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SYNERGISTIC EFFECT OF ULTRASONIC SONIFICATION IN ANAEROBIC DIGESTION OF EXPIRED FOOD PRODUCTS

Abstract: The regulations in force in the European Union require the thermal pre-treatment of substrates containing animal by-products prior to the anaerobic digestion (AD) process. Expired food products (EFP) belong to this category of substrates. Traditionally, the requirement for thermal pre-treatment has been met with waste heat from combined heat and power plants (CHP). However, due to the increasing trend towards biomethane production and the move away from CHP, alternative heating methods need to be explored. The main objective of this study was to evaluate the impact of the dual synergistic effect achieved by ultrasonic-thermal pre-treatment of EFP on the kinetics, efficiency and energy balance of AD. The combined thermal treatment and ultrasonic disintegration at 90 °C resulted in an increase in dissolved phase chemical oxygen demand (COD) by (84.4 ±3.9) % and total organic carbon (TOC) by (56.8 ±6.2) %, leading to final concentrations of (33010 ±1280) mg O_2/L and (10710 ±670) mg C_{org}/L, respectively. After thermal pretreatment of EFP at 70 °C, the methane yield reached (515 ±24) mL/g VS, while at 90 °C it increased to (525 ±22) mL/g VS. The application of ultrasonic thermal pretreatment resulted in a positive net energy gain, with the most efficient variant yielding (4.20 ±0.23) Wh, which was (0.37 ±0.17) Wh higher than the control sample. In contrast, a negative energy balance was observed in the variants where conventional heating methods were used.

Keywords: expired food products, thermal pretreatment, ultrasound disintegration, synergistic effects, anaerobic digestion

Introduction

Food waste has become a widespread and significant problem in industrialised countries, with economic, environmental and social implications. According to the Food and Agriculture Organisation (FAO) of the United Nations, almost one third of global food production does not reach the consumer but is lost at various stages of the supply chain, from production to consumption [1]. In Europe and North America, food losses average (95-115) kg per person per year, while in lower-income regions such as sub-Saharan Africa and South and Southeast Asia, these figures are significantly lower at (6-11) kg per person per year [2]. In the European Union, food waste is estimated at 88 million tonnes per year, which corresponds to an average of 173 kg per capita [3].

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Food waste is not only an economic problem, but also an environmental problem. The processes associated with the production, transport and storage of food require significant consumption of resources, including water, energy, fertilisers and pesticides [4, 5]. In addition, food waste is one of the largest sources of greenhouse gas emissions, second only to the construction and transport sectors [6]. Therefore, it is crucial to implement solutions that either reduce food waste or effectively utilise discarded food products in line with the principles of the circular economy [7]. This concept aims to minimise the negative environmental impact of products and promote the sustainable reuse of available resources, including waste materials [8].

One of the established methods for managing food waste is anaerobic digestion (AD), which enables conversion into organic fertiliser and the production of energy-rich biogas [9]. This solution offers energy, environmental and agricultural benefits [10], is in line with circular economy goals and fulfils the increasing demand for renewable energy production and climate change mitigation measures [11]. AD not only contributes to landfill waste reduction, but also improves the economic and environmental performance of waste management systems [12]. Although the AD of unused, including expired food products (EFP) is well understood, further improvements in process efficiency and technological optimisation are required to fully exploit its potential as an energy substrate.

A significant proportion of EFP consists of animal and meat waste, which requires special treatment for hygienic reasons [13]. The rules for the processing of animal by-products not intended for human consumption are set out in Regulation (EC) No 1069/2009 of the European Parliament and of the Council [14]. One of the recommended procedures is AD, which provides for pre-treatment of the substrate by crushing into particles of no more than 60 mm and subsequent hygienisation at 70 °C for 60 minutes, as laid down in European Commission Regulation No 142/2011 [15]. The thermal treatment of EFP not only ensures hygienisation, but also facilitates the release of organic compounds into the dissolved phase [16]. The resulting hydrolysates are more easily assimilated by anaerobic microorganisms, which improves the efficiency of AD [17]. Traditionally, waste heat from cogeneration plants has been used for thermal treatment, but this option is now significantly limited [18]. This change is being driven by the growing popularity of biogas upgrading technologies for the production of biomethane and its subsequent use in natural gas distribution networks or as fuel for road vehicles [19]. Therefore, there is a need to explore alternative, cost-effective and efficient methods for the thermal pretreatment of EFP.

One possible solution is the use of ultrasonic waves to achieve a dual synergistic effect, where two different but complementary mechanisms improve the overall efficiency of the process. In the context of EFP pre-treatment, this means the simultaneous effect of thermal treatment and ultrasonic disintegration of the organic substrate. Ultrasound generates thermal effects through the absorption of acoustic energy as well as non-thermal effects such as cavitation and mechanical stress, which destroy cell structures and promote the biodegradation of biomass [20]. Cavitation is the formation and collapse of microbubbles leads to localised shock waves and shear forces that further support the AD process [21].

Previous studies on ultrasonic pretreatment of organic substrates have focused predominantly on non-thermal mechanisms, such as cavitation and mechanical disruption, while the thermal effect generated during sonication has been largely neglected or treated as a secondary phenomenon. In the context of the dynamic development of biomethane plants and the decreasing availability of waste heat for substrate hygienisation, this aspect becomes particularly relevant. Therefore, the novelty of the present study lies in the comprehensive evaluation of the synergistic ultrasonic-thermal pretreatment, in which ultrasound is used not only as a mechanical disintegration tool but also as a controllable source of thermal energy, enabling simultaneous fulfilment of hygienisation requirements and enhancement of anaerobic digestion performance.

