

Article

Technological and Energetic Aspects of Multi-Component Co-Digestion of the Beverage Industry Wastes and Municipal Sewage Sludge

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Abstract: In the present study, the co-digestion effectiveness of the selected beverage wastes and municipal sewage sludge in two- and three-component mixtures was evaluated. Orange peels and orange pulp, as well as brewery spent grain were applied as co-substrates to sewage sludge at the following doses: 1.5 and 3.0 g of orange peels, 2.5 and 5 g of orange pulp, and 1.5 g brewery spent grain. Mono-digestion of sewage sludge was used as a control. The experiments were performed under mesophilic conditions in batch reactors. As compared to the control, only in the presence of the highest dose of pulp, brewery spent grain and sewage sludge was the increased methane production of 395 mL CH₄ g^{−1} VS accompanying an additional energy profit of 82% observed. Moreover, in this case, the enhanced volatile solids removal and lower accumulation of p-cymene were found. These results were despite the increased limonene and phenol content in the feedstock, confirming a synergistic effect at the highest dose of pulp, brewery spent grain and sewage sludge.

Keywords: anaerobic co-digestion; orange waste; brewery spent grain; kinetics and biogas production; inhibitors; energy profits



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1. Introduction

Currently, industrial food production generates considerable amounts of by-products, the effective management of which still remains a technological and economical challenge. A significant share of the global market is represented by beverage manufacturing (both alcoholic and non-alcoholic). Despite major technological improvements, this industry is recognised as the most energy- and water-consuming. Moreover, its production is related to substantial CO₂ emissions. Presently, the global beverage market is dominated by the orange juice and beer industry [1–3]. When processing orange juice, about 50–60% of the fresh fruit becomes waste, which includes peel, seeds, pulp and membrane residues [4–6]. In contrast, about 85% of all by-products generated by the beer industry are represented by brewery spent grain [7]. This solid fraction is composed mainly by the husk and pericarp-seed coat that covers the barley grain [8]. Disposal of both solid residues indicates many difficulties for companies. Due to significant moisture content, their properties deteriorate rapidly, making long-term storage impossible; long-distance transport should also be avoided because of the significant costs. Additionally, both types of waste contain a high organic load; for this reason, they cannot be directly discharged into the environment. Therefore, their reuse, recovery and recycling are limited [4,9].

In turn, the afore-mentioned wastes comprise numerous valuable components. Orange waste contains various nutrients, including vitamins A, B and C; minerals (phosphorus, calcium, and potassium); triterpenes; amino acids; phenolic acids and carotenoids [10]. In contrast, brewery spent grain exhibits a significant content of lipids, proteins, minerals

(calcium, phosphorus, magnesium, sulphur, and potassium) and vitamins (folic acid, biotin, niacin, thiamine, choline, riboflavin, pyridoxine, and pantothenic acid), providing a high buffering capacity [7,11,12].

Another interesting pathway is their energetic application. This is particularly important, bearing in mind the current geo-political situation and a need to become independent from conventional energy sources. Anaerobic digestion (AD) is a widespread and well-known technology for effective waste management [13–15]. Compared to other methods of waste recovery such as biodiesel generation and biomaterials production, it allows for both alternative energy production as well as the generation of a valuable by-product (digestate) that might be used as fertilizer [16–18]. However, as a multi-stage and complex process that involves a wide range of bacteria and archaea, it is vulnerable to the instability caused by many factors, including the accumulation of long-chain fatty acids, volatile fatty acids (VFAs), free ammonia and other inhibitors, as well as frequently unfavourable operating conditions [13,18–20].

Due to the valuable composition and significant biogas potential, both orange wastes and brewery spent grain seem to meet the requirements of energy recovery. However, their anaerobic bioconversion may be difficult. Orange waste is characterised by low pH and high biodegradability that together may lead to the fast accumulation of VFAs. Moreover, it has a relatively small amount of protein and fat, containing limonene—a major AD inhibitor which affects the hydrolytic–acidogenic and methanogenic activity [2,9,21,22]. Using brewery spent grain as an AD mono-substrate is ineffective, mainly due to phenol (mainly p-cresol) inhibition [23]. What is more, brewery spent grain contains lignin, commonly known for low bioconversion efficiency related to its fibrous structure, lending itself to rigidity of materials and inhibiting hydrolysis; thus, it requires prolonged retention time, as compared to other substrates [12,24–27]. In order to overcome these difficulties, both by-products should be pre-treated prior to AD. In the case of orange waste, steam explosion and distillation, solvent leaching, as well as biological methods (fungi, alkali application and ensiling) have been involved to remove limonene [22]. In turn, for brewery spent grain, thermal [28] and thermochemical [24] pre-treatments, as well as the addition of trace elements [29], have been studied.

Nonetheless, the application of these methods requires additional investment and operating costs that many facilities cannot afford. In this context, anaerobic co-digestion with other adequate selected waste may be a promising solution. The state-of-the-art shows that both orange waste and brewery spent grain have been co-digested with various by-products. The orange peels were added to residual glycerol, wherein the methane production reached the value of 330 mL CH₄ g^{−1} VS. However, an inhibition occurred at high organic loads [30]. The beneficial results were observed in tertiary mixtures with sewage sludge and biochar addition. In this case, the methane production exceeded the value of 500 mL CH₄ g^{−1} VS [22]. Moreover, citrus pulp was co-digested with multiple agricultural residues, such as corn silage, cattle manure, poultry litter, whey and olive pomace [31]. In this study, at the presence of highest dose of citrus pulp (42%), the enhanced biogas production of 231 mL CH₄ g^{−1} VS was observed. The brewery spent grain was anaerobically treated with sewage sludge and cheese whey [32], azo dye [33], cow dung and pig manure [34], cattle dung [35] as well as Jerusalem artichokes [36]. In those studies, the average biogas productions varied between 290 and 640 mL g^{−1} VS. In turn, an application of ultrasonic cavitation as brewery spent grain pre-treatment method before its AD resulted in four-fold higher methane production as compared to the control reactor [16].

