

MECHANISMS OF DESTRUCTION AND SYNTHESIS OF LIQUID MEDIA, USED IN THE FOOD INDUSTRY UNDER NON-EQUILIBRIUM CONDITIONS

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ABSTRACT

The formation of food liquid medium structures containing at least 70% of disperse particles with high dispersiveness has been considered. The possible formation mechanisms of food liquid medium structure when slow (hydrodynamic) and quick (acoustic) processes create favorable conditions for cavitation have been studied. The possibility to control these processes for initiation of mechanical and kinetic reactions that change the structure of the medium has been demonstrated. The invert syrup has been selected as the study object. The change in the invert syrup structure before and after such cavitation treatment has been recorded with the use of metallographic microscope Nikon Eclipse MA100. The decrease in disperse phase sizes from 2–3 µm to 0.1–0.4 µm along with establishing the high uniformity of component distribution as compared to the syrup without cavitation process treatment has been detected.

1. Introduction

In the existing food production technologies practically all used media, for example, confectionery masses, are produced in large volumes [1] for which the principle of local equilibrium is applied when the formation processes of the treated media structure happen so slowly so that they can be considered as quasi-equilibrium media [2]. And the system is exposed to external impacts in its entire volume in all spatial scales from molecular to macroscopic for a considerable period of time, so the kinetic reactions between the medium components take place in the entire volume until the relevant locally equilibrium values are achieved. These features lead to a range of natural restrictions that prevent obtaining the products with the specified structural and physical & chemical properties [3,4].

The purpose of the work is the formation of food liquid medium structures with large amount of dry substances in the conditions of the combined hydrodynamic and acoustic impacts.

To obtain such products it appears that it is necessary to go beyond the scope of quasi-equilibrium approach, start using mechanisms of non-equilibrium and unsteady structure formation.

This article describes one of the possible approaches to solving the issue, the approach that is based on the combined effect of hydrodynamic and acoustic processes impacts on the structure

of the liquid disperse media (LDM) widely used in confectionery industry in the form of solutions and meltdowns [5].

The possibility to control selective microscopic processes from the macrolevel, in particular, change in macroscopic parameters is related to initiation of mechanical and chemical processes of the LDM spatial structure formation that occur at the microscopic level (Figure 1) [3,6].

When these processes run at the microlevel we hope to get response in the form of change in physical and chemical properties of the media at the macroscopic level. Such mechanisms can be expected to become the basis for manufacturing of new products with specified properties.

2. Materials and methods

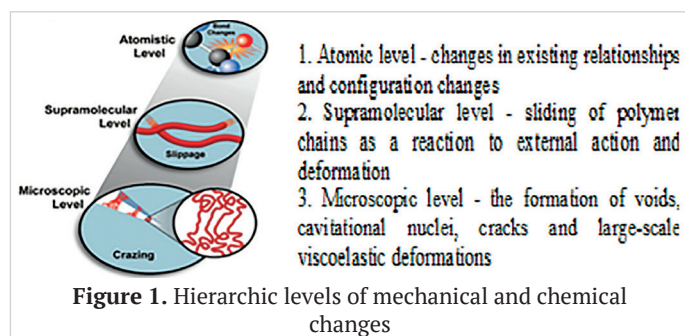
The chosen object of study is the invert syrup with the amount of dry and reducing agents about 78–80%, i. e. with 100 % decomposition of saccharose into glucose and fructose, what is widely used in the production of pastry confectionery products and marshmallow gummy products. The invert syrup produced under the conditions of cavitation impact on 20 samples and monitoring without cavitation impact on 5 samples have been considered.

In the studies the principle of the combined hydrodynamic and acoustic impacts has been applied in the laboratory cavitation machine with ultrasonic transducer fed by the power of 250 W and oscillation frequency of 21–24 Hz.

For the operational control of the process by gravimetric method, the moisture analyzer MB23 (Ohaus, USA) has been used.

The structure and sizes of the disperse particles have been determined using the microscope observation on the inverted metallographic microscope Nikon Eclipse MA100 (with resolution of ×100, ×500 in the reflected light) with the DS-L2 control device for the DS camera head (Nikon, Japan).

The reducing agents have been determined in accordance with GOST 5903–89 «Confectionery. Methods for determination of sugar».