The objective of this study was to evaluate the impact of the dual synergistic effect achieved by ultrasonic-thermal pretreatment of expired food products on the efficiency of anaerobic digestion. The study evaluated changes in dissolved organic matter content as an indirect indicator of pretreatment performance, compared methane production yield in AD and performed a comparative energy efficiency analysis of the tested UTP approach versus conventional thermal pretreatment (CTP).

Materials and methods

Research concept

The study was divided into three stages (S), each differing in the pre-treatment method for expired food products (EFP) prior to anaerobic digestion (AD). In stage 1 (S1), the homogenised EFP did not undergo any thermal treatment. In stage 2 (S2), the EFP underwent conventional thermal pretreatment (CTP), while in stage 3 (S3), the EFP underwent ultrasonic thermal pretreatment (UTP). Both S2 and S3 were further divided into two variants based on the pre-treatment temperature applied. In variant 1 (V1), EFP were treated at 70 °C for 60 minutes, while in variant 2 (V2), treatment was carried out at 90 °C for 60 minutes. After pre-treatment, the EFP were subjected to chemical analyses to evaluate the indirect effects of the method used. Subsequently, the EFPs were subjected to AD in respirometric batch reactors with an organic loading rate (OLR) of 5.0 g VS/L under mesophilic conditions at a temperature of (42 ±1) °C.

Materials

EFP from five distribution points of large retail chains located in Bialystok, Poland, was used for the study. Over a period of four months, EFP samples were taken weekly to determine the proportion of different types of waste, including meat products, fruit and vegetable waste, dairy products and other food residues. In order to develop a substrate mixture that accurately reflects real-life conditions, the field observations were supplemented with data from interviews with retail representatives. The final composition of the EFP mixture used in the experiments consisted of: 40 % meat waste, 30 % dairy products, 30 % fruit and vegetables. Prior to the experiments, the EFP were mechanically pre-shredded to an average particle size of (5.0 ±1.5) mm. The properties of the EFP used in the study are presented in Table 1.

Anaerobic sludge inoculum

The anaerobic sludge (AS) used as inoculum in the fermentation reactors was obtained from a closed anaerobic digestion chamber (ADC) with an active volume of 7300 m^3. The ADC is an integral part of the sludge treatment system and the co-digestion process in the municipal wastewater treatment plant (MWWTP) in Białystok, Poland. The ADC operates at a constant temperature of 42 °C, with an organic loading rate (OLR) of about

(2.2 ±0.3) g VS/dm^3·day and a hydraulic retention time (HRT) of 21 days. The detailed properties of the AS are presented in Table 1.

Table 1

Characteristics of the EFP and AS used in the experiment

Parameter	**Unit**	**Value**	
		EFP	**AS**
pH	[-]	7.9 ±0.2	7.5 ±0.3
Total solids (TS)	[g/L]	74.0 ±7.2	36.8 ±3.3
Volatile solids (VS)	[g/L]	63.0 ±5.7	25.9 ±1.4
Mineral solids (MS)	[g/L]	11.0 ±1.6	10.8 ±1.3
Total carbon (TC)	[g/L]	83.3 ±2.6	11.2 ±0.3
Total inorganic carbon (TIC)	[g/L]	7.5 ±0.3	3.9 ±0.6
Total organic carbon (TOC)	[g/L]	75.8 ±2.4	7.3 ±0.6
Total nitrogen (N_{tot})	[g/L]	8.6 ±0.6	1.2 ±0.3
C/N	[-]	9.8 ±0.3	9.7 ±0.8
Total phosphorus ($P_{tot.}$)	[g/L]	1.7 ±0.4	0.07 ±0.01
Protein	[g/L]	53.9 ±2.7	7.1 ±0.3
Carbohydrates	[g/L]	12.9 ±0.8	0.02 ±0.01
Lipids	[g/L]	83.3 ±3.1	1.4 ±0.2
Total alkalinity	[g $CaCO_3$/L]	6.9 ±0.1	5.8 ±0.2
Volatile fatty acids (VFA)	[g CH_3COOH/L]	0.29 ±0.01	0.27 ±0.02
VFA/total alkalinity	[-]	0.042 ±0.002	0.051 ±0.005

Laboratory setups for the thermal pretreatment of EFP

The pre-grinding and homogenisation of EFP was carried out using a Pulverisette 11 knife mill (Fritsch GmbH, Idar-Oberstein, Germany). A volume of 1.0 L of EFP was fed into the mill and the grinding process was carried out using a titanium knife with four blades at 10,000 rpm for 10 seconds. The CTP and UTP processes were carried out in an IS-1K reactor (InterSonic, Olsztyn, Poland) using heating by electric heaters or ultrasound, depending on the stage of the experiment. A volume of 1.0 dm^3 of pre-homogenised EFP was introduced into the reactor chamber.