Nevertheless, it should be noticed that more favourable results were observed in the tertiary mixtures for both the brewery spend grain and orange waste substrates. Taking into account both the economic factor and the easy implementation in a full scale, the application of sewage sludge as a basic substrate for orange waste and brewery spent grain co-digestion seems to be particularly beneficial. It should be noted that sewage sludge is the main by-product from wastewater treatment plants (WWTPs), generated globally in large quantities [37]. Its treatment is related to a significant operational WWTP cost due

to high energy consumption, while the mono-digestion of sewage sludge results in low methane production, as it corresponds to the substrate characteristics—i.e., deficiency of organic matter, imbalanced C/N ratio (carbon to nitrogen ratio) and presence of inhibitors (heavy metals, pharmaceuticals and pathogens). At many WWTPs, the digesters are usually oversized (even up to 30%), which enables introducing an additional substrate without any investments [18]. The implementation of both beverage wastes as co-substrates for sewage sludge anaerobic digestion might improve the feedstock composition by ensuring a significant amount of organic matter. It should be pointed out that such a study has not yet been conducted.

The basic novelty of the work is such a multi-aspect investigation, estimating the effect of another substrate (brewery spent grain) addition on the efficiency of orange waste and sewage sludge co-digestion. It is worth mentioning that many studies conducted in this field have concerned only two-component mixtures. The works involving additional components are rare—although the use of an additional substrate may allow for the efficient anaerobic bioconversion of orange waste in anaerobic co-digestion, with sewage sludge providing an additional energy gain for the WWTPs. Orange waste could increase the C/N ratio, while brewery spent grain could provide the required buffering capacity. Importantly, each of these indicates a significant biogas potential and contains the micro-elements stimulating the activity of methanogens, and thus contributing to the increase in biogas production. However, anaerobic co-digestion performance and its operational conditions should be constantly monitored due to the presence and effect of inhibitors typical of the co-substrates mentioned.

The aim of this study is to evaluate the effectiveness of the co-digestion of selected beverage wastes and municipal sewage sludge in tertiary mixtures, comparing the results with those for two-substrate configurations. Orange peels and pulp as well as brewery spent grain have been applied as co-substrates. The influence of orange waste and brewery spent grain addition on sewage sludge anaerobic digestion is examined on the basis of biogas/methane yields, kinetics (using four different models) and volatile solids removal (VSR). Additionally, the effects of limonene, phenols and p-cymene are evaluated by Fourier-transform infrared photoacoustic spectroscopy (FT-IR/PAS) analysis. To evaluate the possible energy profits resulting from the implementation of these substrates to the existing digester, the energy analysis is also provided. It should be noted that the proposed technology might be easily implemented on a technical scale without significant financial outlays.

2. Materials and Methods

2.1. Substrates and Inoculum

The sewage sludge and inoculum were collected from a mechanical-biological municipal WWTP in Lublin (Hajdów), Poland. The inoculum originated as effluent sludge from mesophilic digesters. Immediately after collection it was transported to the laboratory and then it was sieved to remove fibres and particles above 5 mm. Subsequently, it was introduced into batch reactors, where it was stored under anaerobic conditions at 37 °C to diminish the non-specific biogas production. The procedure of inoculum preparation was adopted from a study conducted by Angelidaki et al. [38]. This sample was characterised by total solids (TS) and volatile solids (VS) of 18.85 ± 0.23 and 9.95 ± 0.16 g kg⁻¹, respectively, as well as a pH of 7.9 ± 0.1 .

The sewage sludge was a main substrate; it was prepared as a mixture of primary and waste sludge, both thickened, and taken separately from Hajdów WWTP. Immediately after collection, the samples were sieved and mixed in a volumetric ratio of 60:40 v/v under laboratory conditions. Such a proportion is recommended as beneficial for an effective biogas production from sewage sludge.

In the present study, the following beverage solid residues were used as additives for co-digestion with sewage sludge: orange peels, pulp and brewery spent grain. The first two substrates were prepared under laboratory conditions as by-products from a

bench-scale orange juice processor. These were mechanically blended to obtain a particle size of 2–5 mm. Then, these samples were frozen and stored at $-25\text{ }^{\circ}\text{C}$ in a laboratory freezer. Before each experiment, they were thawed. Brewery spent grain originated from a craft brewery located in Lublin, Poland. Before supplying the reactor, it was dried at a temperature of $55\text{ }^{\circ}\text{C}$ for at least for two hours in a laboratory dryer. Such preparation of the substrates was adopted to maintained unchanged co-substrate properties during the experiment. This procedure allowed for the elimination of the substrate composition variability's influence on the obtained results. The composition of the sewage sludge and co-substrates was controlled every time while introducing them into the reactors (Table 2).

2.2. Laboratory Installation and Operational Set-Up

The batch tests were conducted with the specially designed BioReactor Simulator (Bioprocess Control AB, Lund, Sweden). It comprised 6 reactors, with an active volume of 2.0 L. Each digester was equipped with a mechanical stirrer operating on a cycle of 5 min mixing and 25 min resting. In order to maintain a proper temperature, reactors were kept in a water bath. The biogas production was monitored and recorded automatically by using a wet gas flow-measuring unit that operated on the principle of liquid displacement and buoyancy and was integrated with the system for continuous data acquisition. Before the experiments, all reactors were flushed with inert gas (N_2) to achieve anaerobic conditions.

