Abstract: In this study, we evaluate the usefulness of mature landfill leachate (MLL) as a carrier allowing hydrodynamic cavitation (HD) of brewery spent grain (BSG). The HD experiments were conducted using an orifice plate with a conical concentric hole of 3/10 mm (inlet/outlet diameter) as a constriction in the cavitation device. The initial pressure was 7 bar and the number of recirculation passes through the cavitation zone reached 30. The results showed that complex organic matter was degraded and solubilized when cavitating the MLL and BSG mixture. The biochemical oxygen demand (BOD$_5$) increased by 45% and the BOD$_5$/total chemical oxygen demand (COD) ratio increased by 69%, whereas the COD, total solids, and nutrient concentration dropped noticeably. However, Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) revealed the generation of possibly toxic HD byproducts such as aromatic compounds. This seems to indicate that MLL could not be regarded as a suitable carrier for BSG cavitation.

Keywords: hydrodynamic cavitation; brewery spent grain; mature landfill leachate; SEM analysis; FTIR-PAS

1. Introduction

The mashing process that constitutes one of the initial operations in a brewery yields brewery spent grain (BSG) as a byproduct. This process involves solubilization of cereal grains as well as malt, which a prerequisite for appropriate extraction of wort (comprising water and extracted matter) [1,2]. Approximately 15–20 kg of BSG is produced per 100 L of beer, translating into 34 million tons of wet BSG produced each year worldwide [3,4]. BSG constitutes a lignocellulosic material that contains significant amounts of fiber (cellulose, arabinoxylans, and lignin) as well as protein, which correspond to about 70% and 20%, respectively. Additionally, various vitamins (biotin, choline, folic acid, niacin, riboflavin, thiamine, pantothenic acid, and pyridoxine) and minerals (calcium, cobalt, copper, iron, magnesium, manganese, phosphorus, potassium, selenium, sodium, and sulfur) were identified in its content [5]. The usage of BSG as animal food and as part of the human diet has been studied for a long time. Moreover, various health-related benefits resulting from the consumption of BSG compounds have been reported, one of which corresponds to the reduction of postprandial glycemic responses [6]. As a result, numerous scholars conduct studies on the application of BSG in the production of various foods, including bread, pasta, and baked snacks [7–9]. In addition, the raw material contained in BSG can be extracted or produced via chemical reactions to provide the compounds used in industry. BSG was a basis for a new adsorbent media used for the sorption of heavy metal cations [10–12]. Chen and Xiong [13] investigated the use of BSG for removal of as (III) from water. In terms of the application of BSG in energy production, several alternatives...
have been proposed—for instance, thermochemical conversion (pyrolysis, combustion), or its use as a source of different energy carriers, e.g., bioethanol, biogas, syngas, and biomass briquettes [14]. The chemical composition and abundance of BSG make it highly suitable for producing energy. BSG constitutes an effective substrate or cosubstrate for use in anaerobic digestion as a result of its high content of potentially renewable energy, over 300 mL CH\textsubscript{4} per g of total solids (TS) added and the C/N ratio of below 25 [15]. The rate of hydrolysis, biodegradability, and digestibility of BSG may be improved through various forms of pretreatment, enabling to overcome the difficulties related to the lignocellulosic matter conversion [16]. In order to utilize BSG effectively, it is necessary to use appropriate techniques and carry out disruption of the naturally ordered structure and removal of lignin, which results in reduced crystallinity of cellulose and improved material porosity [17,18]. Improving the efficiency of the processes involving the valorization of lignocellulosic materials necessitates the use of pretreatment methods. Depending on the mechanism governing the process, these methods include physical, chemical, biological, thermal, and combined ones [18]. In principle, efficient pretreatment strategies should be characterized by cost efficiency, simplicity, and should generate inhibitory or indigestible compounds. In terms of mechanical pretreatment of recalcitrant compounds, hydrodynamic cavitation (HD) was investigated as a suitable mechanism. HD involves formation, growth and eventual collapse of microbubbles or cavities, which occur over a short time interval and release huge amounts of energy at the transformation site. The cavities are formed when the pressure in a flowing fluid is below the vapor pressure at the operating temperature [19]. Afterwards, due to the pressure increase, microbubbles or bubble clouds collapse downstream from the cavitation device, creating local supercritical conditions that involve temperatures of approximately 10,000 K and pressures reaching up to 1 GPa. Currently, HD is employed in water/wastewater treatment aimed at the removal of pharmaceuticals, persistent organic pollutants, bacteria, microalgae, and viruses [20–25], biogas production [26,27], cell disruption [28,29], pretreatment of sugarcane bagasse [30], and refining of wood pulp [31]. Moreover, setting up HD is more straightforward and economical than in the case of acoustic cavitation [32,33]. Thus, a study on the pretreatment of BSG by means of hydrodynamic cavitation seems to be highly relevant. The high TS content of BSG can be reduced by diluting to a level that is suitable for the cavitation device and pump. In terms of sustainable development, the liquids which could be employed comprise municipal wastewater, certain types of industrial sewage, fluid waste, and probably landfill leachate.

