EFFECTIVE SUSPENSION LAYER IN ULTRASONIC TREATMENT OF PLANT BIORESOURCES

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Abstract. The task of finding the rational parameters of plant raw material processing to increase the production of biofuel efficiency does not lose its importance. Experimental studies on ultrasonic cavitation treatment of plant raw materials in the technology of obtaining a promising second-generation biofuel (biobutanol) were conducted. Rapeseed straw was used as a characteristic crop. The study used an ultrasonic cavitation unit with a capacity of 4.93 litres and emitters with a total power of 720 W and an ultrasonic frequency of 28 kHz. The ultrasound intensity was 2.2 $W \cdot cm^{-2}$. The weighted average particle size of rapeseed straw was 0.78 mm. The dry matter content in the aqueous suspension was 10%. As a result of the study, it is established that the layer of suspension in the working chamber of the ultrasonic cavitator has a significant impact on the efficiency of biobutanol production. The effectiveness of this factor increases with increasing the duration of ultrasonic treatment. Compared with the control, the specific content of biobutanol was 1.22 ± 0.04 $g \cdot l^{-1}$ and 1.24 ± 0.03 $g \cdot l^{-1}$ for the treated layer of 0.03 and 0.12 m, respectively. Fermentation of the untreated material allowed to obtain 0.73 ± 0.04 $g \cdot l^{-1}$ of butanol. However, for the duration of processing at the level of 25 minutes, there was a significant increase in the amount of the obtained biobutanol for the effective layer of suspension in the cavitation chamber at the level of 0.03 m (up to 1.57 ± 0.09 $g \cdot l^{-1}$) at almost unchanged values for the layer of 0.12 m. These trends were confirmed in the treatment of the suspension with 5% dry matter content, where for the effective layer of the suspension of 0.12 m butanol yield was 1.63 ± 0.06 $g \cdot l^{-1}$ increasing to 2.44 ± 0.09 $g \cdot l^{-1}$ for the layer of 0.03 m. The yield of butanol after fermentation of untreated rapeseed straw biomass with 5% dry matter content was 0.24 ± 0.02 $g \cdot l^{-1}$.

Keywords: biobutanol, ultrasound, cavitation, plant raw materials, suspension.

Introduction

The task of finding rational parameters of the processing of plant bioresources in order to increase the efficiency of obtaining different types of biofuels does not lose its relevance [1; 2]. One of the most effective ways to prepare suspensions based on plant bio raw materials, which provides a high degree of destruction of lignocellulosic structures and increases the efficiency of further fermentation in the technology of liquid biofuels, is ultrasonic treatment [3-5].

According to the results of previous studies, important factors determining the efficiency of the process of ultrasonic treatment of plant raw materials, along with the physical and mechanical properties of raw materials are structural and technological parameters of ultrasonic equipment [6].

Based on the results of numerous studies on changes in the intensity of ultrasound in dispersed media, we can conclude that the determining influence is of the parameter of the thickness of the suspension layer on the intensity and efficiency of ultrasonic treatment. In this case, for the cavitators with radiating elements placed on the flat bottom of the working chamber, the intensity of ultrasound in the suspension will decrease functionally depending on the distance from the bottom of this working chamber. A number of authors have obtained dependences for determining the ultrasonic absorption coefficients that reflect the dissipation of ultrasonic energy by dispersed suspensions.

According to G.G. Stokes [7], the ultrasonic absorption coefficient is proportional to the square of the angular frequency and the viscosity coefficient of the suspension. In the development of these studies, it was found that the absorption coefficient is proportional to the longitudinal viscosity, which consists of the dynamic and volumetric viscosity in the absence of the frequency dependence [8]. Studies [9] on the attenuation of sound intensity in suspensions have shown that the mass content of dry matter in the suspension, its viscosity, and frequency of ultrasound have a decisive influence on the attenuation of sound. Analysing and summarizing the results of studies of the distribution of ultrasound of different frequencies in dispersed media, we can assume that for constant frequency conditions for a given liquid or suspension attenuation of ultrasound will be proportional to the distance from its source and will be linear or close to linear [10].