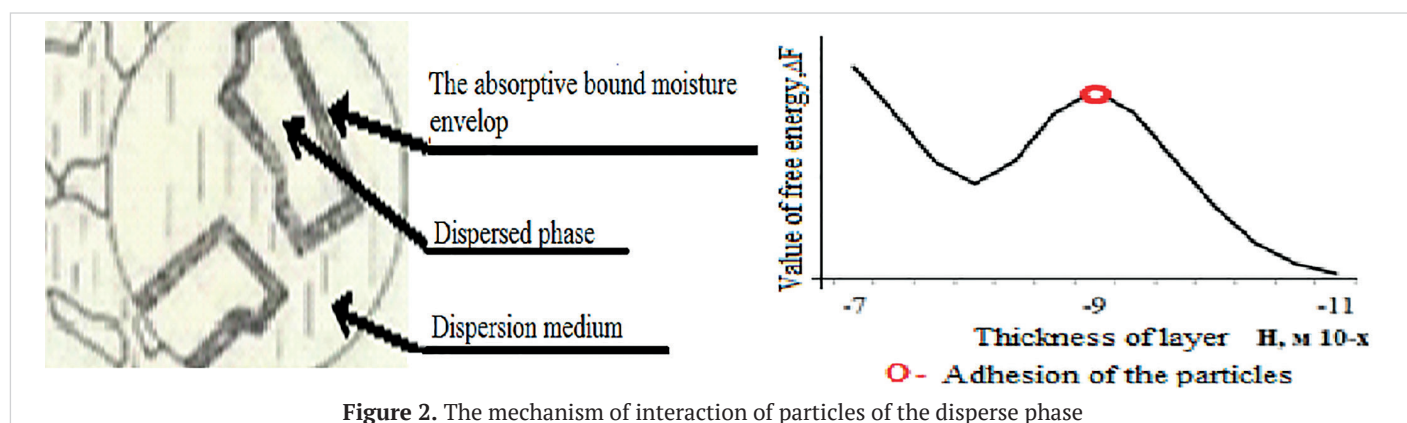


Figure 2. The mechanism of interaction of particles of the disperse phase

The sizes and quantity of particles in the visualization field of the optical microscopy with the same magnification by x500 lens and the set microscope grade scale in μm have been determined in accordance with GOST R8.774–2011 «State system for ensuring the uniformity of measurements. Disperse composition of liquid media. Determination of particle size by dynamic light scattering».

3. Results and discussion

3.1. Structural features of macromolecular media

The used confectionery media, for example, emulsions, invert and concentrated sugar syrups that differ by content of disperse particles of at least 70 % with high dispersiveness and a total absence of translational motion, have the peculiar features of gel [4, 7, 8, 9]. These features can include compressibility, significant amount of solid phase high-molecular particles that are coupled and interlink together by molecular forces forming the macromolecular structures of various configurations and sizes [9]. We will try to demonstrate the occurrence of these properties on the example of production of the invert syrup – the medium that belongs to one of the simplest macromolecular media where the structure formation processes can occur in the simplest way.

In the syrup production process, the absorptive bound moisture envelope is formed around the solid phase particles due to molecular force field that always appears as a result of non-compensated molecular forces in the interphase surface layer [9,10]. The saccharose inversion in the syrup is associated with the increase in the number of molecules, the favorable conditions for particles approach to the distance of $2H$ (disperse medium thickness) are created, and then while the distance between the particles reduces, the deformation processes increase and the free surface energy is accumulated (Figure 2) that results in formation of intermolecular bindings. The strength of these contacts is determined by molecular forces.

The inversion of saccharose with its high concentration of about 80 % is associated with the increased amount of fructose and glucose to ensure favorable conditions for formation of aggregates, chains and clusters of different spatial sizes, and their configuration can change for multiple times under the influence of both internal and external factors (Figure 3).

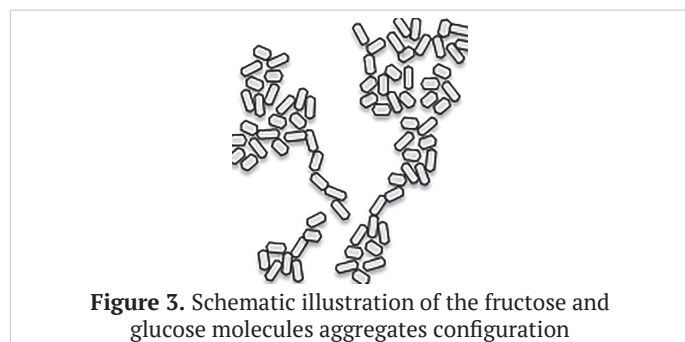


Figure 3. Schematic illustration of the fructose and glucose molecules aggregates configuration

As a result of this process the specific surface area reduces, the density decreases, and simultaneously the cavities of different sizes form. Such cavities with gas phase content are, by their physical nature, the cavitation nuclei which physical characteristics may change with time. All this indicates that the syrup can have the property of compressibility [6,9].