This study investigates the suitability of applying mature landfill leachate as a medium for conducting HD cavitation of BSG in order to enhance its biodegradability. From a sustainable development point of view, the suitable liquids could include municipal wastewater, some industrial sewage as well as landfill leachate, but not water. So far, authors tested municipal wastewater as a carrier for BSG suspension. Another step was to investigate capability of landfill leachate for this purpose. The novelty of this work is applying hydrodynamic cavitation as a method of pretreatment of BSG as well as using mature landfill leachate as a carrier during this process.

The structural modifications were evaluated by means of scanning electron microscopy (SEM). In addition, Fourier transform infrared photoacoustic spectroscopy analysis (FTIR-PAS) was performed to assess the extent to which HD affects the possible generation of new compounds which might affect subsequent treatments.

2. Materials and Methods

2.1. Materials

The landfill leachate employed for suspending BSG was sourced from Rokitno (Lublin, Poland) municipal solid waste landfill which has operated for over 20 y. Three 35 L samples were acquired from the landfill storage tank and promptly transported to the laboratory. The experiments were conducted in triplicate. The essential parameters characterizing the
mature landfill leachate (MLL) composition were studied and the results are shown in Table 1.

Table 1. Composition of mature landfill leachate (MLL) before and after cavitation (average value ± standard deviation).

| Parameter                      | Unit   | MLL before Cavitation | MLL after Cavitation |
|--------------------------------|--------|-----------------------|----------------------|
| Total chemical oxygen demand (COD) | mg L\(^{-1}\) | 6140 ± 83             | 5470 ± 79            |
| Soluble chemical oxygen demand (SCOD) | mg L\(^{-1}\) | 4771 ± 37             | 4948 ± 32            |
| Dissolved organic carbon (DOC)    | mg L\(^{-1}\) | 1486 ± 79             | 1555 ± 69            |
| Biochemical oxygen demand (BOD\(_5\)) | mg L\(^{-1}\) | 249 ± 15              | 306 ± 16             |
| BOD\(_5\)/COD                   | -      | 0.041 ± 0.002         | 0.056 ± 0.002        |
| Total solids (TS)               | g kg\(^{-1}\) | 13.5 ± 0.2            | 13.0 ± 0.1           |
| Volatile solids (VS)            | g kg\(^{-1}\) | 3.7 ± 0.05            | 4.1 ± 0.03           |
| Alkalinity                      | mg L\(^{-1}\) | 13,052 ± 327          | 12,324 ± 308         |
| pH                             | -      | 8.11 ± 0.05           | 8.60 ± 0.02          |
| Volatile fatty acids (VFA)      | mg L\(^{-1}\) | 1178 ± 38             | 1163 ± 40            |
| Total nitrogen (TN)             | mg L\(^{-1}\) | 3705 ± 128            | 3176 ± 106           |
| Ammonium nitrogen (NH\(_4^+\)-N) | mg L\(^{-1}\) | 1707 ± 389            | 1896 ± 302           |
| Total phosphorus (TP)           | mg L\(^{-1}\) | 21.6 ± 13.7           | 21.1 ± 10.5          |
| Ortho-phosphate phosphorus (PO\(_4^{3-}\)-P) | mg L\(^{-1}\) | 19.0 ± 2.8            | 18.4 ± 2.1           |

Conversely, BSG was obtained from a small brewery located in Lublin, which uses barley as a feedstock for beer production. The BSG was sampled three times (1 kg per sampling). The samples were promptly taken to the laboratory and wet-ground by means of a screw conveyor with 2.0 mm mesh. Afterwards, cavitation of the mixture comprising the substrate suspended in 30 L of MLL was performed. In order to avoid exceeding the permissible content of TS in the mixture [34], the maximum dose (30 g wet BSG per L of MLL) was adjusted, taking into account the possible swelling properties of the wet-ground BSG as well as the configuration of the pump and cavitation device. The BSG composition is shown in Table 2, and the main properties of the cavitated BSG and MLL mixture are shown in Table 3.

