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Using the effects of hydrodynamic cavitation for purposeful dynamical action on the supramolecular structures

Evolution of the cavitation cluster and the level of the dynamic cavitation effects in liquid flow within a Venturi nozzle, depending on the design features and the mode of operation of this type cavitator, are considered. The experimental and theoretical investigations have been performed with the view to using the Venturi nozzle as cavitation reactor to efficient influence supramolecular structures in liquid in relation to producing stable liposome dispersions. Structural peculiarities of liposomes, closed biological nanocapsules, as well as bond energy values in these structures have been analyzed. The results of this study prove that using Venturi nozzles in large-scale production of liposome preparations allows increasing production capacity and significant reduction in the mass-related power consumption as compared with traditional acoustic and hydrodynamic methods.

Cavitation is known to be of the most effective ways of intensification of many technological processes related to treatment of liquid products. Various cavitation methods with using acoustic, hydrodynamic or electrohydraulic techniques have presently become widespread for enhancement of hydrodynamic, chemical, biochemical and biophysical processes in different production technologies.

Cavitation processes are usually carried out on a molecular scale. It allows purposefully influence the physical and chemical properties of a processed product. Powerful cavitation actions result in mechanical and thermal breaking up protein molecules, micelles and the bacteria cells, as well as in enhancement of sonochemical reaction, appearance of free radicals and other micro-scale phenomena.

Implementation of cavitation mechanism supposes creation of extremely powerful dynamic pulses in disperse liquid system, which are capable of breaking small solid dispersions and even micro- and nano objects, as well as dramatically affecting the kinetics of chemical and biochemical reactions in liquid solutions

In order to realize the cavitation phenomena it is necessary that pressure in liquid be decreased in a short time to values well below the saturated vapor pressure of the liquid at given temperature ($p_l << p_{sat}(T_l)$), and then be quickly increased to values $p_l > p_{sat}(T_l)$ (Fig.1). It is worth noting that in processes of acoustic or hydrodynamic cavitation the fluid pressure may be reduced to negative values due to the action of stretching stresses (see Fig.1). Under these conditions liquid is known to be in an extremely unstable (metastable) state. Until the condition $p_l < p_{sat}(T_l)$ is satisfied in a bulk of the fluid, there would inevitably be occurred formation and intensive growth of a large numbers of vapor bubbles, so-called cavitation cluster [1].

After rapid increase of liquid pressure to the values of $p_l > p_{sat}(T_l)$ the vapor bubbles are intensively collapsed with radiating local high-amplitude pressure pulses,

