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Sonochemistry of food - area high-energy chemistry which actively is researched now in Russia and Belarus

Sonochemistry as a field of science is relate to the subject of physical chemistry and is a part of high-energy chemistry. Sonochemical method allows to have a direct impact on the reagents in endothermic liquid-phase reactions and do not require heating of the solution containing these reagents. The main factor of sonochemical reactions is the giant pulses of fluid pressure from pulsating of cavitation bubbles - acoustic cavitation. Bubbles in the compression phase is reduced in diameter to nanometer dimensions, the gas-vapor mixture inside them are heated and turns into a plasma, what is accompanied by the emission of photons - the sonoluminescence. These rays can reach the energy of ultraviolet radiation. There are even attempts to produce in cavitation bubbles filled with pairs of deuterated acetone, a inertial thermonuclear fusion [1].

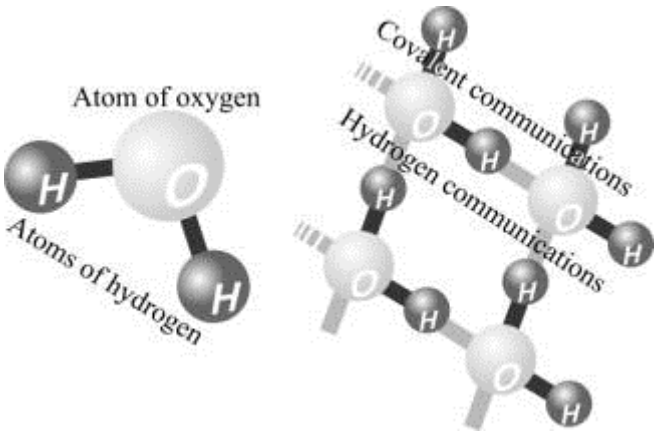
Reactions of hydration , in contrast to the hydrolysis reactions is not accompanied by the dissociations of the molecules, but the modern chemistry of tends to attribute them to the chemical reactions, because, having polarity molecules the water itself causes dissociation into ions of dissolved substances. Using this approach, which limiting the food sonochemistry by reactions aimed at the dipole-dipole and ion-dipole interactions in aqueous solutions, in Russia and Belarus in recent years studies are in this area. Developed unique research methods of sonochemical processes and devices, as well as technologies for food and drug sonochemistry and the sonochemical reactors for their implementation. In 2010, was successfully completed the state sanitary-epidemiological inspection and certification of cavitation reactors special series to implement sonochemical technologies in the food industry.

Setting sonochemical processing of solutions salt used in products from minced meat.

One of the world's leading food sonochemistry scientists – Dr. M. Ashokkumar, Professor, University of Melbourne in 2011 visited his Russian colleagues-researchers. He estimated the

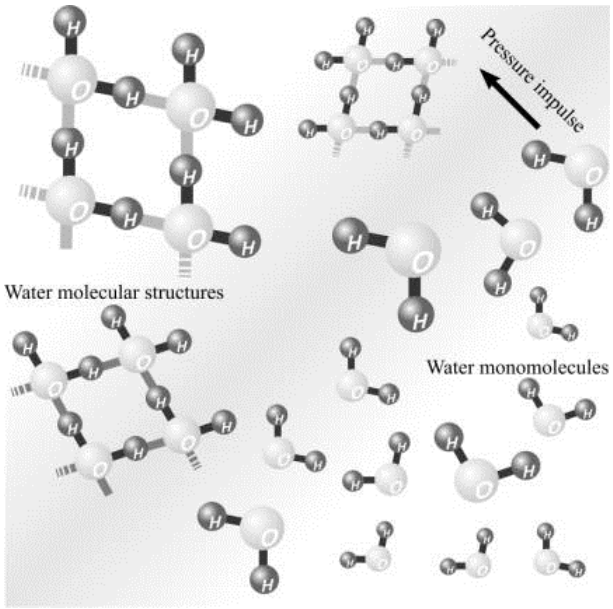
undertaken in Russia the approach to food sonochemistry, praised of their research and myself took part in them [2,3].