In stage S2 (V1, V2), heating was carried out with 500 W electric heaters, while in S3 (V1, V2) ultrasound with a frequency of 35 kHz and a power of 400 W was used. The IS-1K reactor was thermally insulated with a 10 cm^3 thick polystyrene layer to minimise heat loss. The energy consumption for heating was monitored with an Orno OR-WAT-435 wattmeter (Elmak Sp. z o.o., Rzeszów, Poland). The temperature of the EFP in S2V1 and S3V1 was maintained in the range of (70-73) °C, while in S2V2 and S3V2 it was kept between (90-93) °C. The electric heaters or ultrasonic heads were automatically switched on and off as soon as the set temperatures were reached. This was done by a control system co-operating with a Pt100 sensor (Jumo Sp. z o.o., Wrocław, Poland). Based on continuous temperature monitoring (Pt100 sensor), the time required to reach the set temperature was (8 ±1) min for S2V1 (70 °C) and (11 ±1) min for S2V2 (90 °C) when electric heaters were applied. In the ultrasonic variants, the heating time was longer and amounted to (16 ±2) min for S3V1 (70 °C) and (21 ±3) min for S3V2 (90 °C). The pre-treated EFP was then chemically analysed and fed into the AD process to determine the efficiency of methane (CH_4) production.

Measurements of methane production

The methanogenic potential of EFP was determined by measuring the volumetric gas production using the Automatic Methane Potential Test System (AMPTS II, BPC Instruments AB, Lund, Sweden). AD was performed at a constant temperature of (42 ±1) °C in glass chambers with a total capacity of 500 mL equipped with an individual sequential full mixing system with bladeless vertical axis stirrers (100 rpm for 30 seconds, activated every 5 minutes).

The study was conducted with 18 respirometers, replicating in triplicate the experimental variants specified in the methodological assumptions. The tested variants included thermally pretreated EFP: CTP 60 min (70 °C), CTP 60 min (90 °C), UTP 60 min (70 °C), UTP 60 min (90 °C). A control group included: EFP without pretreatment (3 bioreactors), AS only to estimate endogenous CH_4 production (3 bioreactors). At the beginning of the experimental cycle, 200 mL of AS inoculum was added to the AMPTS II respirometers, followed by the corresponding amounts of EFP according to the tested variants. The organic loading rate (OLR) was set to (5.0 ±0.3) g VS/L, calculated with respect to the active volume of anaerobic inoculum (200 mL). This corresponded to (1.0 ±0.05) g VS (approximately (1.17 ±0.06) g TS), which was equivalent to about (16.0 ±0.8) g (≈15.8 ±0.8) mL of fresh mass EFP per reactor, depending on the actual TS and VS content of the substrate (Table 1). Anaerobic conditions in the reactors were achieved by flushing the sludge-substrate mixture with pure N_2 at a flow rate of 100 L/h for 3 minutes.

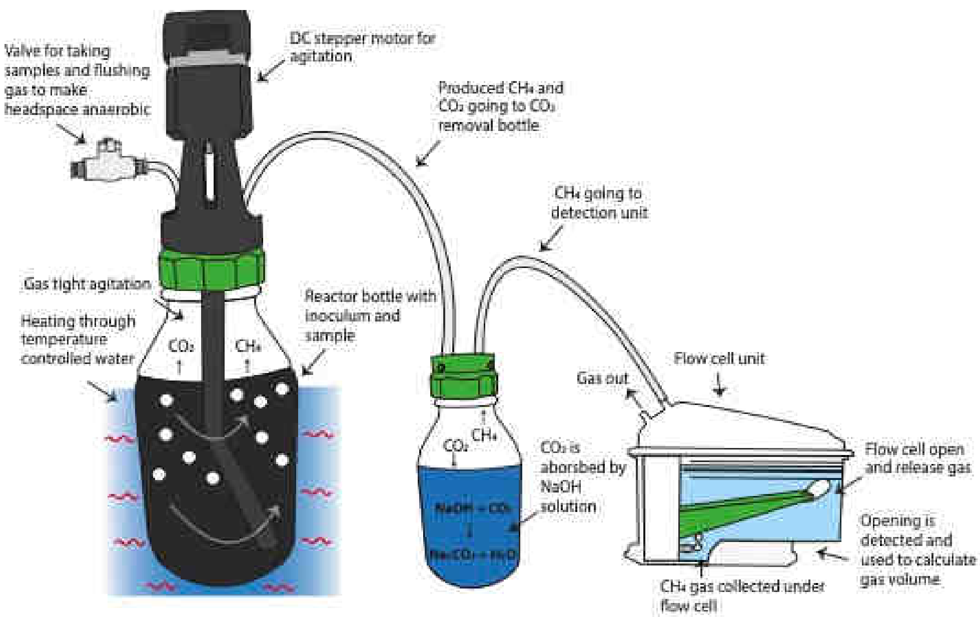

Fig. 1. Scheme of the experimental setup used for the measurements of CH_4 production (https://bpcinstruments.com/)

Gas production was monitored daily using the original bioprocess control software in the AMPTS II system. The software recorded the CH_4 volume under standard conditions (atmospheric pressure 101.3 kPa, temperature 0 °C, humidity 0 %). The respirometric measurements were continued until complete degradation of the available organic compounds. The automated system compared consecutive measurement results and terminated the test when five consecutive measurements differed by less than 1 %. The endogenous biogas production of the anaerobic sludge alone was not taken into account when calculating the CH_4 yield. Methane production was expressed as the volume of gas produced over 20 days, measured in mL per g VS added to the reactors. The CO_2 produced during the AD process was not taken into account in the measurements and further calculations. The experimental setup included a 100 mL sorption module in which the absorption liquid was a 3M NaOH solution, which ensured a CO_2 capture efficiency of over 98 %. The fermentation reactors were connected to the CO_2 absorption units using gas-tight Tygon® tubing supplied as standard equipment with the AMPTS II system (Bioprocess Control). The other components of the experimental system are shown in Figure 1.