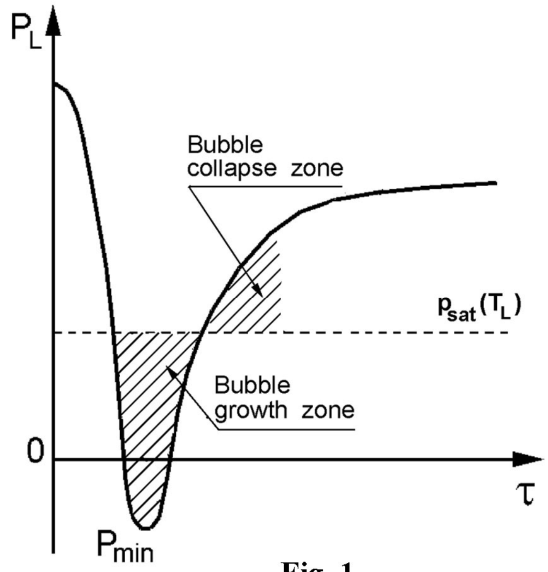

Fig. 1

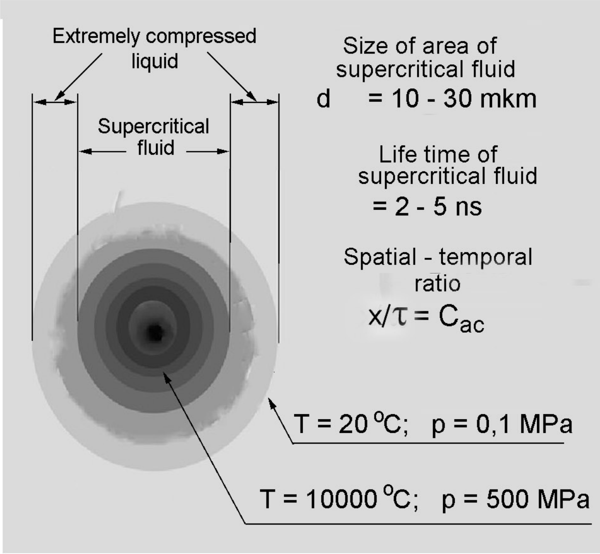

Fig. 2

Fig.1. Characteristics of variation in time of pressure in a local liquid volume for realization the cavitation phenomena.

Fig.2. Schematic presentation of collapsing cavitation bubble in the state of nano-scale and short-lived supercritical fluid.

Characteristic values of size, lifetime, pressure and temperature gradients

which are accompanied by powerful dynamic effects on the nearest microdispersion. Local spatial scope of the cavitation pulse action is about 30 μm. The lifetime of the cavitation cluster is evaluated on a scale of microseconds.

The temporal and spatial scale factor of dynamic effects, which are created by oscillating cavitation cluster, must match the characteristic size of the object and the characteristic time course of biophysical processes.

The characteristic collapse time is much shorter than the characteristic time for heat transfer and therefore this stage of the bubble compression process is considered to be adiabatic. As a consequence, collapsing bubbles are heated to extremely high temperatures. From known estimates maximum values of temperature and pressure inside the collapsing bubbles can exceed 10000 K and 500 MPa, respectively [2-5].

Thus, during the short period of time (of about 10 ns) the very compressed bubble and its nearest environment are in a state of supercritical fluid [2.3].

By definition, a supercritical fluid is any substance at temperature_and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid [5,6]. Water in the state of supercriticall fluids is known to be suitable as a substitute for organic solvents in a range of industrial and laboratory processes.[6]. The most pronounced features of a collapsing bubble in the state of supercritical fluid are demonstrate in Fig.5.

There are a number of interesting unusual phenomena, which take place during the bubble collapse process. Dense plasma is formed inside the supercritical fluid, light is emitted, reactive radical molecules are arisen. Besides, there are developed intricate liquid micro-flows in the inter-bubble space, which are capable to deform or even break up polymer macromolecules, due to dynamic action of shear stresses.

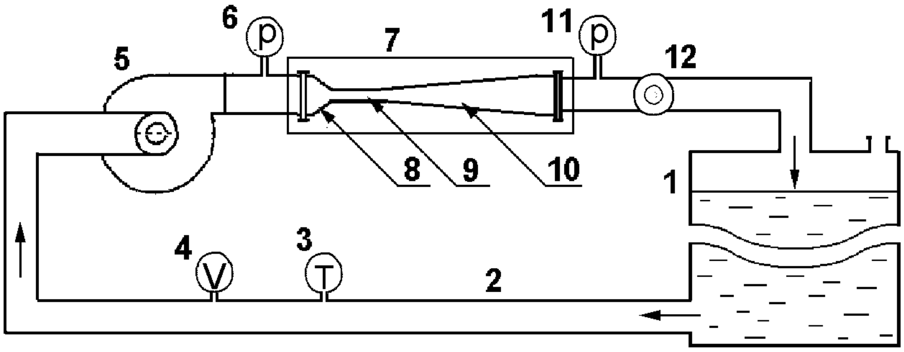

Fig.3. Experimental set-up for generation of hydrodynamic cavitation.
1 – reservoir with processed liquid; 2 – pipeline; 3 – thermometer; 4 –flow rate meter; 5. - centrifugal pump; 6 – manometer; 7. - Venturi tube; 8. convergent cone; 9. throat; 10. diffuser; 11 - manometer; 12. throttle orifice.