In view of the above, we conducted experimental studies on ultrasonic cavitation treatment of plant bio raw materials in the technology of promising second-generation biofuel - biobutanol. The research was devoted to the analysis of the influence of the thickness of the effective layer of suspension in the working chamber of the ultrasonic cavitation unit on the efficiency of disintegration of plant raw materials with subsequent production of biobutanol by fermentation.

Materials and methods

The subjects of the study were the strain of *Clostridium sp.* IMB B-7570 (IFBG C6H 5M) from the "Collection of strains of microorganisms and plant lines for food and agricultural biotechnology" of the Institute of Food Biotechnology and Genomics of NAS of Ukraine, as well as non-grain biomass of the most common crops in Ukraine [11]: soybeans *Glycine max*, rapeseed *Brassica napus*, sunflower *Helianthus L.*, barley *Hordeum*, corn *Zea mays* and wheat *Triticum sp.* (all – the harvest of 2021).

The research used an ultrasonic cavitation unit with a capacity of 4.93 litres with emitters with a total power of 720 W and an ultrasonic frequency of 28 kHz. The ultrasound intensity was 2.2 $W \cdot cm^{-2}$. The laboratory ultrasonic bath consisted of a stainless-steel gastronomic container of standardized size "GN 1/4", at the bottom of which piezoceramic ultrasonic emitters were attached with an operating frequency of 28 kHz and an ultrasonic power of 60 W each (Fig. 1).

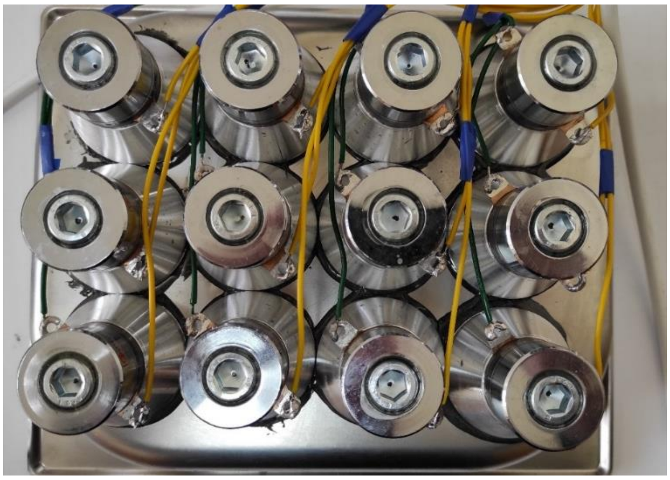

Fig. 1. **Laboratory ultrasonic cavitation unit with emitters (bottom view)**

The laboratory unit was powered by a 1.5 kW ultrasonic generator UCE-NT1500 ("UCE Ultrasonic", China), which provided the set operating time and automatic tuning of the resonant frequency of ultrasonic emitters in the range of 20-40 kHz. The weighted average particle size of vegetable raw materials was 0.78 mm. The dry matter content in the aqueous suspension was 10%.

Preliminary preparation of plant raw materials consisted of its two-stage grinding [12] to a given weighted average size of crushed particles, mixing the whole mass of crushed raw materials, preparation of suspensions with a given dry matter content, and subsequent sonication of the suspension.

The moisture content of raw materials was determined by the weight method [13]. "Elikor-5" crusher ("Electromotor" PJSC, Ukraine) was used for preliminary grinding, and "LZM-1" laboratory mill ("LIS" LLC, Ukraine) was used for the final grinding. The weighted average size of crushed particles of raw materials was determined by sifting laboratory "RLU-3" ("Status" LLC, Ukraine) with a set of laboratory sieves [14, 15]. Plant raw materials were ground to a weighted average particle size of 0.078 mm (passage from the laboratory sieve No. 64, east from the sieve No. 67). The ground raw material was mixed using an available laboratory batch drum mixer for 5 minutes.