3.2. Cavitation dynamics and kinetics of macromolecules

The reviewed microscopic properties of the LDM are diversely represented at the macrolevel and can be used for solving various process tasks. Particularly, the cavitation nuclei dynamics can be controlled in a specified way by duly stimulating their growth and further collapse with the help of the combination of quick and slow hydrodynamic processes [1,11,12]. For example, these processes can be organized in a given manner in the LDM flow in the laboratory cavitation machine (Figure 4).

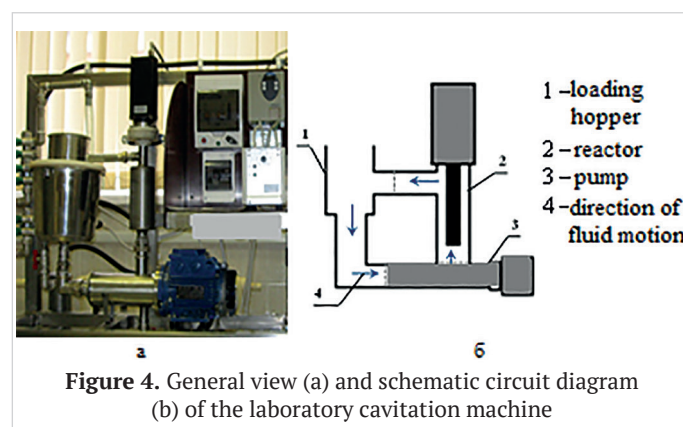
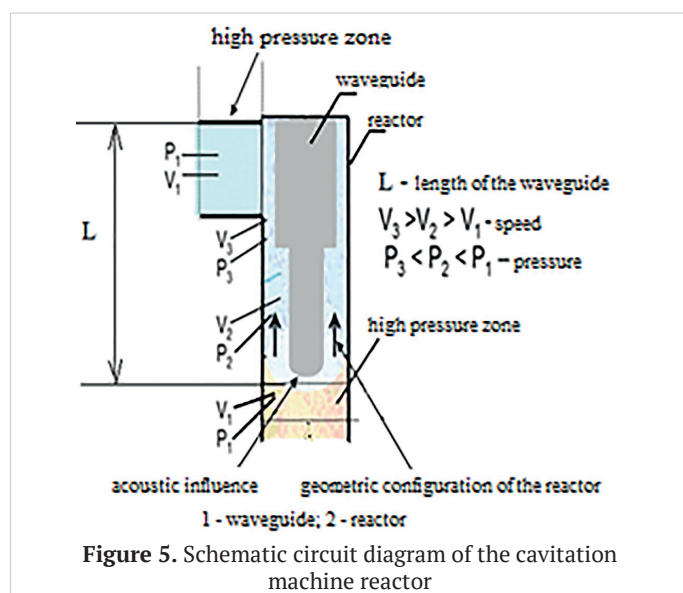


Figure 4. General view (a) and schematic circuit diagram (b) of the laboratory cavitation machine

In this case, the quick process means the acoustic impact with frequency of 21–24 kHz, and the slow process means the parameters change of the medium that flows with the given geometric configuration for specified time (τ_g). In the machine reactor, during the sharp speed increase and pressure drop (from P_1 to P_2 , P_3), the configuration of aggregates changes and the number of bubbles significantly increases (Figure 5).

The pressure increases at the reactor outlet that can lead to bubble collapse with the saved energy release practically in the point, and this, in its turn, can lead to breaking of disperse phase contacts.

It should be expected that such selective impact is capable to initiate the various kinetic reactions changing the structure of the considered media. For example, during the bubble collapse, the released energy can appear to be sufficient for water molecule excitation, ionization and dissociation [1,12,13]. That is why it can be assumed that these water particles colliding with the fragments of the broken macromolecules will join them to form new kinds of materials.



3.3. Prerequisites for structure formation

In order to determine the conditions for implementing such structure formation processes, we will assess in stages the characteristic values of time and spatial scales of the induced wave movements of the LDM and oscillation properties of separate bubbles. Depending on the ratio between the practical values, the different ways of the cavitation nuclei evolution will be implemented.