The occurrence of powerful cavitation effects is directly concerned with the initiation of the water hammer phenomenon on the surface of a collapsing vapour bubble. During 10 ns liquid radial velocity in the vicinity of a collapsing bubble varies from –1500 m/s to +300 m/s and, as a consequence, the value of radial liquid acceleration in the collapse zone exceeds $8\cdot10^{12}$ m/s^2.[2]. So high magnitudes of dynamic parameters and thermal effects of cavitation are likely sufficient to destroy not only the relatively weak intermolecular energy bonds, but also the much more strong intramolecular bonds. Thus, for a protein molecule with a molecular mass 50 kDa maximum inertial force associated with acceleration of ambient liquid, is about 650 pN (pikonewton), whereas the force_necessary_for the fracture of an C–C bond in long-chain molecules is equal to 450 pN [7].

In various hydrodynamic cavitators, such as Venturi tubes, rotary pulsation apparatus, centrifugal pumps and other, the above-mentioned conditions for cavitation occurrence are fully realized [2,8,9]. Industrial use of a particular type of cavitation reactor depends on the given technological challenges posed and on the level of specific energy costs as well [3,9,10].

To study the processes of hydrodynamic cavitation a laboratory setup was designed, which can be regarded as a static type cavitation reactor. As a hydrodynamic cavitator the profiled Venturi tubes have been used. Schematic diagram of cavitation reactor is shown in Fig.3. The circulation loop includes a reservoir with a processed liquid, pipeline, centrifugal pump, Venturi nozzle, as well as measuring instruments (manometers, thermometer and flow rate meter). In operation of the device the liquid, contained in reservoir under atmospheric pressure, circulates with the centrifugal pump through the Venturi nozzle and the pipeline. In the experiment, the pressure values in the inlet and outlet of the nozzle, temperature and fluid flow rate were registered continuously.

The pipe cross section diameter d_0, which was the same at inlet and at outlet nozzle, is equal to 42 mm. Convergent angle β_{con} is 90°, and divergent angle of the diffuser β_{dif} is 12°. The nozzle throat length L_{thr} equals 20 mm. The nozzle length L_0

depends on the specified values of other constructive parameters – d_0, L_{thr}, β_{con}, β_{dif}. The research has been carried out for different values of nozzle throat diameters d_{thr} – from 4 mm to 16 mm.

The pressure at nozzle inlet p_0 can be varied in the range of 2 to 4 bar. In this study the only value of p_0= 4 bar was used. The pressure at nozzle exit p_{ex} (back pressure) was varied by a throttle orifice with changeable cross-section area. To evaluate the degree of back pressure influence on the cavitation cluster behavior a parameter φ_{ex} is introduced, which is defined by the ratio of useful area of the throttle orifice to the cross-sectional area of the pipe, and is given in %. Increasing φ_{ex} from 0 to 100% lowers back pressure value from $p_{ex} = p_0$ to $p_{ex} = p_a$.
Together with back pressure p_{ex} (or area ratio φ_b) throat diameter d_{thr} is one further important factor, affecting the cavitation processes within the nozzle.

When liquid flows through the narrow throat of the nozzle with a sufficient high velocity, the pressure in the liquid drops far below the saturated vapor pressure value, that is, the above condition $p_l << p_{sat}(T_l)$ is satisfied. As a result, a great number of growing vapor bubbles arise there and in the throat outlet a cavitation cluster should be formed. The subsequent rapid increase in pressure inside the diffuser leads to the collapse of the cluster and radiation of high-amplitude pressure pulses.