2.2. Experimental Installation and Methodology

The experiment was performed in a closed-loop arrangement that involved a centrifugal pump that generated pressure as well as a cavitation device, which was connected to a circulation tank by means of pipes. In order to observe the cavitation process underway, a transparent organic glass tube, comprising a steel plate with a conical concentric having the inlet and outlet diameter of 3 and 10 mm, respectively, was assembled. The pump had a maximum operating pressure of 16 bar, a variable speed of 1000–3000 rpm, and a power rating of 2.2 kW; a thyristor regulator enabled to control the output. The cavitated mixture was pumped from the circulation tank (with the volume of 30 L) to the cavitation device and back. The connecting pipes had the inner diameter of 28.76 mm. The following devices comprised the utilized setup: a manometer for inlet pressure \( p_1 \) measurement, control valves, Keller PR-33X piezoelectric pressure gauges (1 mbar resolution) which were connected to the digital data measurement system, and an electromagnetic flow meter (0.05 L min\(^{-1}\) resolution). Keller pressure gauges were used to measure the fully recovered downstream pressure \( p_2 \), which is necessary for calculating the cavitation number. A thermocouple was used to measure temperature. Figure 1 shows the scheme of the employed experimental setup as well as the orifice plate configuration.
Table 2. Composition of brewery spent grain (BSG) (after its pretreatment by milling) [35].

| Parameter                     | Unit     | Average Value ± Standard Deviation |
|-------------------------------|----------|----------------------------------|
| COD                           | g kg⁻¹   | 307.9 ± 9.2                      |
| TS                            | g kg⁻¹   | 223.9 ± 4.3                      |
| VS                            | g kg⁻¹   | 217.2 ± 4.2                      |
| Total carbon (TC)             | g kg⁻¹   | 44.0 ± 2.2                       |
| Inorganic carbon (IC)         | % dry weight | nd                               |
| Total Kjeldahl nitrogen (TKN)| % dry weight | 3.25 ± 0.07                    |
| Cellulose (C)                 | % dry weight | 14.07 ± 0.49                  |
| Hemicellulose (HC)            | % dry weight | 41.07 ± 0.50                  |
| Lignin (LG)                   | % dry weight | 5.13 ± 0.21                   |
| Pectic polysaccharides, phenolic compounds, proteins, and monosaccharides analyzed totally (PPPM) | % dry weight | 39.73 ± 1.14                |
| Monosaccharides (MS)          | g kg⁻¹ TS | 47.54 ± 2.66                   |
| Proteins (P)                  | % dry weight | 20.3 ± 0.42                 |
| Phenolic compounds (PPh)      | g kg⁻¹ TS | 0.23 ± 0.03                    |

*a TOC ≈ TC, nd.—not detected.*

Table 3. Composition of BSG and MLL mixture before and after cavitation (average value ± standard deviation are given).

| Parameter                    | Unit     | Mixture of BSG and MLL before Cavitation | Mixture of BSG and MLL after Cavitation |
|------------------------------|----------|------------------------------------------|----------------------------------------|
| COD                          | mg L⁻¹   | 13,600 ± 420                              | 12,000 ± 307                           |
| SCOD                         | mg L⁻¹   | 6058 ± 102                                | 6139 ± 111                             |
| DOC                          | mg L⁻¹   | 1928 ± 309                                | 2527 ± 343                             |
| BOD₅                         | mg L⁻¹   | 222 ± 17                                  | 321 ± 13                               |
| BOD₅/COD                     | -        | 0.016 ± 0.002                             | 0.027 ± 0.004                          |
| TS                           | g kg⁻¹   | 17.3 ± 0.3                                | 16.7 ± 0.2                             |
| VS                           | g kg⁻¹   | 8.0 ± 0.07                                | 8.2 ± 0.06                             |
| Alkalinity                   | mg L⁻¹   | 12,395 ± 345                              | 13,950 ± 320                           |
| pH                           | -        | 8.26 ± 0.12                               | 8.49 ± 0.07                            |
| VFA                          | mg L⁻¹   | 1811 ± 211                                | 1853 ± 261                             |
| TN                           | mg L⁻¹   | 3573 ± 143                                | 3100 ± 131                             |
| NH₄⁺-N                      | mg L⁻¹   | 1677 ± 394                                | 2730 ± 388                             |
| TP                           | mg L⁻¹   | 24.6 ± 15.3                               | 24.5 ± 15.4                            |
| PO₄³⁻-P                      | mg L⁻¹   | 18.9 ± 2.9                                | 19.7 ± 2.7                             |