Earlier sonochemical is thought only the processes that occur in the gas phase inside the cavitation bubbles [4]. One of the reactions of water, which not accompanied the dissociation of water molecules – the destruction by pulses pressure from the ripple bubbles by molecular structure of water which is formed by hydrogen bonds. The presence of this structure, reminiscent of the structure of ice, even at room temperature was once again confirmed by studies at Leiden University [5] and is associated to the polarity of the water molecules. Reaction which break this structure by mass reagent (water) immeasurably superior of reactions the pyrolysis in vapor phase of bubbles.



The water molecule and molecular structure of water which is formed by hydrogen bonds.

As a result sonochemical reaction dehydration, the water for a while loses structure and becomes thermodynamically nonequilibrium state. In the Institute of Chemical Physics of Russian Academy of Sciences by measuring proton magnetic relaxation in distilled water which was subjected to sonochemical processing in the cavitation reactor, was established how long this water returned to equilibrium. There established the presence in the water after the treatment phases with different molecular mobility, the separate existence of which there is approximately 2-3 *hours*. During this period, energy of cavitation the received by water is transformed into heat of hydration of water molecules themselves, that is, into heat from recovery of hydrogen bonds in an amount corresponding to the thermodynamic equilibrium.



Scheme of destroying the molecular structure of water by cavitation.

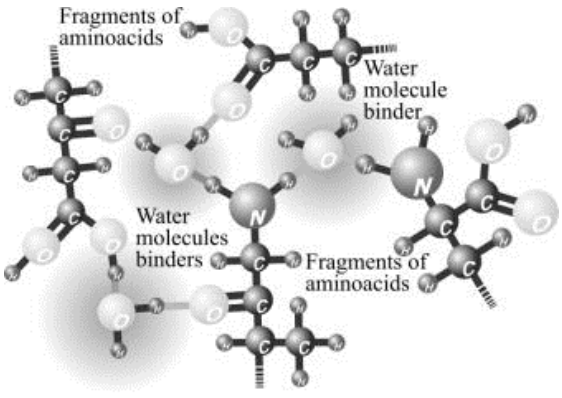
The strong increase in the viscosity of water as the temperature decreases, a paradoxical decrease in density when cooled below +4°*C*, and high in comparison with non-polar liquids, the surface tension is explained with phenomenon the self-hydration. Unrelated molecules of water may to hydrate of biomacromolecules, creating dense hydration shells around them. Hydration is the process of binding water chemicals - chemical reaction, which produces a new substance. Chemistry of biopolymers known that, for example, a protein with a molecular structure of amino acids which have carboxyl –COOH, hydroxyl –OH and amine $–NH_2$ polar groups, is capable as a result of hydration attach up to 40% water by weight. [6] According to the teachings of Acad. V. Vernadsky, the water which is connected in hydration is an integral part of the protein. It naturally increases mass of protein, because actions the mechanisms similar to those that occur during its synthesis and almost equally well how strong peptide bonds. Food raw materials in today for the most part kept in the dried or frozen, that is, has the loss of natural moisture or losing a bond with her. Therefore, finding the ability to manage the hydration of biopolymers solves a huge problem - reducing the number or excludes from food, nonfood substances, which are traditionally used to artificially increase the binding of water and in this way their mass.

Hydration process management has become one of the main directions of development of food and drug sonochemistry in Russia [3]. Hydration capacity of water in relation to other substances depends on content in water of unstructured phase. When a source of energy of disintegration of the the hydrogen bonds is disappears, they again begin to recover in the amount corresponding to the thermodynamic equilibrium, returning the absorbed energy as heat self-hydrations. The hydrogen bonds disintegration by impulse of pressure cavitation occurs as is shown in figure:

$$H_2O + H_2O + ... + H_2O \rightleftarrows m(H_2O)_n + 25\frac{n \cdot m}{N_A}\ kJ, \quad (1)$$

where: m – the number of molecular water associates in the reaction; n – the number of water molecules is forming a stable associates; N_A – Avogadro's number.