Analytical methods

Determinations of total solids (TS), volatile solids (VS), and mineral solids (MS) were performed using the gravimetric method in accordance with the PN-EN 15935:2022-01 standard [22]. The contents of inorganic carbon (IC), total carbon (TC), total organic carbon (TOC), and total nitrogen (TN) were analysed using a Flash 2000 analyser (Thermo Scientific, Waltham, MA, USA). Total phosphorus (TP) was determined colourimetrically at a wavelength of 390 nm using a DR 2800 spectrophotometer (Hach-Lange GmbH, Düsseldorf, Germany) after prior sample mineralisation. The total protein content was calculated by multiplying the TN concentration by a factor of 6.25. Reducing carbohydrates were determined spectrophotometrically using anthrone reagent (0.2 g anthrone/100 mL concentrated H_2SO_4). Prior to analysis, samples were subjected to acid hydrolysis of polysaccharides (1 M H_2SO_4, 100 °C, 1 h), followed by cooling and neutralisation to pH 4-5. After addition of the anthrone reagent, the mixture was heated in a water bath (95-100) °C for (8-10) min. Absorbance was measured at 600 nm using a DR 2800 spectrophotometer (Hach-Lange GmbH, Düsseldorf, Germany). Calibration was performed using standard glucose solutions, yielding a linear response within the analysed concentration range. Lipids were extracted using a Soxhlet apparatus (Buchi, Flawil, Switzerland), and their content was determined based on the mass difference before and after extraction. The pH value was measured using an HQ11D pH meter (Hach-Lange GmbH, Düsseldorf, Germany). The concentrations of chemical oxygen demand (COD) and TOC in the dissolved phase were determined after filtering the H-LSPW sample using a vacuum membrane filtration set (Advantec MFS, Inc., Dublin, CA, USA). TOC was analysed using a TOC-L analyser (Shimadzu, Kyoto, Japan), while COD was measured spectrophotometrically (DR 2800, Hach-Lange GmbH, Düsseldorf, Germany). Total alkalinity was determined using a titration method, and volatile fatty acids (VFA) were analysed photometrically using the 0-50 Nanocolor kit. The biogas composition, including CH_4 content, was monitored using a gas chromatograph (GC, 7890A Agilent, Santa Clara, CA, USA).

Computational methods

The actual energy input (E_INPUT) was determined using the Orno OR-WAT-435 wattmeter (Elmak Ltd., Poland). The energy output (E_CH_4out) derived from CH_4 production was calculated as follows:

$$E\_CH_4out = Y\_CH_4out \times E\_CH_4 \times M\_VSinR \text{ [Wh]} \quad (1)$$

where: Y_CH_4out - methane yield [mL/g VS], E_CH_4 - energetic value of methane [Wh/mL], M_VSinR - VS supplied to the respirometer [g VS].

The unit energy input (E_Uin) per unit of VS mass was calculated using the formula:

$$E\_Uin = E\_INPUT/M\_VSin \text{ [Wh/g VS]} \quad (2)$$

where: E_Uin - specific energy input per unit VS [Wh/g VS], E_INPUT - specific energy input [Wh], M_VSin - VS mass [g VS].

The total energy input into the respirometer (E_TOTinR) was determined with the following equation:

$$E\_TOTinR = E\_Uin/M\_VSinR \text{ [Wh]} \quad (3)$$

where: E_TOTinR - specific energy input delivered to the respirometer [Wh], E_Uin - specific energy per unit VS [Wh/g VS], M_VSinR - VS mass introduced into the respirometer [g VS].

The net energy gain (E_NET) was calculated using:

$$E\_NET = E\_CH_4out - E\_TOTinR \text{ [Wh]} \quad (4)$$

The degree of organic matter solubilisation [%] was calculated using equation [23]:

$$\text{Degree of COD or TOC solubilisation} = [(sCODS1 \text{ or } sTOCS1 - sCODS0 \text{ or } sTOCS0)/(CODT0 \text{ or } TOCT0 - sCODS0 \text{ or } sTOCS0)] \cdot 100 \quad (5)$$

Here, sCODS0/sTOCS0 represents the soluble COD/TOC before the pretreatment EFP [mg/L], sCODS1/sTOCS1 corresponds to the soluble COD/TOC after pretreatment EFP, and CODT0/TOCT0 denotes the total COD/TOC concentration [mg/L] in TS of raw EFP.

The rate (r) of the (AD) process, defined as the daily CH_4 increase, as well as the kinetic constants (k), which describe the estimated rate, were calculated using an iterative approach with linear regression. The equation used to model biogas/methane yield is as follows:

$$Y(t) = -Y_{max} (e^{-kt} - 1) \quad (6)$$

where: Y - yield of CH_4 [mL N/g VS_added·day], Y_{max} - maximum achievable production of CH_4 [mL N/g VS_added], k - kinetic constant [1/day], t - time [day].

The rate of CH_4 production (r) was calculated by multiplying the kinetic constant (k) by the maximum potential of gas metabolite generation during the AD process, normalised per unit of VS introduced to the respirometer. This calculation assumes a first-order kinetic model.

Statistical analysis

The statistical evaluation of the obtained results was carried out using the STATISTICA 13.3 PL software package. Differences between groups were assessed through a one-way analysis of variance (ANOVA), while Tukey's test was employed to determine the significance of differences between the analysed variables. A significance level of $p = 0.05$ was applied for all tests.