The study involved investigating the prospects for BSG biodegradability improvement via hydrodynamic cavitation. In the course of the process, 30 recirculation passes were carried out through the cavitation zone; the applied inlet pressure amounted to 7 bar. The pressure (marked as \( p_1 \) in Figure 1) was constantly maintained and controlled by means of a manometer. The operating time was shorter than 30 min, enabling to reduce the costs and energy consumption. The employed configuration, orifice plate, and process conditions were previously found to be optimal for improving the biodegradability of the cavitated medium (nevertheless, optimization is beyond the scope of this paper). The primary goal was to reduce the consumption of energy as well as ensure that the index of biodegradability was significantly higher than that of raw (uncavitated) substrate. The orifice plate exhibited the following hydraulic characteristics: total area of holes—
7.0686 mm², constriction parameters—1.333 mm⁻¹ and 0.0023 for α and β₀, respectively, total perimeter of holes—9.42 mm, flow rate—0.49 L s⁻¹, and orifice velocity—69.32 m s⁻¹. The cavitation number (Cᵥ) was obtained using the formula: 

\[ Cᵥ = \frac{p_2 - p_v}{0.5 \rho v_0^2} \]

where \( p_2 \)—fully recovered downstream pressure, \( p_v \)—vapor pressure of the liquid, \( \rho \)—liquid density, and \( v_0 \)—orifice velocity. In the course of the cavitation, the temperature of the liquid at first equaled 20 °C; however, it was raised throughout the experiments, since the system was not cooled in the course of operation. The observed downstream pressure equaled 95821 Pa, while the related cavitation number amounted to 0.039. The literature comprises numerous sources reporting that cavitation takes place at \( Cᵥ \leq 1 \). The lower the cavitation numbers, the better the results obtained. However, Šarc et al. [36] reported that incorrect results may be obtained if the cavitation conditions are equated with the cavitation number. The recommendation of these authors was to describe the following parameters: medium temperature, flow rate, cavitating geometry, cavitation number (indicating the method as well as location of the performed pressure measurements), and—ideally—the contents of solid and gas particles as well as the graphs of pressure fluctuation. The biodegradation improvement through cavitation involved increasing the BOD₅/COD ratio (that is, the biodegradability index, BI) and increasing the concentration of organic compounds that are easily degradable (BOD₅ and SCOD). Moreover, the analysis took the differences between the basic parameters characterizing the mixture of BSG and MLL into account. The FTIR-PAS analysis was carried out to examine the possible changes in organic matter that might have taken place due to cavitation. A control experiment involving cavitation of leachate was carried out according to the aforementioned procedure to check the benefits of this process. The analysis encompassed the following parameters characterizing MLL, as well as the raw and cavitated BSG and MLL mixture: COD, BOD₅, volatile solids (VS), TS, total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), and the pH value. The supernatant of the mixture underwent the same procedure and determined parameters were included: volatile fatty acids (VFA), SCOD, alkalinity, ammonium nitrogen (NH₄⁺-N), as well as ortho-phosphate phosphorus (PO₄³⁻-P). A 0.45 µM pore-size filter was used to obtain the supernatant samples. It was necessary to determine these parameters because they were required to characterize the feed in the anaerobic digestion. The parameters considered in the BSG measurements, included: COD, total Kjeldahl nitrogen (TKN), TC, TS, VS, IC, PPh, LG, HC, MS, C, and P.

**Figure 1.** Experimental installation and orifice plate configuration: 1—circulation tank, 2—pump, 3—hydrodynamic cavitation reactor, 4—orifice plate, 5—piezoelectric pressure gauge, 6—valve, 7—manometer, 8—electromagnetic flow meter.
2.3. Composition Analysis

2.3.1. Substrate Characteristics Analysis

The analyses involving determination of the compositions of MLL, as well as the cavitated and raw BSG and MLL mixtures, were performed in line with Standard Methods for Examination of Water and Wastewater [37]. This applied to the TS, BOD₅, VS, pH, and alkalinity determinations. Certain analyses were conducted by means of the FIAsstar 5000 and FOSS analytical methods (for PO₄³⁻-P and NH₄⁺-N). A Shimadzu TOC-5050A total organic carbon analyzer with Shimadzu Solid Sample Module was used to determine the IC and TC characterizing the lyophilized samples. The value of TOC corresponded to the difference characterizing the related parameters. Ortho-phosphate was studied in line with ISO/FDIS 15681-1, whereas ammonium was examined according to ISO 11732. In turn, a HACH DE 3900 spectrophotometer was employed to measure SCOD, COD, TN, VFA, and TP. An electronic pH meter was used to establish the pH value. Standard methods were applied to measure the BSG parameters, including VS TS, and COD [37]. Before further analysis, the BSG and MPW mixtures, both cavitated and raw, were lyophilized by placing the 50 mL samples at −25 °C in a laboratory freezer and subsequently drying them at 56 °C by means of an Alpha 1–4 freeze dryer. A modified Van Soest analysis was used to determine the HC, C, and LG contents [38,39]. This method allows for separating the cell wall fractions (and dietary fiber fractions) by means of neutral (sodium dodecyl sulphate, EDTA, pH 7.0) as well as acidic (cetyltrimethyl ammonium bromide in 1 N H₂SO₄) detergent solutions. The neutral solution enables to remove sugars (PPPM), proteins, polysaccharides, and phenolic compounds. Then, hemicelluloses were removed using the acid detergent. Afterwards, sulfuric acid was applied to perform solubilization of cellulose. The Kjeldahl method was employed to determine the nitrogen content of the lyophilized samples. The Kjeltec system (FOSS Tector 8200) was used to prepare and measure the utilized samples. The conversion factor, amounting to 6.25, allowed determining the content of protein from nitrogen. The PPh content was established using a modified Folin—Ciocalteau colorimetric method. The methods and related procedures mentioned above were described in detail in Montusiewicz et al. [35].