Since the heat of vaporization of water is equal to 44 *kJ/mol*, then she may be to devoid of structure by heating. But if the goal is to increase the degree of hydration of biopolymers, which are themselves unstable to thermal denaturation, thermal fracture mechanism of hydrogen bonds is not acceptable. There are many known ways of destruction of the structure of water without her heating. These include all methods of mechanical action, such as processing in a colloid mill or in a disintegrator of rotary type, and sometimes transfer the energy using the polarity of water molecules [7]. A researcher working with the water is prepared by the last way for kneading dough on baking, found that thickness of the hydration shells of protein molecules is reduced and formed a more flexible structure of the protein. This supports the hypothesis of the structuring of protein by means hydration [8]:



The structuring of protein by means hydration

These techniques improve the solvent power of water is doing by means changing her energy state at the expense of energy transformation different nature, temporarily deducing it from thermodynamic equilibrium. The advantage of sonochemical effect in is that the original chemical composition of the water does not matter. On the contrary, the water may contain dissolved in any amount or suspended solids and they will not be lost in the process of disintegration, as in the case of membrane cleaning and do not to form undesirable chemical compounds as at electrolysis. The latter is particularly important because for foods the content of mineral substances and the content of useful trace elements is controlled by dissolving them in incoming water. The cavitation in water is accelerate dissolution, ions of dissolved substances get the dense hydration shells, which reduces their ability to participate in unwanted chemical reactions. This is another advantage ofsonochemistry.

Known a method of processing grain aqueous solution of propionic acid before placing it into storage [9] and the method of wetting grain with water (his conditioning) at production from it flour [10]. In these methods, the liquid is exposed to ultrasound. Acoustic processing power is not set explicitly, but in the second case is required to form hydroxyl ions and synthesis of hydrogen peroxide which is known to be implemented in two ways:

$$OH + OH \rightarrow H_2O_2 \quad (2)$$

$$O + HOH \rightarrow H_2O_2, \quad (3)$$

where one of its part formed from of the synthesized hydroxyl ions, in the other is involved dissolved in the water oxygen [11]. Therefore in [10] is provided preliminary oxygen saturation of water by means forced aeration. The remaining hydroxyl ions in the water further destroy the structure of the grain due to the effect of ion cracking. A hydrogen peroxide has detrimental effect on the microflora and decomposed by enzymes of grain. Decomposition has explosive character, which also destroys the endosperm of kernels. But this method of preparation of water for hydration food stuff which include fats is not suitable, because they can oxidize, leading to a deterioration of taste and reduce the shelf life of products prepared from hydrated that way biomass. In Russia and Europe was patented a sonochemical method of hydration of proteins meat by water which processed in cavitation reactor at the amplitude of the sound pressure in the 2 ... 23 times higher than the hydrostatic pressure in him [12]. This method is not widely adopted due to short shelf life of foods, such as sausages made with its use, even though it saves raw materials [13].

In Russia created the method sonochemical processing of brine [14] and sonochemical method of processing the water and water solutions to hydration biomass [15]. In they hydrogen peroxide is not synthesized in significant quantities, because the amplitude of the ultrasonic reactor pressure does not exceed twice the value of the hydrostatic pressure in the liquid. But the decrease of the pressure amplitude of ultrasound which causes cavitation and whose square of which is proportional the acoustic power of the process, has led to a drastic decrease of performance of the sonochemical processing. From the general physics we know that necessary for any action energy is equal to the product of the power of the impact on its duration. Therefore, such methods in the production of, for example, meat products have been used only in catering [13], where produced small quantities of products.

But there is a way of hydration of biopolymers by sonochemical processed water or solutions on its basis [16]. In it sonochemical processing carry out in the cavitational reactor with an average amplitude of sound pressure of the elastic wave exceeding hydrostatic pressure not less