Each bottle was supplied with 1.4 L of inoculum and 0.4 L of sewage sludge. The substrate-to-inoculum ratio was adopted based on a procedure given by Angelidaki et al. [38]. In order to evaluate the co-digestion efficiency, a separate control series (R1) was provided, wherein no co-substrates were added. In R2–R5, the anaerobic co-digestion of sewage sludge and orange waste in a two-component system was studied. In turn, in R6–R8, three-component co-digestion was evaluated. The adopted operational set-up is shown in Table 1. The study was conducted under mesophilic conditions ($37\text{ }^{\circ}\text{C}$) and lasted 21 days. The experiments were repeated three times under unchanged operational conditions; for each one, new samples of inoculum and sewage sludge were taken and prepared in the same manner.

Table 1. Experimental settings.

Series	Feedstock Composition	Component Volume			Additive Mass	Feedstock Volume: Additive Mass L:g	VS Load in Feedstock g kg ⁻¹
		Sewage Sludge L	Orange Pulp	Orange Peels g	Brewery Spent Grain		
R1	sewage sludge (control)	0.4	-	-	-	-	14.21 ± 4.88
R2	sewage sludge + orange pulp		2.5	-	-	1:6.25	14.41 ± 4.49
R3	sewage sludge + orange pulp		5.0	-	-	1:12.5	14.84 ± 4.61
R4	sewage sludge + orange peels		-	1.5	-	1:3.75	14.68 ± 4.80
R5	sewage sludge + orange peels		-	3.0	-	1:7.5	15.39 ± 6.09
R6	orange peels + brewery spent grain	0.4	-	1.5	1.5	1:3.75:3.75	16.57 ± 7.10
R7	sewage sludge + orange pulp + brewery spent grain		2.5	-	1.5	1:6.25:3.75	16.05 ± 1.48
R8	sewage sludge + orange pulp + brewery spent grain		5.0	-	1.5	1:12.5:3.75	16.31 ± 1.8

2.3. Analytical Methods

Feedstock and digestate composition were monitored by analysing the following parameters: total chemical oxygen demand (COD), TS, VS, total nitrogen (TN) and total

phosphorus (TP). The soluble chemical oxygen demand (SCOD), VFA, alkalinity (ALK), ammonia nitrogen ($\text{NH}_4^+ - \text{N}$) and orthophosphate phosphorus ($\text{PO}_4^{3-} - \text{P}$) were measured in supernatant. The soluble fraction was obtained by centrifugation of the samples at 4000 r min^{-1} for 30 min. The composition of substrates was examined after their collection. For each one, the analogous parameters, as listed above, were included. TS and VS were determined using the Standard Methods for the Examination of Water and Wastewater [39]. Other analyses were performed using Hach Lange UV-VIS DR 3900 (Hach, Loveland, CO, USA) and cuvette tests. The pH values were monitored using a HQ 40D Hach Lange multimeter (Hach, Loveland, CO, USA).

In order to examine the biogas composition, a ThermoTrace GC-Ultra gas chromatograph provided by Thermo Fisher Scientific (Milan, Italy) was applied. It was equipped with a conductivity detector fitted with divinylbenzene (DVB) packed columns (RTQ-Bond). The parameters for the analyses were: 50°C for the injector and 100°C for the detector; the employed carrier gas was helium, with a flow rate of $1.5 \text{ cm}^3 \text{ min}^{-1}$.

Trace GC Ultra PolarisQ (Thermo Electron, Italy) was used to analyse the limonene and p-cymene contents. The parameters of the capillary column were: Supelco ($30 \text{ m} \times 0.25 \text{ mm ID} \times 0.25 \mu\text{m}$). The spectra were taken under the following conditions: transporter gas helium, with a flow rate of $1.5 \text{ cm}^3 \text{ min}^{-1}$; injection volume of 1 mL. The inlet temperature was initially 40°C . It was then raised by 5°C/min to reach the level of 250°C , where it was kept for 3 min. In order to estimate the peak areas, the CHROM-CARD software was involved.

2.4. Kinetic Modelling

The kinetic evaluation was performed using four different models: Hyperbolic, modified Gompertz, cone and logistic growth. Their equations are presented below:

- Hyperbolic

$$P(t) = P_m \cdot \left(\frac{k \cdot t}{1 + k \cdot t} \right), \quad (1)$$

- Modified Gompertz

$$P(t) = P_m \cdot \exp \left(-\exp \left(\frac{R_m \cdot e}{P_m} \exp(\lambda - t) + 1 \right) \right), \quad (2)$$

- Cone

$$P(t) = \frac{P_m}{1 + (k \cdot t)^{-n}}, \quad (3)$$

- Logistic growth model

$$P(t) = \frac{P_m}{\left(1 + \exp \left(4 \cdot R_m \cdot \left(\frac{\lambda - t}{P_m} \right) \right) + 2 \right)}, \quad (4)$$

where:

- $P(t)$ is the cumulative methane production ($\text{mL CH}_4 \text{ g VS}^{-1}$);
- P_m is the methane production ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS}$);
- R_m is the maximum methane production rate ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS d}^{-1}$);
- e is a constant (2.71828);
- λ is the lag phase (d);
- n is the dimensionless shape factor;
- k is rate constant (d^{-1}).

To indicate the suitability of the model, the root-mean-square error (RMSE) was applied. It was estimated using the following equation [40]:

$$\text{RMSE} = \sqrt{\frac{(P_{\text{exp}} - P_{\text{mod}})^2}{N}}, \quad (5)$$

where:

- P_{exp} is the methane production achieved in the experiment ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS}$);
- P_{mod} is the methane production achieved in kinetic evaluation ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS}$);
- N is a number of measurements.