2.3.2. SEM Analysis

The morphology of samples was investigated using a Hitachi SU 3500 scanning electron microscope at an accelerating voltage of 20 kV t nb. The monochromatic images showing the difference in the electron flux were obtained by means of a secondary electron detector. This enabled to examine the microstructures as well as the surface topography of the considered samples. The SEM analysis was conducted in vacuum, with the working distance of approximately 5.1 mm and the pressure valve of 50 Pa. Prior to being used, the studied samples were sputter coated with a thin layer of gold.

2.3.3. FTIR-PAS Analysis

Afterwards, the samples were subjected to lyophilization prior to conducting Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS). The FTIR-PAS spectra, performed at room temperature over the range of 4000–400 cm⁻¹ at the resolution of 4 cm⁻¹ and maximum source aperture, were recorded using a Bio-Rad Excalibur 3000 MX spectrometer via MTEC 300 photoacoustic detector (with a helium atmosphere in the detector). The spectra were normalized by calculating the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard. A stainless steel cup with the internal diameter of 10 mm was filled with a sample (thickness < 6 mm). Prior to the data collection, the photoacoustic cell was flushed for 5 min with dry helium. The interferograms obtained from 1024 scans were averaged for each spectrum; therefore, a favorable signal-to-noise ratio was achieved. Microsoft Excel 2010 software was used to create the graphs showing the obtained data, whereas the statistical analysis was carried out through the Student’s t-test performed with Statsoft Statistica software package (version 12). The differences with the p-values under 0.05 were considered statistically significant.
3. Results and Discussion

3.1. Characteristics of MLL, BSG and Their Mixture

Several parameters of the MLL (Table 1), i.e., high strength of COD, low biodegradability index (BOD<sub>5</sub>/COD ratio < 0.1), high alkalinity, and significant concentration of NH<sub>4</sub><sup>+</sup>-N were validated by comparison with other literature reports [40,41]. The diminished BOD<sub>5</sub>/COD ratio (BI index) as well as high pH and alkalinity levels seem to confirm that landfill leachate may be classified as “mature”—in other words, as being generated in the final phase of waste stabilization (final maturation). In turn, the relatively high COD, VFA, and NH<sub>4</sub><sup>+</sup>-N values indicate that some of the landfill sections may remain in the former phase of stabilization characterized by a continual methane formation [42].

The samples of BSG were wet-ground before their hydrodynamic cavitation. The main goal was to diminish the particle size and damage the complex structure of cell walls. The pretreated BSG exhibited the characteristics which were in line with the data provided by Mussatto [43]; however, lignin indicated a low concentration of 51.3 g kg<sup>-1</sup> TS, which was possibly connected with the unknown barley processing technology. The BSG addition to MLL, even in low amounts, as applied in the conducted experiments, contributed to marked increases in the majority of parameters (Table 3). The biodegradability index exhibited the opposite trend, which most probably resulted from the introduction of the greater content of refractory lignocellulosic compounds that are typical for BSG. Although wet-milling was performed beforehand, leading to partial matter fragmentation and solubilization of matter, there was a significant, 2.5-fold reduction in the BI index following suspension of the BSG in leachate. The low value (0.016) obtained for the mixture showed that its direction onto anaerobic digesters prior to efficient pretreatment should be avoided.

3.2. Effects of HD on the Biodegradability of BSG and MLL Mixture

The efficiency of HD was evaluated on the basis of the differences between the parameters characterizing the BSG and MLL mixtures prior to and following cavitation. Table 3 shows the related characteristics.