To prepare the suspension purified tap water was used, the corresponding mass fraction of crushed vegetable raw materials, taking into account its humidity. Laboratory scales were used for weighing raw materials [16].

The specific yield of butanol per unit volume of suspension ($g \cdot l^{-1}$) was investigated depending on the height of the suspension layer (h, m), the duration of ultrasonic treatment of the suspension (t, min.) and the dry matter content of the suspension (s, %).

The duration of ultrasonic treatment of the suspension was 5 and 25 minutes, the dry matter content of 5 and 10%, the height of the suspension layer 0.03 and 0.12 m. After ultrasonic disintegration, the raw material was immediately sent for cultivation. The confidence level of the obtained data was 95%.

Results and discussion

At the first stage, experimental studies of six species of native and sonicated non-grain plant biomass as a substrate for the cultivation of the butanol-producing strain *Clostridium sp.* IMB B-7570 were conducted. For each type of raw material, the accumulation of butanol in the culture fluid after 72 hours of fermentation was determined (Fig. 2).

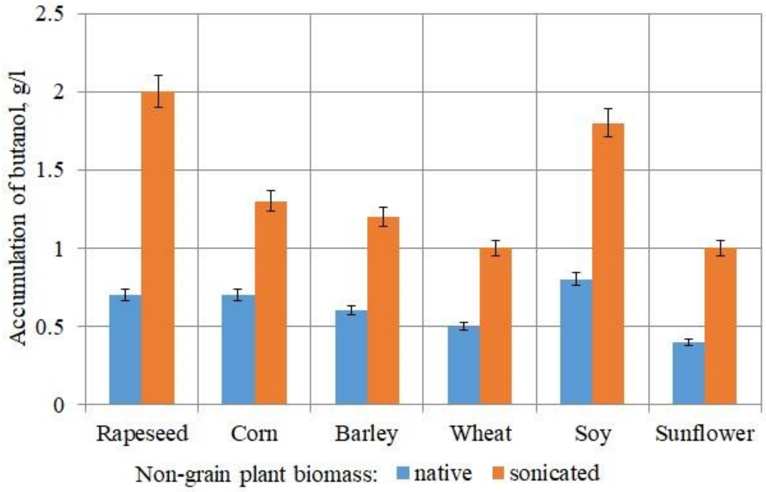

Fig. 2. **Accumulation of butanol by strain *Clostridium sp.* IIR B-7570**

It was found that culturing the strain on pre-sonicated biomass increases the accumulation of butanol in the culture fluid. It is important to establish the parameters of pre-treatment of vegetable raw materials, in particular, grinding and ultrasonic treatment, in which the yield of butanol in the cultivation process would be greatest. After fermentation of the producer strain of *Clostridium sp.* IMB B-7570 in the culture fluid all three products were found of the acetone-butanol-ethanol process.

It was found that the largest accumulation of butanol (over 0.7 $g \cdot l^{-1}$) was with the use of crushed rapeseed and soybean biomass (100 $g \cdot l^{-1}$) as a substrate. In this case, ethanol and acetone were present in small amounts – 0.05 $g \cdot l^{-1}$ and 0.02 $g \cdot l^{-1}$, respectively. Therefore, the results of previous experimental studies have shown that among all the studied crops the most promising for ultrasonic treatment, followed by use as a substrate for biobutanol, is rapeseed biomass.

Further experimental studies were conducted on rapeseed straw harvested in 2021. An ultrasonic bath with emitters with a total power of 720 W and an ultrasonic frequency of 28 kHz was used in the research. The weighted average particle size of rapeseed straw was 0.78 mm.