2.5. FT-IR/PAS Analysis

The samples of feed and digestate were collected from the reactors for FT-IR/PAS (Fourier-transform infrared photoacoustic spectroscopy). First, they were dried via sublimation (i.e., lyophilised). The 50 mL samples were frozen at a temperature of -25°C in the laboratory freezer and subsequently dried at -56°C by means of an Alpha 1–4 freeze dryer. The FT-IR/PAS spectra of the lyophilised samples were obtained by using a Nicolet 6700 spectrometer and a Gasera PA301 photoacoustic cell in the $3800\text{--}700 \text{ cm}^{-1}$ range, resolution 4 cm^{-1} , at room temperature. Dry helium was utilized to purge the photoacoustic cell prior to the collection of data. By computing the ratio of a sample spectrum to the spectrum of a carbon black standard, the spectra were normalised. A stainless-steel cup with a diameter of 10 mm was filled with the sample that had a thickness of less than 3 mm. Interferograms of 1024 scans were averaged for the spectrum; thus, a good signal-to-noise (S/N) ratio was provided. The smoothing functions were not used. All spectral measurements were performed with at least three repetitions.

2.6. Statistical Analysis

All performed analyses were performed in triplicates; the average values and standard deviation are given in tables and figures. For statistical analysis, ANOVA (Shapiro-Wilk's, Levene's and Tukey's tests were included) was performed with Statsoft Statistica software (v 13). The significance level was assumed at $p < 0.05$. All kinetic constants were established using a non-linear regression method. The strength of the relationships between the results was determined using Pearson's correlation coefficient (R) and determination coefficient (R^2).

3. Results and Discussion

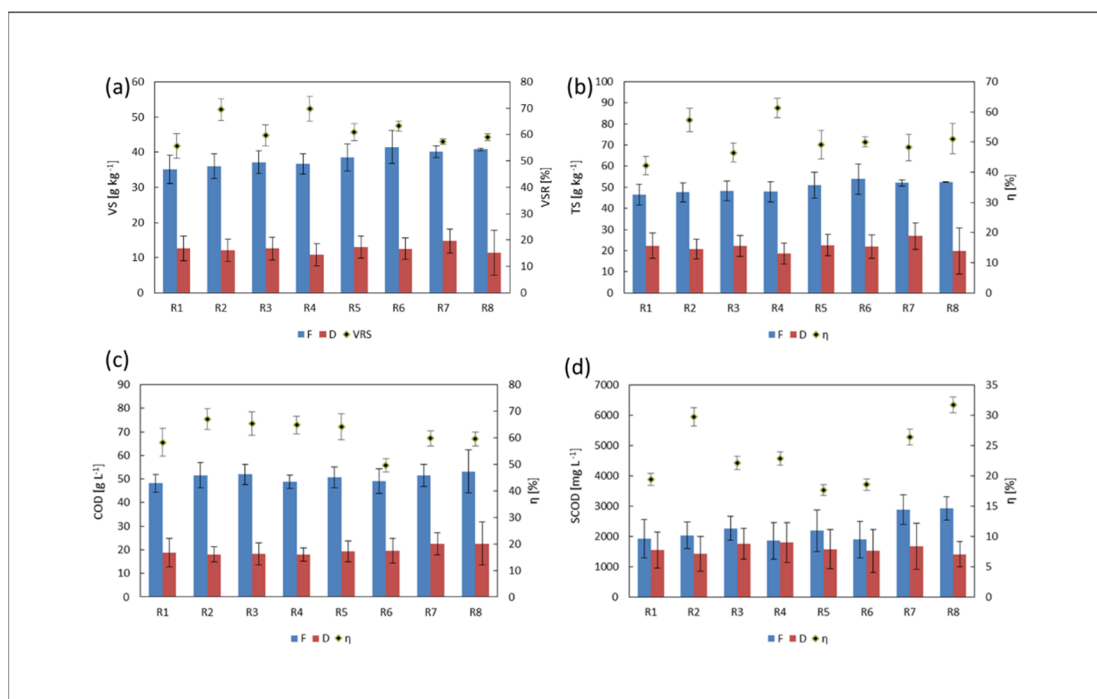
3.1. Characteristics of Substrates and Organic Removal

The characteristics of the applied substrates are presented in Table 2. The used orange wastes indicated similar composition. Both orange peels and pulp were characterised by a low pH, relatively high organic content and comparable nutrient contents. The major differences were observed for TS, VS and phenol and limonene content. It should be pointed out that the orange peels presented an enhanced concentration of inhibitors: phenol and limonene, which might be problematic in anaerobic bioconversion. In turn, brewery spent grain was characterised by the highest organic content as well as nitrogen and phosphorus concentrations. Moreover, to other applied substrates, it indicated an enhanced alkalinity.

The composition of feedstock and digestate is shown in Figure 1. Introducing co-substrates resulted in an increase in the VS, TS and COD contents as compared to the control (sewage sludge only), and the highest enhancements were observed for VS and TS in three-component anaerobic co-digestion.

Table 2. Composition of the substrates used in the experiment (average values and standard deviation are given).