As far as the HD results are concerned, the concentration of SCOD and DOC (soluble organic compounds) as well as ammonia nitrogen were increased, showing efficient decomposition and solubilization of complex organic matter. A high increase in the NH<sub>4</sub><sup>+</sup>-N concentration (62%) seems to indicate the effective degradation of proteins. Simultaneously, a noticeable drop in the COD, TN, and TS values was observed. These findings are in line with the review reports frequently indicating HD as an effective method for degrading complex organic compounds [20,44]. In the case of biodegradability, substantial BOD<sub>5</sub> (45%) as well as BOD<sub>5</sub>/COD ratio increases were noted. The latter was improved from 0.016 to 0.027 through HD, i.e., in 69%. A control (blank) test was carried out, involving the cavitation of MLL, to verify the possibility of applying mature landfill leachate for suspending BSG to aid in its hydrodynamic cavitation. It should be emphasized that HD also had an effect on the composition of MLL (Table 1). The average values of the parameters were altered; however, the trend (i.e., downward or upward) was maintained in the majority of cases and the differences in percentage were comparable (for COD, TN, TS) or much lower (for BOD<sub>5</sub>, DOC, NH<sub>4</sub><sup>+</sup>-N) than in the cavitated MLL and BSG mixture. Alkalinity, which was reduced by 6% as a result HD, in contrast to the 12.5% increase in the case of the mixture, constitutes an exception. This tendency was also noted for PO<sub>4</sub><sup>3-</sup>-P and TP, but differences were not as pronounced. As far as biodegradability is concerned, both BOD<sub>5</sub> and BOD<sub>5</sub>/COD ratio increased in the course of HD. The increases reached 23 and 36.5%, respectively. They were much lower in comparison to the BSG and MLL mixture. However, the BSG addition greatly improved the biodegradability index following cavitation, its value was low nevertheless, which indicates issues in the biochemical treatment of this substrate. Additionally, the high concentration of NH<sub>4</sub><sup>+</sup>-N, which increased as a result, may subsequently inhibit the anaerobic digestion. Simpson and Ranade [45] reported that the cavitation effect is dependent upon numerous factors, including the cavitation device geometry, properties of the liquid, and operational param-
eters. Bis et al. [46] showed that the orifice plate with a conical concentric hole having 3 mm inlet and 10 mm outlet diameter, as well as the cavitation number equal to 0.033, can be used to achieve enhanced biodegradability of MLL. Hence, this cavitational constriction was adopted in this work. It was reported that the organic degradation by HD can proceed via two main mechanisms [47]. One involves direct decomposition of the organic material through increased temperature and high pressure (thermolytic pathway), whereas the other consists in the oxidation by OH* radicals produced in the course of HD. The orifice plate with a single concentric hole used in the experiments contributed to the growth of bubbles, rapid pressure recovery, and greater cavitation intensity due to its geometry [45]. In turn, such conditions favored oxidation of volatile hydrophobic substances in the gas phase, but limited the hydroxyl radicals diffusion outside the bubbles, and thus their reaction with the nonvolatile BSG compounds in the mixture. Moreover, BSG is widely known as a source of phenolic compounds, which have the antioxidant and free radical scavenging properties [48]. The phenol reduction degree is largely influenced by a change in the value of pH. At pH values ≥ 10, the reduction does not take place. In contrast, in the pH range of 9 > pH > 3, the phenol reduction degree increases with decreasing pH value [49]. Petković et al. [50] reported that the HD technology with no additional chemicals is not capable of achieving a complete phenol reduction because the OH* radicals are generated in insufficient amounts for the oxidation of phenol. Increases in pH (from 8.26 to 8.49), BOD$_5$ from 222 to 321 g m$^{-3}$, which occurred simultaneously with a COD reduction from 13.6 to 12 g L$^{-1}$ (Table 3) proved that the presence of antioxidants probably limited the oxidation of the easily biodegradable organic compounds, which were released as the products of recalcitrant organic matter decomposition. However, beside the oxidation processes initiated by OH* radicals, capture reactions proceed and the acceptors of these radicals are mainly bicarbonate and carbonate ions. Hence, higher alkalinity promotes the limited oxidation by radicals. Therefore, the thermolytic pathway of BSG decomposition was predominant. Hence, the improved BSG biodegradability seems to result from the physical effects, such as high temperature and pressure, rather than from the chemical effects of HD. The results of the present study were compared with different HD lignocellulosic biomass pretreatment methods, which are shown in Table 4.