In the first phase of this research the change in pressure and fluid velocity along the Venturi nozzle length, as well as the liquid volumetric flow have been determined for given values of constructive and regime parameters - d_p, L_{thr}, d_{thr}, β_{conf}, β_{dif}, p_a, p_0, p_{ex} and φ_{ex}. On this stage of our investigations distilled water at 20°C was used as a model liquid. The values of fluid flow velocity and pressure in an arbitrary section of the Venturi nozzle were determined theoretically. The problem was solved in the one-dimensional formulation with the coordinate x directed along the axis of pipe. The origin of x is in a cross-section of the pipe at a specified distance ahead of inlet of the convergent cone. In the given cross-section liquid pressure $p_l(0) = p_0$ and velocity $v_l(0) = v_0$, where v_0 is the flow velocity in the pipe with diameter d_0. From the condition, that volumetric flow rate in the loop is to be constant, it follows, that in any cross-section of the nozzle with coordinate x the fluid velocity $v_x = v_0 d_0^2 / d_x^2$, where d_x is nozzle diameter in this cross-section. The Bernoulli's equation for the initial cross-section and for a cross-section of the nozzle with coordinate x can be written as

$$p_0 + \rho_l \frac{v_0^2}{2} = p_x + \rho_l \frac{v_0^2}{2} \frac{d_0^4}{d_x^4} + \left(\zeta_{fr} + \zeta_{loc}\right) \cdot \rho_l \frac{v_0^2}{2} \frac{d_0^4}{d_x^4}, \tag{1}$$

where ρ_l is the liquid density; $\zeta_{fr} = \lambda \cdot x / d_x$ is the friction factor, corresponding to frictional pressure losses between these cross-sections; $\lambda = f(\mathrm{Re})$ is the pipe friction coefficient; ζ_{loc} is the local resistance coefficient, corresponding to hydraulic losses due to sudden change of cross-section area.

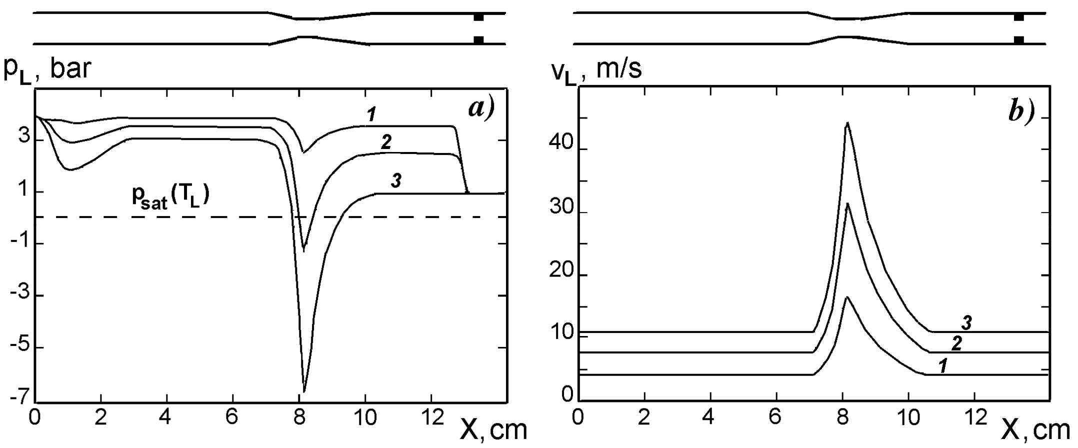

Fig.4. Variation in pressure p_l *(a) and velocity* v_l *(b) of non boiling water flow along the Venturi nozzle length at different values of orifice to pipe area ratio* φ_{ex}*: 1 – 25%; 2 – 50%; 3 – 100%. Operation parameters:* d_{thr} *=18 mm;* p_0*=4 bar;* T_l *=20°C.*

The fluid pressure in a cross-section with a coordinate x is given by

$$p_x = p_0 - \left[\left(1+\zeta_{fr}+\zeta_{loc}\right)\frac{d_0^4}{d_x^4}-1\right]\rho_l\frac{v_0^2}{2}. \tag{2}$$