Parameter	Unit	Orange Peels	Orange Pulp	Brewery Spent Grain
Chemical oxygen demand (COD)	mg L ⁻¹	10,185 ± 304	11,750 ± 233	33,600 ± 678
Volatile fatty acids (VFA)	mg L ⁻¹	611 ± 20.2	432.5 ± 15.2	608 ± 10.9
pH	-	4.35 ± 0.2	4.33 ± 0.1	5.01 ± 0.3
Alkalinity (ALK)	mg L ⁻¹	27.1 ± 7.28	35.3 ± 6.08	242.0 ± 2.83
Total solids (TS)	g kg ⁻¹	235.09 ± 0.50	155.18 ± 0.23	937.78 ± 0.32
Volatile solids (VS)	g kg ⁻¹	224.41 ± 0.87	149.28 ± 0.47	878.21 ± 0.77
%VS	% dry weight	95.5	96.2	93.7
Total nitrogen (TN)	mg L ⁻¹	92.05 ± 15.49	111 ± 12.73	739.4 ± 93.7
Total phosphorus (TP)	mg L ⁻¹	16.87 ± 0.38	19.37 ± 0.89	433.25 ± 54.6
Ammonium nitrogen (N-NH ₄ ⁺)	mg L ⁻¹	4.57 ± 0.13	3.96 ± 0.17	2.83 ± 0.25
Ortho-phosphate phosphorus (P-PO ₄ ³⁻)	mg L ⁻¹	14.7 ± 0.14	14.95 ± 0.88	223.75 ± 2.64
Phenol	mg L ⁻¹	60.1 ± 6.5	36.1 ± 4.24	49.9 ± 0.4
Limonene	µg g ⁻¹ TS	297 ± 5.1	50.3 ± 2.1	nd.

**Figure 1.** Content of VS (a), TS (b), COD (c) and SCOD (d) in feedstock (F) and digestate (D), as well as related removal efficiencies (average values and standard deviations are given).

This observation was related to the enrichment of feedstock with brewery spent grain (Table 2) by 18, 14 and 16% for VS, as well as 15, 12 and 12.5% for TS in R6, R7 and R8, respectively. Considering COD, in two-component anaerobic co-digestion, the major increase of 7% was found in the presence of both orange pulp doses, while in three-component series it was 10% when involving 5 g of orange pulp and 1.5 g of brewery spent grain (R8). Similarly, the highest growths for SCOD of approx. 50% occurred in R7 and R8 at both doses of orange pulp mixed with brewery spent grain.

In relation to sewage sludge mono-digestion, the VSR and TS removal were improved every time (Figure 1a,b), although to a lesser extent in the series with brewery spent grain. The highest increases were found in the lowest co-substrates doses (with comparable VS loads to control). An increased organic load in feedstock might result in poor process performance and promote the process instability caused by VFA accumulation. In particular,

this effect might occur in anaerobic co-digestion with easily biodegradable substrates such as fruit and other food wastes [41–43]. Nevertheless, such an effect was not observed when analysing the VFA in digestate (Table 3).

Table 3. The pH values and ALK, VFA, phenol, limonene and p-cymene concentrations in feedstock (F) and digestate (D) (average values and standard deviation are given).

Parameter	Unit		R1	R2	R3	R4	R5	R6	R7	R8
ALK	mg L ⁻¹	F	844 ± 17.7	847 ± 24.5	854 ± 33.8	852 ± 25.5	876 ± 35.3	894 ± 52.2	996 ± 15.1	907 ± 24.4
		D	4547 ± 183.2	4893 ± 212.4	5240 ± 233.8	4942 ± 209.7	4984 ± 219.9	4131 ± 122.0	4796 ± 158.4	4636 ± 348.2
VFA	mg L ⁻¹	F	560 ± 15.2	566 ± 11.2	578 ± 18.4	540 ± 31.3	593 ± 61.7	642 ± 77.5	677 ± 51.3	804 ± 35.7
		D	239 ± 18.0	335 ± 16.8	325 ± 47.2	324 ± 47.4	338 ± 20.0	238 ± 17.6	252 ± 22.2	250 ± 22.1
pH		F	6.23 ± 0.05	6.30 ± 0.04	6.22 ± 0.04	6.01 ± 0.14	6.04 ± 0.08	6.02 ± 0.08	6.08 ± 0.01	6.02 ± 0.01
		D	7.44 ± 0.01	7.42 ± 0.01	7.41 ± 0.02	7.43 ± 0.02	7.43 ± 0.03	7.44 ± 0.02	7.45 ± 0.02	7.44 ± 0.01
phenol	mg L ⁻¹	F	7.4 ± 0.6	9.9 ± 1.9	8.4 ± 0.7	7.6 ± 0.7	9.7 ± 0.9	15.0 ± 2.3	24.4 ± 2.5	24.6 ± 2.4
		D	8.6 ± 0.64	9.5 ± 0.72	10.0 ± 1.1	10.1 ± 1.07	9.4 ± 0.75	9.5 ± 0.85	10.5 ± 0.97	10.1 ± 0.97
limonene	ppb	F	51.9 ± 12.2	198.2 ± 21.0	246.0 ± 39.7	558.1 ± 38.18	1098.8 ± 20.9	835.1 ± 22.4	513.2 ± 34.4	689.5 ± 19.4
		D	17.0 ± 1.3	30.1 ± 7.6	37.6 ± 3.4	36.1 ± 3.5	51.1 ± 2.3	22.8 ± 2.6	37.7 ± 4.6	27.0 ± 9.9
p-cymene	ppb	F	31.1 ± 4.2	43.7 ± 3.5	33.6 ± 3.6	35.5 ± 0.3	32.4 ± 2.3	37.7 ± 1.3	34.8 ± 0.8	33.7 ± 0.7
		D	16.7 ± 3.1	44.5 ± 2.1	44.7 ± 3.7	3797.6 ± 68	9024.5 ± 250	3119.3 ± 78	542.3 ± 21	143.6 ± 15.3

The results in terms of VSR were consistent with other studies. Serrano et al. [44] performed the mesophilic anaerobic co-digestion of sewage sludge and orange peels mixed at a proportion of 70:30 (wet weight), achieving the VSR of 76%; in sewage sludge, the mono-digestion was only 53%. Martínez et al. [22] evaluated the anaerobic co-digestion of sewage sludge and orange peels, as well as sewage sludge, orange peels and biochar addition. At HRT of 20 days, VS was removed by 63 and 49% in the two- and three-component systems, respectively.