**Table 4. Comparison of different hydrodynamic cavitation (HD) lignocellulosic biomass pretreatment methods.**

| References         | Aim of Work               | Substrate                  | Process Parameters                  | Results                                                                 |
|--------------------|---------------------------|----------------------------|-------------------------------------|-------------------------------------------------------------------------|
| Zieliński et al.   | Biogas yield improvement | *Sida hermaphrodita* silage + cattle manure | Reactor type—rotor disintegrator, electric motor with a power of 4 KW at 2800 rpm | No change in the chemical composition of the lignocellulose biomass after cavitation was observed |
| Hilares et al.     | Lignin reduction improvement | Sugarcane bagasse | Reactor type—orifice, inlet pressure—3 bar, temperature—70 °C, catalyst—0.3 M NaOH | 51.52% of lignin removal                                               |
| Hilares et al.     | Lignin reduction improvement | Sugarcane bagasse | Reactor type—orifice, inlet pressure—3 bar, temperature—64 °C, catalyst—0.48 M NaOH | 60.4% of lignin removal                                               |
| Montusiewicz et al.| Improvement of biodegradation index | BSG + primary treated municipal wastewater | Reactor type—orifice, inlet pressure—7 bar, temperature—20 °C | BSG biodegradability index increased from 0.074 to 0.091 |
| Thangavelu et al.  | Lignin reduction improvement | Corncob | Reactor type—orifice, inlet pressure—0.5 bar, temperature—30 °C, catalyst—Laccase enzyme: 6.5 U g$^{-1}$ of biomass | 47.44% of lignin removal                                               |
| Kim et al.         | Lignin reduction improvement | Reed | Reactor type—orifice, inlet pressure—5 bar, temperature—77 °C, catalyst—3.0% NaOH | 35%–42% of lignin removal                                               |
| Present study      | Improvement of biodegradation index | BSG + MLL | Reactor type—orifice, inlet pressure—7 bar, temperature—20 °C | Improvement in both the BOD$_5$ value and BOD$_5$/COD ratio (i.e., 45% and 69%, respectively) |

The use of hydrodynamic cavitation as a pretreatment method is known in the literature. There is not much research concerning the use of leachate or other liquid waste as a carrier in the process of hydrodynamic cavitation of lignocellulose waste such as BSG.
The only one is the authors' own study on BSG cavitation with the use of primary treated municipal wastewater as a carrier. Therefore, it is difficult to discuss these results.

3.3. Morphological Structure of Raw and Cavitated Material

The effectiveness of cavitation in enhancing the BSG biodegradability could result from the structural modification, and thus the SEM analysis was involved. The SEM images are presented in Figure 2.

![SEM images of BSG](image)

**Figure 2.** SEM images of BSG: (a) original untreated sample; (b) milled sample; (c) cavitated sample.

The untreated BSG was characterized by rigid and highly ordered fibrils (Figure 2a). This observation is in line with the findings of Mussato et al. [56]. The BSG structure was changed through primary grinding (Figure 2b), resulting in partial fragmentation of fibers and opening of the cell walls; however, the main structure remained intact, whereas the
cells of the smallest particles were disrupted. According to Reis et al. [57], the milling of BSG affects the structure of arabinoxylans (i.e., degree of polymerization and degree of branching). With the decreasing of the BSG particle size, the smallest and more branched polymers are extracted. The cavitated samples have a different morphology, as observed in Figure 2c, which continued reducing the particle size, disrupting the cells, and making their appearance distinctly different, probably due to the effect of intense shockwaves that could break molecular bonds. As a result of cavitation, the BSG surface became roughened and less porous, while the fiber structures were more accessible to enzymes due to their disintegration (Figure 2c). The explanation is that the HD causes the change of the structure of the BSG by the mechanical effect on the area surrounding the bubbles. The effect is represented by a huge shear force which acts to break and disintegrate matter and to reduce the particle size, and chemical effect on the material inside the bubble; this results from the extreme induced temperature and pressure [58].

3.4. FTIR-PAS Analysis

The FTIR-PAS spectra of examined samples are presented in Figure 3. While analyzing the spectra, it is noticeable that the MLL with and without the BSG addition before and after the HD process reveals some differences in the position and intensity of the peaks in all FTIR-PAS spectra. The addition of BSG, though not clearly visible on the spectra, changes the spectral characteristic of the MLL. The spectra of the mixture of MLL and BSG differ from those without the addition of BSG. There is a clear change in the intensity of -OH groups, both within 3600–3000 cm$^{-1}$ (Figure 3a) and within the fingerprint region (Figure 3b). The first range is also the range of the N-H groups vibrations. In this second range, the change in the intensity of -OH bands (1372 and 1315 cm$^{-1}$) is also visible. The amount of hydroxyl groups is lower in the case of samples with BSG addition. It has been established that the availability of hydroxyl groups is crucial for the immobilization of enzymes on the BSG via covalent bonding. Consequently, a smaller number of OH groups results in the lower availability of BSG for enzymes produced by the microorganisms. The analysis of the FTIR-PAS spectra allows to conclude that HD does not cause an increase in the number of OH groups in the samples with BSG, compared to the samples containing only MLL.