In the nozzle outlet diameter $d_x = d_0$ and the pressure $p_x = p_{ex}$. Substituting these values into equation (1), we find the inlet flow velocity

$$v_0 = \sqrt{\frac{2\left(p_0 - p_{ex}\right)}{\rho_l \sum\left(\zeta_{fr}+\zeta_{loc}\right)}}, \tag{3}$$

where $\sum\left(\zeta_{fr}+\zeta_{loc}\right)$ is the sum of all frictional and local hydraulic resistances in the range $\left(0 < x < L_0\right)$. [11]

A special computer program has been developed to calculate the distribution of liquid pressure $p_l(x)$ and flow velocity $v_l(x)$ along the Venturi nozzle using the equations (2) and (3). In Figures 4 some results of these calculations are shown with respect to flow of non-boiling water through the nozzle for given regime parameters.

From Fig.4-a it can be seen that with increasing useful area of the throttle orifice φ_{ex} flow rate v_l rapidly increases and fluid pressure p_l sharply drops in the nozzle throat. When area ratio $\varphi_{ex} > 50\%$ (p_{ex} < 2,6 bar) the above condition $p_l < p_{sat}\left(T_l\right)$ is satisfied inside the throat and, in accordance with Fig.1, there should arise and grow a large number of vapor bubbles. In the diffuser the fluid pressure quickly increases up to values $p_l > p_{sat}(T_l)$ and on this account the intensive collapse of the cluster would be observed. Lifetime of the cavitation clusters, their oscillation frequency and amplitude values of the pulses are_significantly affected by such operation parameters as d_{thr}, p_0, p_{ex} and T_l.

To investigate the dynamic cavitation effects two our earlier models of bubble dynamics have been used [2]. One of these has been produced to adequately predict

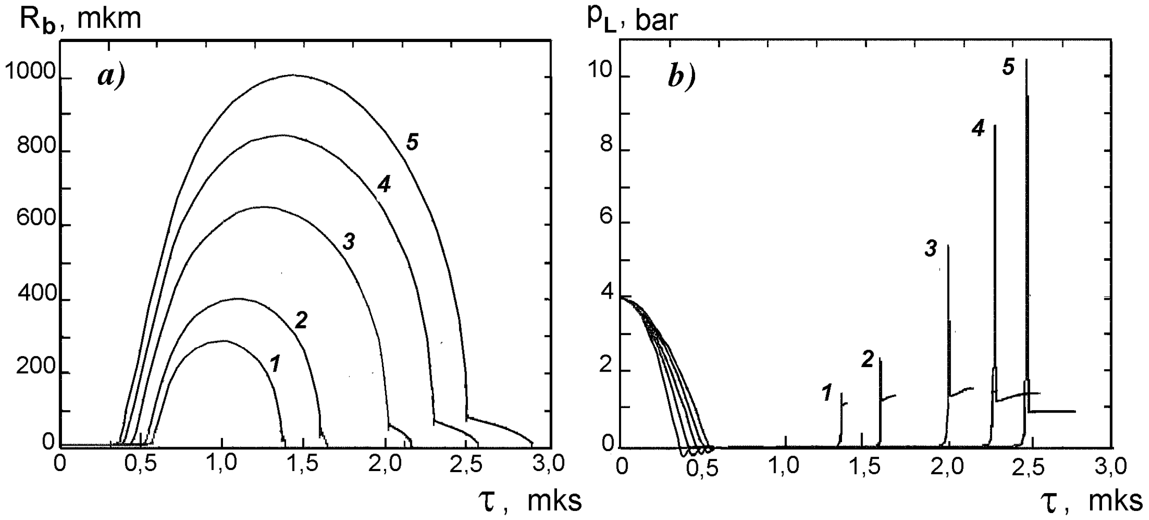

Fig.5. Variation with time in the bubble radius in a monodisperse bubble cluster R_b (a) and the volume averaged liquid pressure within the cluster $\overline{p}_l$ (b) during water flow through the Venturi nozzle at different values of the back pressure p_{ex}: 1 – 2,75 bar; 2 – 2,50 bar; 3 – 2,00 bar; 4 – 1,50 bar; 5 – 1,00 bar.