In the linear approximation, the natural frequency of bubbles oscillation for adiabatic process is determined by the ratio [14]: $\omega_b = v_s/b$, where b is the practical radius of the bubble, $v_s = \sqrt{3\gamma p/\rho}$, here γ — the adiabatic exponent for the gas in the bubble, p — gas pressure in the bubble, ρ — density of the liquid surrounding the bubble. As it was mentioned above, the quick dynamic process means the acoustic impact with practical frequency ω (see Fig. 4) that is responsible for the bubble energy excitation that is implemented by

$$\omega \gg \omega_b. \quad (1)$$

Furthermore, the length of this acoustic excitation wave λ must be less than the practical size of the bubble (or, at least, commensurately), i.e. the following ratio must be observed

$$\lambda \ll b. \quad (2)$$

In this case, the acoustic dispersion and resonance absorption of the acoustic waves by the bubbles are possible. In the opposite case which is likely to be implemented in the considered experiment, the oscillating mode will be implemented in the entire area of the acoustic impact. And the excitation can transfer from acoustic vibrations to bubbles in the entire impacted medium in general and during the time less than ω^{-1} .

In the case being considered, the slow process is the change in macroscopic properties of the liquid in the given geometric configuration, controlling the growth and collapse of bubbles. As it can be seen from Fig. 4 and Fig. 5, the main change in flow rate and pressure takes place in the waveguide area due to change in the tube cross-section. Let's assume the maximum rate V_3 in the waveguide area as the practical flow rate, and the length of the waveguide L as the practical spatial scale, then the value $\tau_s = \frac{L}{V_3}$ can be taken as the measure of the slow process.

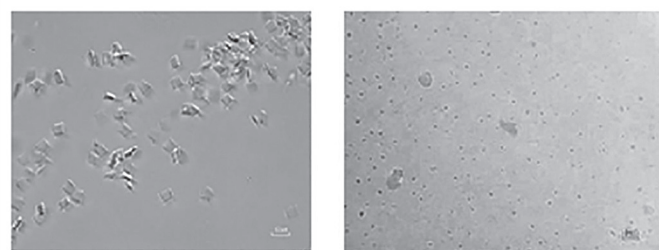
Then the condition $\tau_s \gg \omega^{-1}$ will determine the possibility of the bubble dynamics control due to change in hydrodynamic parameters of the flow. It is convenient to reformulate this ratio in the following form:

$$\frac{L\omega}{V_3} \gg 1. \quad (3)$$

Therefore the ratios (1)-(3) determine the allowable technical parameters of the system when the energy excitation of cavitation nuclei with acoustic waves and control of their dynamics are possible.

3.4. Practical results

The conducted experiments with invert syrup in the machine illustrated in Figure 4 and Fig. 5 have demonstrated the dispersiveness change with the combination of hydrodynamic and acoustic cavitation. It has been established that the sizes of the produced glucose and fructose aggregates decreased: the particles with practical sizes of about 0.1–0.4 μm were observed (Figure 7). And the produced medium is characterized by high uniformity of component distribution of 92–94% as compared to the syrup without cavitation treatment.



a) size of particles $d = 2-3 \mu\text{m}$ ($\times 500$) b) size of particles $d = 0.1 - 0.4 \mu\text{m}$ ($\times 500$)
Figure 7. Structural change of the invert syrup produced without cavitation impact (a) and with cavitation impact (b)

4. Conclusions

It has been demonstrated that the combination of quick acoustic and slow hydrodynamic impacts makes it possible to control the structure formation processes in the food media. One of possible mechanisms is related to the gas bubble formation in the studied medium with its further collapse when the bubble energy is released in the amount that is commensurable to the practical molecular scale (see Figure 1). This selective impact is capable to initiate various kinetic reactions changing the structure of the considered media [1,12,13].

That is why processes of this type can become the basis of advanced technologies in obtaining products with given properties and structure. For example the technology of making the pastry confectionery with the use of invert syrup to produce emulsion also in the conditions of the combined cavitation effects is associated with the decrease in saccharose particle size from 25 to 6 μm and increase in their quantity almost by 75 times. This provides the output of finished products with a new changed coagulation and crystallization structure with modified properties: increased absorptivity, high strength along with crumbliness and significantly reduced recyclable waste. In the future it is supposed to develop the technology of «green» fruit jelly on the basis on the invert syrup with the use of fresh fruits and vegetables to preserve native vitamins and minerals.

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