Results and discussion

Concentration of organic compounds in the dissolved phase

Analysing changes in the concentration of organic compounds in the dissolved phase is an indirect method for evaluating the effects of substrate pretreatment techniques applied prior to the anaerobic digestion process [24]. The main objective of pretreatment is to dissolve compact organic structures, fragment them and improve the transfer of organic matter to the liquid phase, thereby increasing the bioavailability of the substrate for anaerobic microorganisms, especially hydrolytic and acidogenic bacteria [25]. The efficient conversion of organic compounds into volatile fatty acids (VFAs) directly determines the rate and efficiency of methanogenesis and contributes to improved stability of the digestate [26]. The most commonly used indirect indicators for evaluating the effectiveness of pretreatment include COD and TOC [26].

In S1, where EFP was not subjected to thermal pretreatment, the analysed parameters characterising the concentrations of organic compounds were as follows: (17,900 ±930) mg O_2/L (COD) and 6,830 mg/L (TOC) (Table 2). The application of conventional thermal pretreatment (CTP) in S2V1 and S2V2 led to a significant increase in COD and TOC concentrations. No significant differences were observed between S2V1 (70 °C) and S2V2 (90 °C) depending on the applied CTP temperature. The COD concentrations in the dissolved phase reached (30,070 ±840) mg O_2/L and (30,980 ±950) mg O_2/L respectively (Table 2). The proportion of dissolved COD after CTP was (68.0 ±2.8) % in S2V1 and (73.1 ±3.1) % in S2V2.

Table 2

Effect of the applied pretreatment on the degree of solubilisation and the changes in the concentration of organic compounds in the dissolved phase

Stage/ Variant	COD			TOC		
	Concentration [mg/L]	**Increase [%]**	**Solubilisation [%]**	**Concentration [mg/L]**	**Increase [%]**	**Solubilisation [%]**
S1	17,900 ±930	-	-	6,830 ±410	-	-
S2V1	30,070 ±840	68.0 ±2.8	11.1 ±0.5	9,330 ±430	36.6 ±4.6	6.9 ±0.9
S2V2	30,980 ±950	73.1 ±3.1	12.0 ±0.5	9,970 ±570	45.9 ±5.7	8.6 ±1.1
S3V1	31,720 ±770	77.2 ±2.4	12.6 ±0.4	10,010 ±630	46.5 ±6.3	8.8 ±1.2
S3V2	33,010 ±1280	84.4 ±3.9	13.8 ±0.6	10,710 ±670	56.8 ±6.2	10.7 ±1.2

The application of a combined thermal and ultrasonic disintegration process (UTP) at 70 °C (S3V1) resulted in a (77.2 ±2.4) increase in dissolved COD content, reaching (31,720 ±770) mg/L (Table 2). However, this change was not statistically significant compared to CTP implementation. A significantly higher COD transfer efficiency (84.4 ±3.9) % to the dissolved phase was observed in S3V2 (90 °C), resulting in a concentration of (33,010 ±1,280) mg/L. Similar trends were observed for TOC concentrations. The highest increase in dissolved TOC, reaching (56.8 ±6.2) %, was recorded in S3V2. In this case, the UTP allowed a TOC content of (10,710 ±670) mg/L (Table 2). In raw EFP, TOC concentrations of (6,830 ±410) mg/L were measured. The other pretreatment options resulted in dissolved TOC concentrations between (9,330 ±430) mg/L (S2V1) and (10,010 ±630) mg/L (S3V2). TOC concentrations increased by (36.6 ±4.6) % to (46.5 ±6.3) % (Table 2). The values in this group were statistically comparable, but significantly higher than in untreated EFP.

Ultrasound treatment is an effective method for cell disruption prior to anaerobic digestion (AD) [27]. The effect of ultrasound is primarily generated by ultrasonic cavitation, which leads to strong shear forces, strong turbulence, high temperature and pressure in a certain area [28]. The effectiveness of the sonication process also depends on parameters such as the ultrasonic power, the exposure time and the type of raw materials used [29].

In the studies by Gadhe et al. [30], the effectiveness of ultrasonic pretreatment of food waste was investigated. The maximum increase in the concentration of dissolved COD, which reached 56.51 %, was achieved with an 8 % TS content, a sonication time of 15 minutes, ultrasonic frequency of 20 kHz and a power of 1200 W. The results were lower than those presented in this study, in which a maximum increase of 84.41 % in dissolved COD concentration was recorded under the UTP conditions for 60 minutes at 90 °C (S2V2). Lower efficiency in increasing dissolved COD was also reported by Joshi and Gogate [31], who studied the effect of different operating parameters for UTP, such as treatment time (between 2 and 14 minutes), power density (0.2-1.0) W/mL, duty cycle (20-80) % and substrate loading (3-11) % w/v on food waste disintegration. The largest increase in dissolved COD (61.5 %) was observed under optimal UTP conditions: 10 min irradiation time, 0.4 W/mL power density, 60 % duty cycle and 7 % w/v substrate loading. Yue et al. [32] also examined the effect of UTP pretreatment of food waste with a power of 10 to 500 W. The COD content in untreated food waste was (10,240 ±280) mg/L, while after increasing the energy input, the dissolved COD concentration increased from (16,200 ±260) mg/L to (26,680 ±1060) mg/L. The maximum increase in dissolved COD was 160.5 % and was therefore almost twice as high as the value determined in this study.