Considering the COD and SCOD, their removal was also improved as compared to the control, wherein a significant drop referred to the latter and reached 36 and 64% in R7 and R8, respectively. The increases might point to the effective consumption of soluble organics via anaerobic co-digestion. The exceptions were the reactors supplied by the orange peels and brewery spent grain (R6), as well as the highest orange peel dose (R5), wherein a declining trend occurred. It seems to indicate that the process inhibition was caused by the high concentration of p-cymene (Table 3) as a product of limonene conversion. Importantly, in R5 and R6, the highest concentrations of this compound in the feedstock were found.

3.2. Inhibitors Presence

To evaluate the influence of the co-substrate application on the process stability, the following parameters were analysed: the pH value, ALK, VFA concentration and the VFA/ALK ratio (Table 3).

It should be noted that all of the analysed parameters reached the values recommended for adequate methanogenic activity [45]. Stable process performance was also confirmed by the VFA/ALK ratio, which reached values much below 0.3, ranging from 0.052 to 0.068 in all anaerobic co-digestion series, with the highest values found in the two-component system.

Due to the possible inhibitory effect, the contents of the phenolic compounds in the feedstock and digestate were also analysed [46]. Their negative influence on the AD process is connected to the damage of microbial cells through changing the membrane permeability, which might lead to the leakage of intra-cellular components and the inactivation of essential enzymatic systems [47]. However, its toxicity is dependent upon several factors, such as: concentration, micro-organisms' consortium and acclimatization period [48].

The application of orange pulp and orange peels increased the content of phenols in the feedstock; however, the difference was of no statistical significance. The significant changes were found in the three-component anaerobic co-digestion. In R6, the concentration was enhanced twice, while in R7 and R8, more than three-fold increases were noticed. It was not surprising due to the composition of substrates used and their doses (Tables 1 and 2).

Compared to the feedstock compositions in R1, R3 and R4, a slight increase in the phenol content in the digestate was found. In the remaining series, the concentration of phenols

decreased, indicating their metabolization through anaerobic co-digestion. Importantly, the major removal efficiency of approx. 57% was noted in the anaerobic co-digestion of orange pulp and brewery spent grain. Some studies have indicated that the presence of easily biodegradable substrates might improve the degradation of recalcitrant compounds, such as phenol; this effect is related to the occurring co-metabolism and presence of enzymes involved in these mechanisms [49–51]. This observation also confirmed the synergistic effect occurring between substrates.

In the present study, the limonene and p-cymene contents were also analysed. This was due to the possible inhibitory effect of limonene, which is related to the occurrence of cymene which is generated during biotransformation of the former in AD [21]. Inhibition is expected because essential oils might accumulate in the cell membrane and change its fluidity, resulting in increased permeability and finally lead to leakage of the cell contents [52].

The application of both orange wastes resulted in a significant increase in the limonene concentration, as compared to sewage sludge. There were 3.8, 4.7, 10.7, 21.1, 16.1, 9.9 and 13.3-fold increases in feedstock for R2, R3, R4, R5, R6, R7 and R8, respectively—the greatest increase being in the presence of orange peels. The major increment was obviously related to the application of the highest orange peel dose. In turn, the p-cymene content was at a low level. The introduction of co-substrates slightly increased its concentration in the feedstock, with the exception of R2. As shown in Table 3, in all series, limonene was efficiently degraded in the AD process. The related removal efficiencies were 67, 85, 85, 94, 95, 97, 93 and 96% in R1, R2, R3, R4, R5, R6, R7 and R8, respectively. Simultaneously, a significant increase in the p-cymene content of the digestate was noted. The exception was a control series fed with sewage sludge, wherein its removal was observed. Furthermore, the major increases indicating the accumulation of p-cymene through anaerobic co-digestion were observed in the presence of orange peels, and they corresponded with both the high content of limonene in the feedstock (R4, R5 and R6) and the orange peel dose.

In three-component anaerobic co-digestion, using orange pulp and brewery spent grain as co-substrates (R7 and R8), and despite a significant content of limonene in the feedstock, a lower accumulation of p-cymene has been recorded. This seems to indicate the greater flexibility of such a configuration and its usefulness in metabolizing the by-products generated through the biotransformation of limonene. The synergistic effect in anaerobic co-digestion of orange pulp, brewery spent grain and sewage sludge was confirmed. The obtained results are consistent with other studies that suggested the co-digestion strategy for reducing the toxicity of individual substrates [53]. The previous studies have indicated that anaerobic micro-organisms exhibit some adaptability to the inhibitory effect of essential oils, while its extent depends on various factors such as the type of substrate and kind of inoculum, as well as the temperature [54].

The beneficial effect observed in the batch system needs to be confirmed each time in the semi-flow configuration, where operational factors (i.e., organic loading rate and hydraulic retention time) significantly affect the anaerobic co-digestion performance. In such systems, the process inhibition might occur more rapidly due to the continuous supply of the substrate, the accumulation of toxicants and insufficient biomass adaptation. Accordingly, studies in future would continue to involve a semi-flow mode.

3.3. Biogas and Methane Productions

The results of biogas and methane production are presented in Figure 2 and Table 4. As is shown in Figure 2, in all reactors, the peak related to decomposition of carbohydrates occurred within the first three days of the experiment. The highest initial growth was found at both orange peel doses. As compared to the control, the decrease in daily biogas and methane yields were observed only in the presence of the lowest dose of orange pulp (R2), with the subsequent enhancement between 4 and 10 days of the experiment. Moreover, between 17 and 20 days, a minor additional peak was noticed in the cases of R3, R4 and R5.