![Figure 3. Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) spectra of the MLL with and without the BSG addition before and after HD in the (a) 4000–2400 and (b) 2000–600 cm$^{-1}$ range.](image-url)
indicates the decomposition of these groups during the cavitation process (Figure 3a). These observations are consistent with the data presented in Table 3, which indicate a visible ammonification in the cavitated mixture. The IR analysis of the amide groups bands—more precisely, the vibrations of N-H (amide II band) in the fingerprint region—is practically impossible, because this band has weak-to-medium intensity in this range and is generally too close to the strong carbonyl band (amide I band) to be resolved [59]. The bands that are invisible in the spectrum of the same sample prior to cavitation also appear in the spectrum of the cavitated MLL and BSG mixture. These include the bands at 1600 and ~1500 cm\(^{-1}\), showing the presence of aromatic compounds. HD might produce or release aromatic compounds that are comprised in the material following the cavitation in a greater amount in comparison with the original material. Nevertheless, in the case of the MLL samples, the intensity of bands showing the presence of peptide groups, oxygen, and aromatic rings in the IR spectrum of MLL following cavitation was decreased, which can be regarded as the proof of the reduced number of the compounds comprising these functional groups, but in the case of the samples with the BSG addition, the intensity of the bands in 2000–600 cm\(^{-1}\) (Figure 3b) remains almost unchanged. A slight increase in the bands’ intensity is most probably caused by changes in the density of the sample, since the substances with smaller particle size (fragmentation caused by cavitation) generate a stronger photoacoustic signal.

3.5. Energy Efficiency of Hydrodynamic Cavitation

Regardless of the type of pretreatment, the economic aspects of the whole treatment (both the adopted pretreatment and the subsequent suggested treatment), including the costs and possible technological/energy profits, have to be considered. It is obvious that the HD is linked to the energy consumption, and thus its energy input should be determined for a proper evaluation of the energy balance in the entire treatment system. The energy efficiency of cavitation reactors should be evaluated based on the concentration and type of the pollutant; in the study this concerned the removed COD (COD\(_{\text{rem}}\)). The cavitation yield of unit energy input is expressed as [44]:

\[
\text{Cavitation yield (mg COD}_{\text{rem}}\text{ J}^{-1}) = \frac{\text{amount of organic pollutants degraded}}{P_m \cdot t}
\]

where \(P_m\) is the electrical power consumption—power input (J s\(^{-1}\)), and \(t\) is the operation time (s). The related experimental values for the mixture of BSG and MLL were as follows: the power input 949 J s\(^{-1}\) (at 7 bar inlet pressure), the cavitation time 1836 s, and the total energy supplied 1.74 \(\times\) \(10^6\) J, whereas for the sole MLL, these were 689 J s\(^{-1}\), 1700 s, and 1.17 \(\times\) \(10^6\) J.

The BSG and MLL mixture had the cavitation yield of 4.14 \(10^{-2}\) mg J\(^{-1}\), whereas in the case of MLL, it dropped to 2.65 \(10^{-2}\) mg J\(^{-1}\). In comparison with the findings shown by Mishra and Gogate [60] as well as Saharan et al. [61], who investigated the Rhodamine B and orange-G dye degradation via hydrodynamic cavitation, both of these values are much greater. The authors reported that the application of orifice plate with 2 mm centric hole resulted in the cavitation yields of 1.16 \(10^{-6}\) and 2.12 \(10^{-6}\) mg J\(^{-1}\), respectively. According to Tao et al. [44], acoustic cavitation has higher energy efficiency in small-volume operation in comparison to hydrodynamic cavitation, but the energy distribution in the HD reactor is relatively homogeneous. What is more, the HD allows continuous operation and the volume of the treated liquid is larger. Overall, the HD shows certain advantages in large-scale systems and is more likely to realize industrial operation. In order to further enhance the efficiency, the HD should be combined with other AOPs, additives or biological treatment.

4. Conclusions

While evaluating the usefulness of mature landfill leachate as a carrier for the hydrodynamic cavitation of brewery spent grain, two following aspects need to be taken into account: biodegradability enhancement and formation of potentially toxic HD byproducts.
Regarding the first point, a beneficial effect was observed, since hydrodynamic cavitation of BSG suspended in MLL ensured significant increases in both the BOD$_5$ value and BOD$_5$/COD ratio (i.e., 45% and 69%, respectively), making the BSG more available for subsequent anaerobic digestion. Moreover, the concentration of soluble organic compounds (expressed as DOC) increased, indicating an effective decomposition and solubilization of complex organic matter. This was also confirmed by the analysis of the sample morphology which showed visible destruction of the BSG structure. Unfortunately, the second issue seems to look much worse, since an adverse effect occurred in this case. The FTIR-PAS analysis indicated some bands referring to aromatic compounds in the spectrum of the cavitated mixture of BSG and MLL. These were not visible in the related spectrum before cavitation or in the spectrum of cavitated MLL. Thus, in the case of the mixture mentioned, hydrodynamic cavitation led to the formation of new compounds that would most likely negatively affect the subsequent biological treatment. Considering this, the MLL could not be regarded as a suitable carrier for BSG cavitation.

Future perspectives of the research concern evaluating other carriers for hydrodynamic cavitation of BSG, among them agroindustrial wastewater, sewage sludge supernatant, and processing water from waste management installations.

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