Methane fermentation

Various pretreatment methods, including mechanical techniques (such as ultrasonication, high pressure and lysis), thermal processes, chemical treatments (e.g. ozonation and alkaline treatment) and biological methods, can be applied to process solid waste prior to AD [33]. These processes improve the solubilisation of organic matter, which can effectively increase the conversion rate, thereby increasing the efficiency of biogas production [34].

The efficiency of methane production from untreated EFP was (418 ±30) mL/g VS (Fig. 2). The AD rate (*r*) was (86.1 ±4.2) mL CH_4/g VS·day and the rate constant (*k*) was (0.21 ±0.02) 1/day (Table 3). Regardless of the temperature, the application of CTP had no significant effect on the overall methane fermentation efficiency of the tested EFP. In S2V1 (70 °C), methane production was (425 ±27) mL CH_4/g VS and in S2V2 (90 °C) (434 ±29) mL CH_4/g VS (Fig. 2). However, the kinetic parameters of the process increased significantly. The fermentation rates after application of CTP were (96.4 ±6.7) mL CH_4/g VS·day (*k* = 0.23 ±0.01) for S2V1 and (112.1 ±9.1) mL CH_4/g VS·day (*k* = 0.26 ±0.02) for S2V2 (Table 3). The efficiency of methane production from food waste after conventional thermal treatment has been the subject of many studies. For instance, Li et al. [35] conducted experiments in which food waste was thermally treated at temperatures between 80 °C and 120 °C prior to AD. They found that thermal treatment at these temperatures improved the degradation of organic matter and led to a 20 % increase in CH_4 production compared to untreated food waste. Similar results were reported by Xie et al. [36], who showed that heating the substrate to

90 °C for 30 min increased hydrolysis and nutrient availability to the methanogenic microorganisms, resulting in a (15-25) % increase in biogas production.

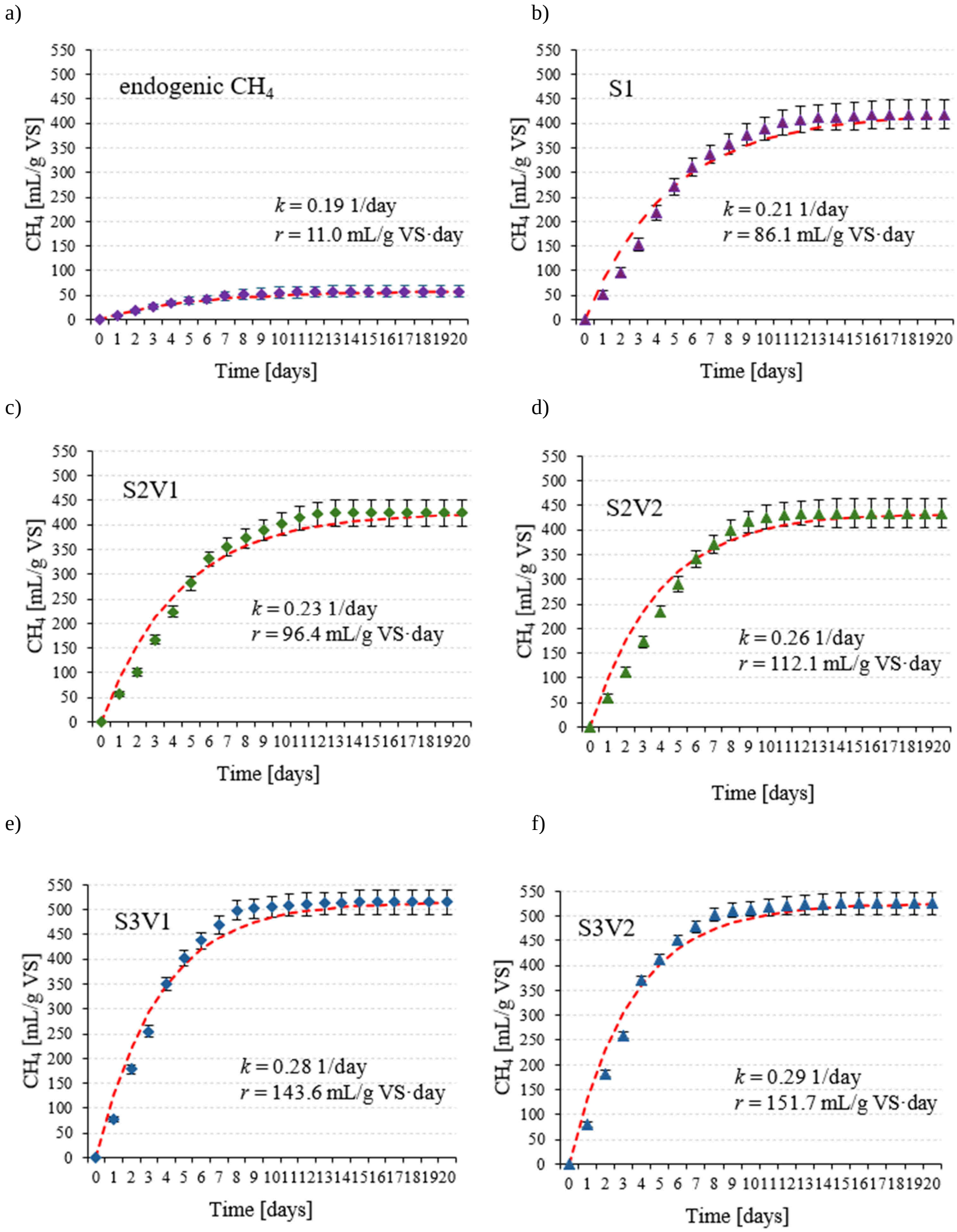

Fig. 2. The actual and model curves characterising the AD of EFP as a function of the experimental variant: a) endogenous CH_4, b) S1, c) S2V1, d) S2V2, e) S3V1, f) S3V2