Such fluctuations might result from the decomposition of the more complex compounds such as proteins and lignocellulose presented in the co-substrates [55].

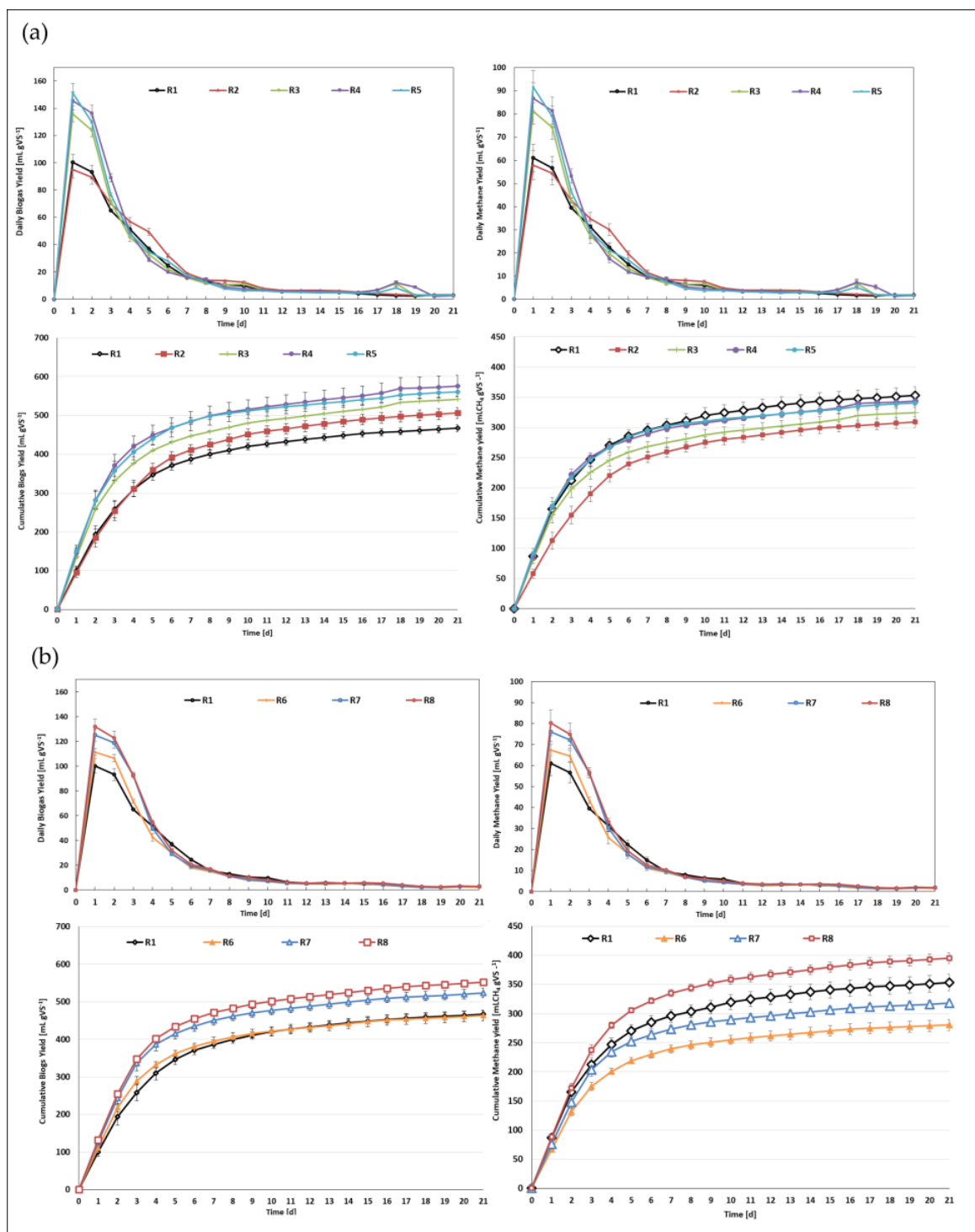


Figure 2. Daily biogas and methane yields, as well as cumulative biogas and methane productions in two- (a) and three- (b) component co-digestion series (average values and standard deviations are given).

Table 4. The results of experimental data in terms of biogas/methane productions as well as estimated kinetic parameters.