A total of four experiments were performed to investigate the effect of the suspension layer height and treatment time on the specific yield of butanol per unit volume of suspension (Table 1). The dry matter content of the suspension was 10%.

Table 1

Specific yield of butanol per unit volume of suspension ($g \cdot l^{-1}$)

Experiment number	**Duration of the suspension ultrasonic treatment t, min**	**Height of the suspension layer h, m**	**Specific yield of butanol per unit volume of suspension B_V, $g \cdot l^{-1}$**
1	25	0.03	1.57
2	25	0.12	1.16
3	5	0.03	1.22
4	5	0.12	1.24

As a result of the experimental studies, it was found that the suspension layer in the working chamber of the ultrasonic cavitator has a significant effect on the efficiency of biobutanol production.

It has been found that the effectiveness of this factor increases with increasing the duration of ultrasonic treatment. Studies have shown that with a duration of treatment of 5 minutes, the effect of the suspension layer on the production of butanol is not significant.

Compared with the control, the specific content of biobutanol was 1.22 ± 0.04 g·l^{-1} and 1.24 ± 0.03 g·l^{-1} for the treated suspension layer of 0.03 and 0.12 m, respectively (Fig. 3). Fermentation of the native raw material allowed to obtain 0.73 ± 0.04 g·l^{-1} of butanol. However, with a duration of treatment of 25 minutes, there was a significant increase in the amount of biobutanol obtained for the effective layer of suspension in the cavitation chamber at 0.03 m (up to 1.57 ± 0.09 g·l^{-1}) at almost constant values for the layer of 0.12 m.

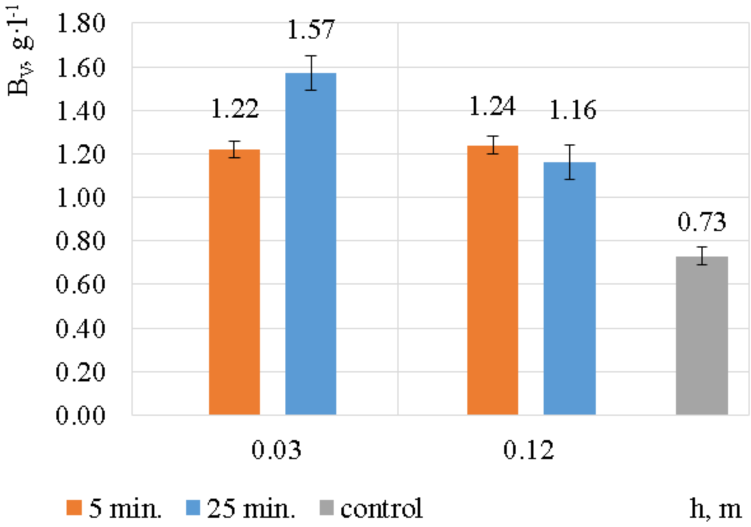

Fig. 3. **Specific yield of butanol per unit volume of suspension, g·l^{-1}** (10% dry matter)

These trends were confirmed in the treatment of the suspension with a dry matter content of 5% and the effective layer of the suspension of 0.12 m, where butanol yield was 1.63 ± 0.06 g·l^{-1} with increasing to 2.44 ± 0.09 g·l^{-1} for the layer of 0.03 m (Fig. 4). The yield of butanol after fermentation of untreated rapeseed straw biomass with 5% dry matter content was 0.24 ± 0.02 g·l^{-1}.