These results showed a higher efficiency of methane production compared to the results presented in this study, where conventional heating to 90 °C (S2V2) led to a 3.83 % increase in CH_4 production compared to untreated EFP. On the other hand, Wang et al. [37] found that thermal treatment above 150 °C could negatively affect anaerobic fermentation. High temperatures can lead to the formation of toxic compounds such as furfural and 5-hydroxymethylfurfural, which inhibit the activity of methanogenic microorganisms and reduce methane production.

A significantly higher efficiency of anaerobic degradation of EFP (food waste) was observed in S3, where the temperature increase was achieved by the ultrasonic disintegration process (UTP). In S3V1 (70 °C), CH_4 production was (515 ±24) mL/g VS, with an observed rate (*r*) of (143.6 ±11.6) mL CH_4/g VS·day and a rate constant (*k*) of (0.28 ±0.02) 1/day (Table 3). In S3V2 (90 °C), CH_4 production reached (525 ±22) mL/g VS, with a rate of (151.7 ±13.3) mL CH_4/g VS·day (Fig. 2). Control measurements of the biogas composition showed that the CH_4 content was in a narrow range between (61.7 ±2.1) % (S1) and (64.6 ±2.0) % (S3V2) (Table 3). The observed differences were not statistically significant.

Table 3

CH_4 yield and kinetic parameters characterising the AD of EFP

Stage/ Variant	**Parameter**			
	CH_4 yield [mL/g VS]	**CH_4 [%]**	***k* [1/day]**	***r* [mL/g VS·day]**
Endogenic CH_4	58 ±11	48.3 ±3.7	0.19 ±0.01	11.0 ±1.4
S1V1	418 ±20	61.7 ±2.1	0.21 ±0.02	86.1 ±4.2
S2V1	425 ±27	63.5 ±1.2	0.23 ±0.01	96.4 ±6.7
S2V2	434 ±29	62.9 ±2.1	0.26 ±0.02	112.1 ±9.1
S3V1	515 ±24	63.4 ±1.7	0.28 ±0.02	144 ±12
S3V2	525 ±22	64.6 ±2.0	0.29 ±0.02	152 ±13

Ultrasonic treatment is considered an environmentally friendly technology compared to conventional chemical extraction/processing methods [38]. Neumann et al. [39] have shown that sonication of food waste at frequencies of (20-40) kHz can increase CH_4 production efficiency by up to (25-40) % compared to untreated substrates. The results obtained are comparable to those presented in this study for the most effective variant, S3V2, where a 25.6 % increase in CH_4 production was observed. Yue et al. [32] showed that CH_4 production efficiency increased from 726.85 mL CH_4/g total volatile solids (TVS) to 927.97 mL CH_4/g TVS by increasing the ultrasonic energy from 1000 kJ/kg to 50,000 kJ/kg during a 30-day anaerobic fermentation of food waste. Joshi and Gogate [31] observed an almost twofold increase in biogas production after 15 days in AD of food waste assisted by sonication compared to conventional heating. The increase in biogas production correlated with the increased power of ultrasound (UT), and the application of sonication resulted in increased cell wall porosity, which promoted more efficient nutrient transfer from the fermentation medium to the microbial cells. In the study by Quiroga et al. [40], daily CH_4 production increased by 31 % in samples subjected to sonication (power 400 W, frequency 24 kHz) during anaerobic co-digestion of food waste, cattle manure and sewage sludge, reaching a value of 432 mL CH_4/g VS. This result was significantly lower than the value obtained by the authors of this manuscript in the mono-digestion of food waste in the S3V2 variant, where CH_4 production reached (525 ±22) mL CH_4/g VS. Higher results were presented by Ormaechea et al. [41], who indicated an about twofold increase in CH_4 production efficiency for co-substrates subjected to ultrasonic pretreatment compared to materials that were not subjected to sonication.

No strong correlations were found between the CH_4 production yield and the concentration of organic compounds in the dissolved phase in any of the experimental variants (S1 - S3V2). The coefficient of determination (R^2) for the relationship CH_4 yield/COD concentration was 0.03816, while for the relationship CH_4 yield/TOC concentration R^2 was 0.4711 (Fig. 3). A significantly better linear fit was found for variants in which the tested EFPs were subjected to pretreatment in S2 and S3. In this case, the relationship between the yield of AD and the concentration of dissolved COD was strong with an R^2 value of 0.8774, and for TOC it was 0.7316 (Fig. 3).