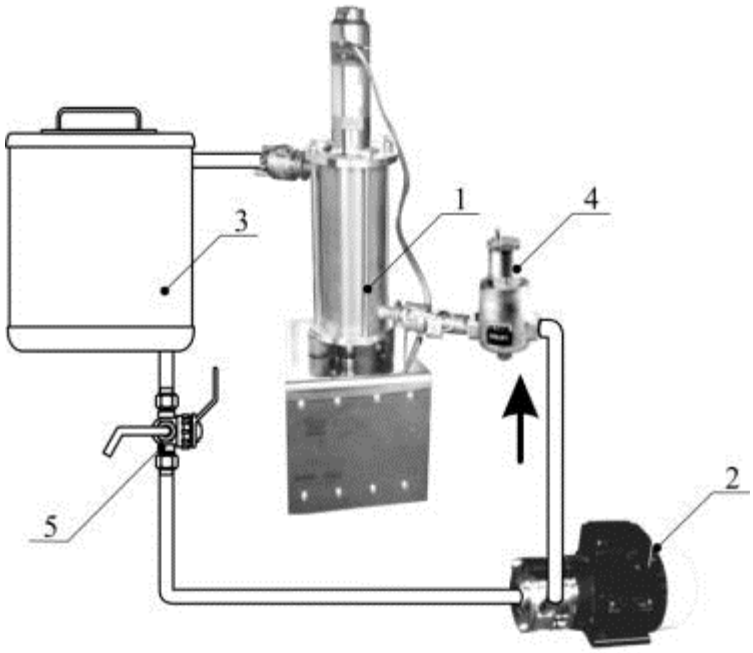
than in 5,5 times. In the description of this method examples of its implementation are given. In the first example at hydration of proteins of a gluten of grain of wheat is received the increase in weight of a crude gluten and reduction of the general microflora. It is known that the adipose component of the grain is in its embryo, which prior to processing of grain into flour is separated from the grains. Therefore, the method has shown here a positive result. In the second example sonochemical treatment of an aqueous suspension of mustard seeds to extract from it the substances used in the manufacture of mayonnaise, microbiological purity of the suspension medium and the content of organic acids in it increased. In the following example as a result of water processing for preparation of a brine at production semi-finished products from chopped meat the content of microflora in forcemeat decreased, fat – is increased. It is known that the analysis of the content of fat in foodstuff and semi-finished products is carried out methods of extraction by Soxhlet and Randall. Therefore it is possible to assume that the paradoxical increase in the content of fat in meat is connected with the increased extractability of products of its oxidation which formed at hydration by processed water. The given examples of implementation [16] confirm that oxidizers in water nevertheless are formed in sufficient quantities for oxidation of fats in a hydrated biomass.

Problem of the last researches conducted by us is search of a way of decrease in the content in the processing water, including, which being the environment of solution or disperse system, oxidizers like hydrogen peroxide without decrease in acoustic power of the sonochemical processing, and without to reduction its productivity.

In [11] are given experimental data about H_2O_2 exit depending on the spent energy at synthesis by ultrasonic fluctuations. Is noted, what hydrogen peroxide exit strongly depends on a chemical composition of water, in particular, from the content in it the dissolved oxygen of air. Later was a published result of researches about an exit the hydrogen peroxide in the two-factorial experiment [8]. By means of it it is established that this exit is optimized by function of two variables. Existence of a local maximum is explained with by heating of water from internal friction, decrease in the contents in it of oxygen and thermal decomposition at increase H_2O_2 in time of processing and acoustic power high over optimum values. It is known also that coincidence of collapse of cavitational bubbles practically any primary diameter in water from the end of the period of an acoustic wave which causing cavitation is comes with amplitude of pressure approximately equal to five hydrostatic pressure [13]. It is a so-called mode of sinperiodic cavitation. At increase above this value the potential energy responsible for the size of a cavitational erosion and a sonoluminescence both in singlebuibble and in multibubblle cavitation remains to constant, and the kinetic changes only. Thus, the mode of sinperiodic cavitation is most energetically favorable. But, as it was shown above, usage [16] in the food industry is hinder the education in hydrogen peroxide water in significant quantities. If to consider that the exit of hydrogen peroxide depends on the content in water of the dissolved oxygen of air, there was a hypothesis that is possible to lower it, previously having subjected water or water solution of deaeration.

In [17] is described the fact of an invariance of permanganat oxidability of solutions of free organic acids, which is subjected sonochemical processing with an amplitude of acoustic pressure no more than 2 *atm*. Influence of processing on hydration ability of water was estimated there by efficiency of dissolution of tableted NaCl. Therefore experimental check of correctness of this hypothesis it was carried out as follows.