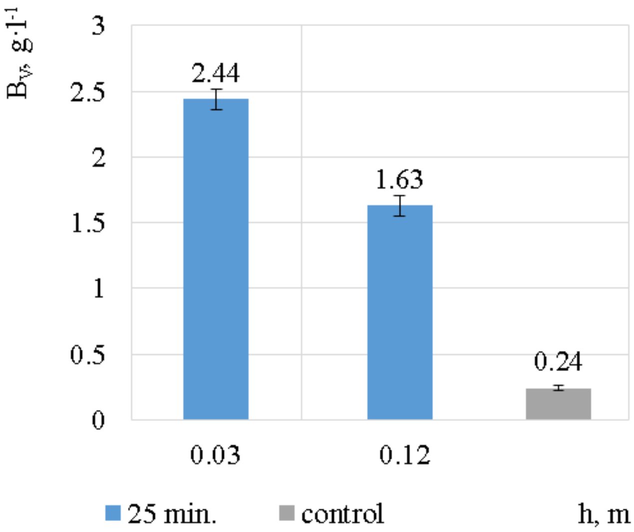

Fig. 4. **Specific yield of butanol per unit volume of suspension, g·l^{-1}** (5% dry matter)

Therefore, the results of the experimental studies have shown the feasibility of ultrasonic treatment of rapeseed biomass and its use as a substrate for biobutanol. At the same time, high processing efficiency and higher yield of biobutanol were observed at the thickness of the effective suspension layer at the level of 0.03 m.

This figure correlates with the results of other studies that link the effective cavitation effect of ultrasound in dispersed media with the distance from the emitter that does not exceed the length of the harmonic ultrasonic wave. For experimental conditions at an assumed speed of sound in the medium at 1500 $m \cdot s^{-1}$ and an ultrasound frequency of 28 kHz, the harmonic wavelength will be about 0.054 m.

Therefore, the obtained results confirm the data that the effective cavitation effect of ultrasound occurs in the layer close to the emitter, the size of which is comparable to the wavelength of ultrasound in the medium. The effective treatment of a significantly larger layer of suspension is caused by mechanical mixing of the layers under the action of ultrasound.

Conclusions

1. Among all the studied crops the most promising for ultrasonic treatment with subsequent use as a substrate for biobutanol is rapeseed biomass.
2. As a result of the research, it was found that the thickness of the suspension layer in the working chamber of the ultrasonic cavitator has a significant impact on the efficiency of biobutanol production. The effectiveness of this factor increases with increasing the duration of ultrasonic treatment for more than 5 minutes.
3. The specific content of biobutanol at 5 minutes of treatment of substrates with 10% dry matter content of shredded to 0.78 mm rapeseed straw was 1.22 ± 0.04 $g \cdot l^{-1}$ and 1.24 ± 0.03 $g \cdot l^{-1}$ for the treated layer of 0.03 and 0.12 m, respectively. Fermentation of the raw material allowed to obtain 0.73 ± 0.04 $g \cdot l^{-1}$ of butanol.
4. At the duration of treatment at the level of 25 minutes, there was a significant increase in the amount of the obtained biobutanol for the effective layer of suspension in the cavitation chamber at 0.03 m (up to 1.57 ± 0.09 $g \cdot l^{-1}$) at almost constant values for the layer of 0.12 m When treating the suspension with the dry matter content of 5% for an effective suspension layer of 0.12 g, the yield of butanol was 1.63 ± 0.06 $g \cdot l^{-1}$ increasing to 2.44 ± 0.09 $g \cdot l^{-1}$ for the layer of 0.03 g. The butanol yield after fermentation of untreated rapeseed straw biomass with 5% dry matter content was 0.24 ± 0.02 $g \cdot l^{-1}$.
5. The effective cavitation effect of ultrasound occurs in the layer close to the emitter, the size of which is comparable to the wavelength of ultrasound in the environment.

Author contributions

Conceptualization, V.B. and S.S.; methodology, S.S., V.B. and O.T.; validation, O.T., V.B. and V.K.; formal analysis, V.B and S.S.; investigation, V.B., S.S., O.T. and V.K.; data curation, O.T. and V.K; writing – original draft preparation, V.B.; writing – review and editing, V.B., S.S., O.T. and V.K.; visualization, V.B. and O.T.; project administration, V.B. and S.S.; funding acquisition, V.B. All authors have read and agreed to the published version of the manuscript.

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