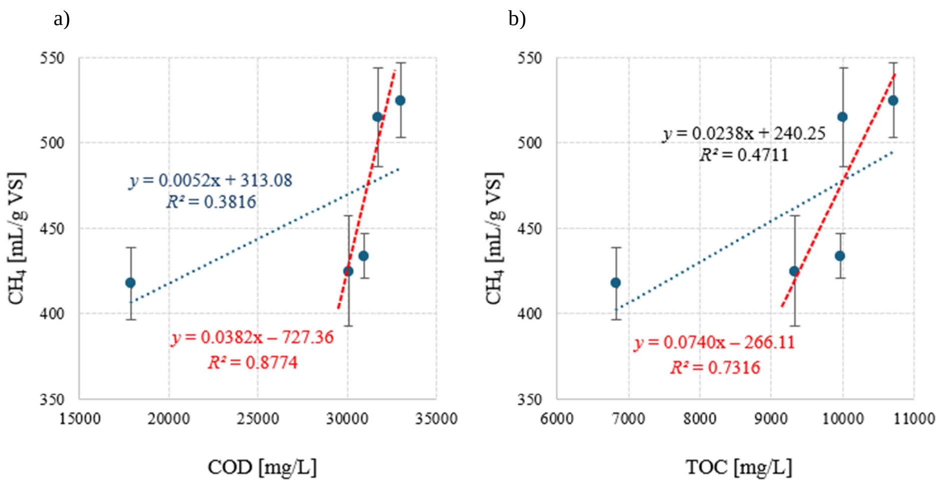

Fig. 3. The relationship between a) CH_4 yield and COD concentration and b) TOC concentration in the dissolved phase

Estimation of the energy balance

Calculations taking into account the CH_4 production and the calorific value of this biogas component (0.00917 Wh/mL) show that the variants in which UTP was used in the pre-treatment process of EFP had the highest energy efficiency. The gross energy production (E_CH4out) in S3V1 was (4.72 ±0.22) Wh, while in S3V2 it was (4.81 ±0.20) Wh (Table 4). The energy consumed (E_TOTinR) for the pretreatment of EFP fed into the anaerobic chambers with UTP was (0.518 ±0.026) Wh and (0.682 ±0.034) Wh, respectively (Table 4). The net energy gain (E_NET) in S3V1 was (4.20 ±0.23) Wh and in S3V2 it was slightly lower at (4.13 ±0.21) Wh. In S1, where the AD process was carried out with raw EFP that had not undergone any pretreatment, the E_NET obtained was significantly lower at (3.83 ±0.27) Wh (Table 4).

The experiments performed showed that the use of CTP variants led to lower energy efficiency, even compared to the control sample. For S2V1 and S2V2, the E_NET values obtained were (3.44 ±0.23) Wh and (3.41 ±0.26) Wh, respectively, 0.39 Wh and 0.42 Wh lower than for S1 (Table 4). Therefore, it should be recognised that the necessary pre-treatment of substrates containing animal products may limit the energy efficiency of biogas plants from the point of view of the processes applicable to AD. However, it is important to emphasise that the results obtained on a laboratory scale in batch reactors are only a very preliminary and estimated basis for further research. More reliable data for a thorough life cycle assessment (LCA) and life cycle cost analysis (LCC) as well as an in-depth energy and economic balance can be obtained by testing under real conditions. Pilot studies reduce the differences and uncertainties associated with scaling up the process.

Table 4

Estimated analysis of energy efficiency for the tested experimental variants

Parameter	**Stage/Variant**				
	S1	**S2V1**	**S2V2**	**S3V1**	**S3V2**
Y_CH_4out [mL/g VS]	418 ±30	425 ±27	434 ±29	515 ±24	525 ±22
E_CH_4 [Wh/mL]	0.00917				
M_VSinR [g VS]	1				
E_CH_4out [Wh]	3.83 ±0.27	3.89 ±0.24	3.98 ±0.26	4.72 ±0.22	4.81 ±0.20
E_INPUT [Wh]	0	116.6 ±4.8	150.2 ±7.2	136.3 ±6.5	179.3 ±7.1
M_VSin [g VS]	263 ±3.8				
E_Uin [Wh/g VS]	0	0.443 ±0.022	0.571 ±0.028	0.518 ±0.026	0.682 ±0.034
M_VSinR [g VS]	1				
E_TOTinR [Wh]	0	0.443 ±0.022	0.571 ±0.028	0.518 ±0.026	0.682 ±0.034
E_NET [Wh]	3.83 ±0.27	3.44 ±0.23	3.41 ±0.26	4.22 ±0.23	4.13 ±0.21

Conclusion

Current regulations in the European Union require the thermal pre-treatment of organic substrates containing animal by-products before they are subjected to anaerobic digestion (AD). One group of such substrates is expired food products, which are produced on a large scale, especially in large companies and food discounters. Until now, thermal pre-treatment has mainly been carried out using waste heat from combined heat and power (CHP) plants. However, due to the conversion of biogas plants to the production of biomethane and the decreasing use of CHP, there is a need to look for alternative heating methods.

The presented study confirms the synergistic effect of simultaneous heating and ultrasonic disintegration on the technological performance and energy balance of anaerobic digestion of expired food products. The monitoring of changes in the concentration of organic compounds in the dissolved phase led to conclude that both the temperature applied during pre-treatment and the technology used have a decisive influence on the degree of solubilisation. The use of ultrasonic disintegration proved to be more effective in transferring organic substances from the solid to the liquid phase.

The highest CH_4 yield was achieved in the anaerobic digestion of expired food products subjected to thermal pre-treatment in combination with ultrasound. These variants also had the highest values for parameters describing the kinetics of anaerobic biodegradation. The higher technological effects of anaerobic digestion were reflected in a higher net energy production. The highest energy efficiency was found in the variants in which the synergistic effect of ultrasonic disintegration and thermal treatment was tested. The exclusive use of conventional heating methods enabled an increase in technological efficiency in terms of CH_4 production, but the energy consumption resulted in a lower net yield than in the control variant.

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