ultrasonic power of 500 W, which corresponds to a processing intensity of 9 W cm^{-2} (mode M4, Fig. 4). These modes ensure the maximum uniform distribution of fat globules of an average diameter within the range of 6–8 μm.

We undertook the first complex theoretical and practical studies of how the shapes and positions of absolutely fixed boundaries influence

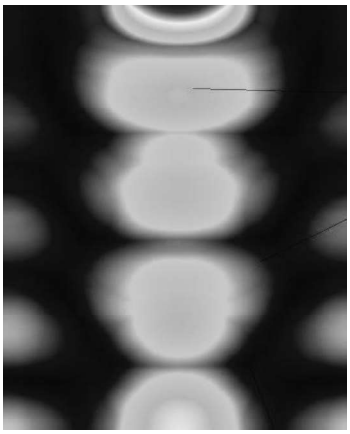

Figure 5. Distribution of oscillation amplitudes of medium pressure.

the propagation of oscillations in a activating liquid medium (food emulsion). We carried out a finite element simulation for the obtained wave equation of oscillation propagation in order to find the distribution of acoustic pressure and the degree of cavitation development in technological volumes. We obtained a visual image (Fig. 5) of the distribution of the amplitudes of pressure oscillation in the medium. It allows for the design of flow working chambers of technological volumes with optimal geometrical dimensions which avoids zones in which the process medium remains unprocessed and thus leads to a decrease in the performance of the device as a whole.

With the help of a specially developed measuring bench, we determined the optimum shapes and sizes of technological volumes for ultrasonic cavitation processing of food emulsions.

To this purpose, longitudinal shifting of the end reflecting boundary (placed opposite the radiator) was constructively generated in order to realize the modes of both a travelling and a stationary wave. The optimal values for the size of process chambers were determined: the diameter should be at least 130 mm; the length of a process chamber should be at least 230 mm.

On the basis of the obtained theoretical data, we developed a design of an acoustic cavitation industrial device for acting on food emulsions, which differs from its analogues in that it has a setup cylindrical wave acting through solid walls of the tunnel for transmitting processed liquid.

CONCLUSIONS

The research resulted in the development of a model of ultrasonic emulsification, which enables the determination of the dependence of the diameter of emulsion droplets on the exposure time and intensity of the action. The analysis of the model allowed us to establish that the optimal time for ultrasonic emulsification is 40 minutes.

In order to obtain an emulsion droplet diameter of less than 20 μm in a carrier phase having a viscosity like that of water (1 mPa·s), the action intensity should be at least 5 W cm^{-2}, while for a liquid with the viscosity of 40 mPa·s, a droplet diameter of less than 20 μm is achieved under the action intensity of 8 W cm^{-2}.

The obtained results may be used to select the modes of operation of ultrasonic technological equipment and to design a process chamber, which would provide the required residence time of an emulsion in the device.

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