Operation parameters: d_{thr} =8 mm; p_0=4 bar; T_l =20°C.

the behavior of a single vapor bubble in viscid compressible liquid after changing external pressure. A complete set of ordinary equations includes the conservation equations and a state equation for the gaseous phase. Heat and mass transfer through the interface is considered in the term of molecular-kinetic theory. The model is applicable over all the temperature range of liquid phase existence right until the critical point. Another model, constructed on the basis of the first one, is intended for analyses of micro-flow patterns in liquid phase between the bubbles and allows a detailed description on a microscopic scale the both pressure and velocity fields in the inter-bubble liquid space of the cluster.

Within the framework of these models the change of radius of a separate bubbles $R_b(\tau)$ in a cavitation cluster can be determined, as well as the pressure in the liquid phase inside the cluster $\overline{p}_l(\tau)$ averaged over the cluster volume.

In order to calculate the dependences $R_b(\tau)$ and $\overline{p}_l(\tau)$ in a specific cavitation process inside the Ventura nozzle it is necessary to found an equation that describes the variation with time in external liquid pressure $p_{l\infty} = f(\tau)$, concerned with variation in flow velocity $v_x(x)$. The external pressure $p_{l\infty}(\tau)$ in the vicinity of a separate bubble, moving with the flow, can be calculated with the aid of the experimental dependence $p_l = f(x)$ in the form of the equation (2). The temporal τ and spatial x coordinates are related by the correlation $\tau = x/v_x$. Such approach provides a means for estimating the effects of cavitation in the Venturi nozzle.

In Fig.5 the radius of a separate bubble $R_b(\tau)$ in monodisperse cluster and averaged pressure in the inter-bubbly space within the cluster $\overline{p}_{l(\tau)}$ are presented as function of time τ for different values of back pressure p_{ex}, conditioned by area ratio

φ_{ex}. Back pressure at outlet the nozzle is shown to dramatically affects the maximum size of the bubbles, the cluster lifetime and the amplitudes of the cavitation pulses. It allows the prediction of_the optimum operation conditions for cavitation processing of a material, taking account of the reducing energy consumption.

The practical task of the given study is to substantiate the possibility of using the Venturi nozzle, as a cavitation reactor, for making fine-dispersed microbiological materials with unique properties. The subject of particular interest, both from scientific and practical points of view, are supramolecular structures formed by the molecules of phospholipids. Phospholipids are that of a set of complex organic amphiphilic compounds, the molecules of which, being in water, have the ability to self-organize to form closed spherical shells, what is known as liposomes.

Liposomes are closed nanocapsules, the surface of which is formed by phospholipid bilayers membrane with thickness of 4 nm. Diameter of unilamellar liposome is generally from 20 to several hundred nanometers. This structure allows the liposomes to capture and hold inside some volume of continuous liquid phase (water) and dissolved components. The inner volume of an aqueous liposome can include drugs, peptides, proteins, nucleic acids, which enables practical use of liposome to deliver them to specific organs and cells [12]. Today liposomes are used in pharmacology and medicine, food industry, agriculture and to address urgent environmental problems. Liposome production moves to the stage of large-scale production, requiring high-performance equipment with low energy consumption.

Formation of the liposome particles is carried out under mechanical dispersing the slurry of the swollen phospholipides, when the molecules spontaneously combine, to form more complex supramolecular aggregates with a thermodynamically favorable configuration of molecules. [3, 4, 5].

The known methods of dispersing the phospholipide suspension for the making of liposomes (shaking, ultrasonic processing, mixing with agitators) seem to be unfit for the industrial production of liposomal preparation because of their low capacity and undue energy consumption. The hydrodynamic cavitators, in particular, the Venturi nozzles, are expected to be perspective in the production of liposome drugs from the viewpoint of energy conservation.

Depending on the composition and processing method, the phospholipids form the following nanostructures: or large multilamellar liposomes (d_{lp}=0,5$\div$10 μm), or relatively large unilamellar liposomes (d_{lp}=150$\div$500 nm), or small unilamellar those (d_{lp}=150$\div$500 nm).