Expenses of energy necessary on sonochemical water processing are established in [15]. At the room temperature they make about 2 $kW \times h/m^3$. In reactor described in [17] is installed the magnetostriction converter with an electric power of 630 *W*, its absolute productivity makes 0,16 m3/h. Productivity of the reactor of the *Oil Tech Production OY* company (Tallinn) in [18], used in experiments, with piezoelectric converters is equal 1,08 m^3/h, that is amplitude of sound pressure here is 2,6 times more and is equal to amplitude of sinperiodic cavitation. Considering it, prepared three identical samples of solution of 0,4 *mg/l* tannin which strongly predisposed to oxidation by hydrogen peroxide. The permanganat oxidability of solution measured by a method of Kubel, made 5,2 mgO_2/l. The first sample considered control and within 3 *min* in experimental installation



Experimental installation with the cavitational reactor of the company *Oil Tech Production OY*:
1 – reactor; 2 – pump; 3 – to a receiver;
4 – deaerator Caleffi 551; 5 – three-running crane.

recirculated it by means of the pump via the reactor which was disconnected, receiver and turning on deaerator after the pump. Method [16] was doing out on the second sample with recirculating of solution within 1 min. The solution by means of the pump passed via the switched-on sonochemical reactor, a receiver and at the deaerator. Hypothesis checked on the third sample is processing it as follows: within 2 *min* solution recirculated by means of the pump via the switched-off sonochemical reactor, a receiver and deaerator, then for 1 *min* turned on the reactor. In all three cases after the expiration of time of processing the pump disconnected, the crane to solution plum and measured on ISO 8467 permanganate oxidability. In total five series of experiences were doing. Results are shown in the table in the form of average values with ranges of mean square deviations.

Table

PARAMETER	UNIT	VALUE		
		Sample 1	Sample 2	Sample 3
Permanganate oxidability	mgO_2/l	5,12±0,05	2,31±0,07	5,09±0,05

From the table it is visible that permanganate oxidability of samples 1 and 3 is almost identical whereas at a sample 2 it is lower. It means that the part of tannin was oxidized by the hydrogen peroxide which formed in the course of sonochemical processing. Further compared results of dissolution of the tablets NaCl during identical time by immersion them in the processed and non processed water. Results for sample 3 is similar to a photo from [17]. It is visible that the difference of reduction of volume of tablets dissolved in usual and to the sonochemical processed water is almost identical. But in a sinperiodic mode it was required to time for sonochemical processing much less.

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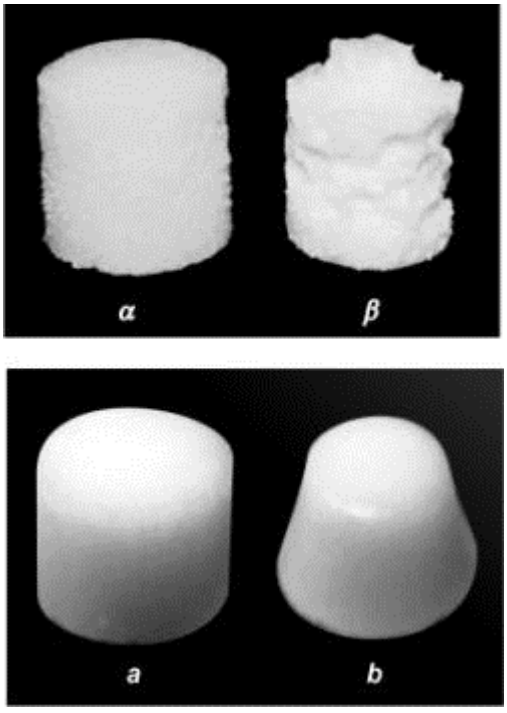

Tableted NaCl after exposure to normal water *a* (*a*) and water, which subjected sonochemical processing *b* (*b*) in accordance with [17] (top) and with [16], but with deaeration (bottom).

The experiments have confirmed the validity of the hypothesis, as the yield of hydrogen peroxide really depends on the content in the water of dissolved oxygen. This allows you to use in the food sonochemistry most energetically favorable mode the sinperiodic cavitation [13] subjecting the water or an aqueous solution of forced deaeration. At the same time hydration and solvent power of water can not fall off and time for sonochemical processing required less than traditionally accepted in food sonochemistry. That is use in the food industry the sonochemistry will be absolutely safe, if the take action which prevent the formation of hydrogen peroxide in water way remove from the solution the atmospheric oxygen.

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