Multilamellar liposomes aggregations are linked by weak van der Waals forces with binding energy of the order of 1$\div$4 kJ/mol, which is two orders of magnitude less than the intramolecular bonds in the phospholipid molecule. Stability of multilamellar liposomes is determined by the energy of hydrogen bonds, ionic, ion-dipole, hydrophobic interaction, energy bonds of which does not exceed 40kJ/mol. At sufficiently strong action on the multilamellar liposome aggregations the unilamellar liposomes are formed, which are the smaller the higher is the impact intensity. For making the unilamellar liposomes of required size the dynamic action level should

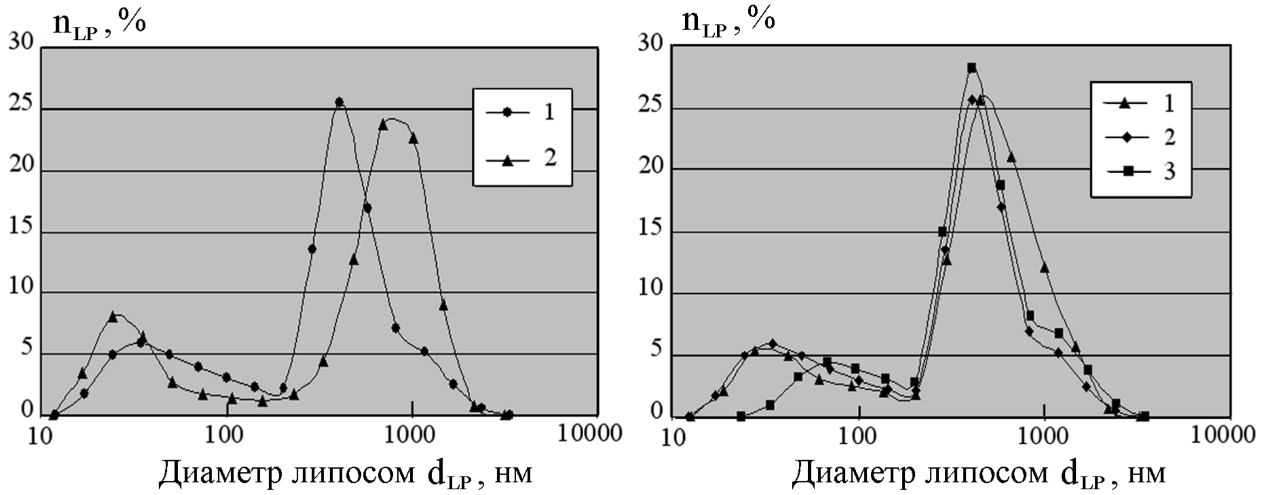

Fig.6. Size distribution of the liposome nanoparticles in aqueous suspension of phospholipides after cavitation processing in the Venturi nozzle.

Operation parameters: p_0 *=4 bar;* T_l *=40°C.*

a) Influence of the nozzle throat diameter d_{thr} *: 1 – 10 mm; 2 – 16 mm.. (*φ_{ex} *=75%)*

b) Influence of area ratio φ_{ex}*: 1 – 25%; 2 – 75%; 3 – 100%.. (*d_{thr} *=10 mm)*

correspond to the amount of energy for breaking the bonds. It is of importance that extremely strong effects can lead to undesirable disruption of unilamellar liposomes which is necessary to overcome the binding energy of about 100 kJ/ mol.

For this reason in cavitation technologies of production unilamellar liposomes with a required diameter the range optimum operation parameters is rather short

Experimental studies on the cavitation treatment of phospholipid dispersions in a Venturi nozzle for obtaining liposome nanostructures were carried out on the above mentioned laboratory set-up (see Fig.3). As an object of the study the aqueous suspension of phospholipids with concentration of 5% was used. It was required to make stable liposomes with mean diameter of about 500 nm.

Experiment were done at constant values of inlet pressure p_0=40 bar and liquid mixture temperature T_l=40°C for three values of area ratio φ_{ex}: 25%, 75% and 100%. The latter allows the estimation of back pressure influence on the cavitation intensity. The throat diameter d_{thr} could change in the range from 4 mm to 16 mm

The degree of influence of the cavitation effects, arising in the Venturi nozzle, on the efficiency factor of phospholipid processing was evaluated through the size of the formed liposomes, whose diameter was measured by method of photon-correlation spectroscopy. The liposome sizes were recorder after threefold circulation of the liquid mixture through the nozzle.

Some results of this experimental investigation of the liposome formation are shown in Fig.6. It seen that the curve of size distribution exhibits two distinct areas of liposome diameter. One of them is that of small unilamellar liposomes ($30 \div 50$ nm) and another is a more extensive area with a large amount of large uni- and multilamillar liposomes ($150 \div 1000$ nm).

From Fig, 6,a it can be seen that with decreasing the throat diameter d_{thr} from 16 mm to 10 mm the mean diameter of the liposomes $\overline{d}_{lp}$ is reduced from 650 nm to 490 nm, or almost 1.5 times. When decreasing the throat diameter d_{thr} to 4 mm, the liposome diameter $\overline{d}_{lp}$ was reduced only to 450 nm, but most of the phospholipid dispersion proved to remain crude even after tenfold recirculation. Therefore, further reduction in the size of the dispersion requires unjustified high energy costs.

In Fig.6,b it can be observed that variation of area ratio φ_{ex} from 25 to 100% slightly influences the liposome diameter both in the area of small particle size and in that of large liposomes. The analyses have shown high stability of the resulting liposomes. The liposome dispersion remains unchanged after 7 days incubation of the samples at 4°C.

The results of the laboratory tests proved that the geometry of the Venturi nozzle device and regime processing parameters significantly affect the intensity of the cavitation process and the degree of dispersion that allows to propose and substantiate the optimum conditions of the process with respect to the set of technological problems.

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Застосування ефектів гідродинамічної кавітації для спрямованого динамічного впливу на супрамолекулярні структури

АНОТАЦІЯ

Розглянуто еволюцію кавітаційного кластера та рівень динамічних кавітаційних ефектів в потоці рідини всередині сопла Вентурі в залежності конструктивних характеристик та режимних параметрів кавітатори цього типу. Експериментальні та теоретичні дослідження проведено з метою обґрунтування можливості застосування сопла Вентурі як кавітаційного реактора для ефективного впливу на супрамолекулярні структури в рідині відповідно до одержання стабільних ліпосомних препаратів, які використовуються сьогодні як ефективний засіб транспортування мікродоз ліків або біоактивних речовин, до клітин живих організмів. Проаналізовано специфічні структурні особливості ліпосом, які являють собою замкнені нанокапсули з товщиною мембранної стінки 4 нм, а також величини енергії зв'язку в цих структурах. Показано, що створення кавітаційних реакторів на основі сопла Вентурі для промислового виробництва ліпосомних препаратів має значно підвищити продуктивність і суттєво зменшити питомі енергетичні витрати у порівнянні з існуючими традиційними методами.

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Использование эффектов гидродинамической кавитации для целенаправленного динамического воздействия на супрамолекулярные структуры

АННОТАЦИЯ

В данной статье рассматривается эволюция кавитационного кластера, а также уровень динамических кавитационных эффектов в потоке жидкости в сопле Вентури в зависимости от конструктивных особенностей данного сопла и от режима работы кавитатора этого типа. Конечная цель работы заключается в использовании сопла Вентури в качестве кавитационного реактора для направленного воздействия на супрамолекулярные структуры применительно к созданию требуемых стабильных коллоидных дисперсий в заданном диапазоне размеров. Рассматриваются возможности и преимущества использования кавитационных эффектов сопла Вентури в производстве липосомных препаратов.