Model	Parameters	Unit	R1	R2	R3	R4	R5	R6	R7	R8
Modified Gompertz	P_m	mL g ⁻¹ VS	337.3	296.7	305.6	323.7	323.9	267.7	302.8	376.9
	R_m	mL g ⁻¹ VS	59.00	44.33	53.67	64.66	64.00	50.86	61.63	69.82
	λ	d	−0.43	−0.30	−0.49	−0.32	−0.34	−0.30	−0.20	−0.25
	R ²	-	0.9885	0.9938	0.9847	0.9858	0.9891	0.9898	0.9904	0.9911
	RMSE	-	9.2	7.0	11.0	11.5	9.6	7.4	8.7	10.6
Hyperbolic	P_m	mL g ⁻¹ VS	403.2	373.3	364.2	382.4	380.6	318.8	359.5	453.7
	k	d ⁻¹	0.368	0.259	0.378	0.420	0.430	0.388	0.405	0.360
	R ²	-	0.9978	0.9959	0.9979	0.9964	0.9969	0.9962	0.9946	0.9954
	RMSE	-	28.8	37.2	22.8	22.4	23.1	22.1	24.1	33.7
Cone	P_m	mL g ⁻¹ VS	372.7	328.6	342.7	353.9	351.6	290.5	325.0	408.4
	k	d ⁻¹	0.412	0.319	0.415	0.463	0.471	0.437	0.454	0.413
	n	-	1.29	1.41	1.21	1.32	1.34	1.39	1.47	1.44
	R ²	-	0.9996	0.9996	0.9980	0.9973	0.9992	0.9994	0.9988	0.9992
	RMSE	-	11.2	11.4	10.4	6.0	6.4	5.8	4.1	7.6
Logistic growth model	P_m	mL g ⁻¹ VS	334.3	293.3	302.7	320.8	321.5	265.4	300.1	373.4
	R_m	mL g ⁻¹ VS	55.30	42.12	50.29	61.88	59.99	48.28	59.49	66.86
	λ	d	−0.49	−0.30	−0.55	−0.32	−0.38	−0.31	−0.17	−0.24
	R ²	-	0.9797	0.9869	0.9752	0.9768	0.9807	0.9815	0.9827	0.9819
	RMSE	-	11.0	9.0	12.7	13.2	11.0	8.7	10.2	12.6
Experimental data	BP	mL g ⁻¹ VS	467.0 ± 9.4	506.3 ± 13.8	541.5 ± 15.5	575.8 ± 27.7	561.1 ± 11.4	463.4 ± 14.4	523.5 ± 12.8	552.2 ± 20.8
	P	mL CH ₄ g ⁻¹ VS	353.3 ± 14.2	308.9 ± 8.8	324.7 ± 11.2	343.6 ± 16.8	341 ± 6.9	280.5 ± 9.5	317.8 ± 6.6	395.2 ± 9.4
	GPR	mL g ⁻¹ VS d ⁻¹	22.3 ± 2.0	24.1 ± 3.3	25.8 ± 3.7	27.4 ± 1.6	26.7 ± 2.7	22.1 ± 2.4	24.9 ± 3.1	26.3 ± 2.9
	MPR	mL CH ₄ g ⁻¹ VS d ⁻¹	16.8 ± 1.2	14.7 ± 2.1	15.4 ± 2.7	16.3 ± 7.7	16.2 ± 1.7	13.3 ± 1.3	15.1 ± 1.6	18.8 ± 3.2
	Methane content	%	62.3 ± 1.37	61.0 ± 0.38	59.8 ± 2.18	59.7 ± 0.98	60.7 ± 0.62	60.4 ± 0.93	60.8 ± 1.29	60.9 ± 0.93

The cumulative biogas production was improved in almost all of the co-digestion series. The statistically significant increments of 23, 20 and 18% were achieved in R4, R5 and R8, respectively, as compared to sewage sludge mono-digestion. Moreover, it should be pointed out that in R7, supplied by a lower dose of orange pulp and brewery spent grain, the enhancement of 12% occurred as compared to the control reactor (R1); however the observed change was of no statistical significance. The achieved increases were attributed to the introduction of co-substrates rich in organic matter, improving C/N and providing deficient micro- and macro-elements. This was favourable for the anaerobic co-digestion performance, which was indicated by the enhanced values of the biogas production rate (GPR) (Table 4). Ensuring optimal conditions for anaerobic micro-organisms contributed to enhancing the microbial activity, resulting in increased biogas production.

A different trend was observed in the tertiary mixtures in the presence of sewage sludge, orange peels and brewery spent grain (R6); therein, a comparable result to sewage sludge mono-digestion was found. This tendency occurred despite improved feedstock composition, as well as high VSR. It might indicate process inhibition related to the lowest pH in the feedstock and the presence of both limonene and phenol (Table 3). Moreover, in this case, micro-organisms were additionally involved in the transformation of complex compounds present in brewery spent grain, also contributing to the lower biogas production. This seems to be confirmed by the GPR value, which was the lowest among all the experiments (Table 4). The explanation might be the fact that cellulose, hemicellulose and lignin, as well as the interactions of these components, create a highly resistant structure for AD microbes [25]. Importantly, in the presence of both orange pulp and brewery spent grain, there was no adverse effect observed, which testifies to their proper selection for anaerobic co-digestion with sewage sludge.

It is not a surprise that the application of carbohydrate-rich substrates resulted in a reduction of the methane content in the biogas (Table 4). This obviously influenced the results in terms of methane production (Figure 2).

As compared to sewage sludge mono-digestion, an improvement of 12% was observed only in the presence of the highest dose of orange pulp and brewery spent grain (R8), accompanied by the highest MPR value. In turn, a major, statistically significant drop of 26% was found in three-component anaerobic co-digestion with orange peels and brewery

spent grain, also confirming the process inhibition visible in the lowest MPR and cumulative methane production (Figure 2).

The results in terms of biogas/methane production, as well as the process disturbances, correspond to the previous studies referring to the application of citrus wastes in the anaerobic digestion process. The methane potential of various citrus peels varied between 353.9 and 398.2 mL CH₄ g^{−1} VS [21]. However, in this case, process inhibition was observed for a limonene content higher than 200 mg kg^{−1}. In turn, the AD of pre-treated orange peels by steam distillation resulted in the production of 230 mL CH₄ g^{−1} VS. The higher values of 400–600 mL CH₄ g^{−1} VS were observed under thermophilic conditions [6]. In a semi-flow system, Serrano et al. [44] evaluated the mesophilic anaerobic co-digestion of sewage sludge and orange peels mixed at a proportion of 70:30 (wet weight). The achieved methane yield was 165 mL CH₄ g^{−1} VS, and the VSR reached 76%. Nevertheless, in this case, at the highest organic loads, the methane production decreased due to ammonia inhibition. Martinez et al. [22] supplemented the two-component mixture with biochar to overcome the limitation of the anaerobic degradation of sewage sludge and citrus peels. The enhanced values of 500 and 704 mL CH₄ g^{−1} VS were observed in the presence of 10 and 30 g of biochar, respectively. The methane potential of sewage sludge and orange peels mixed at a VS ratio of 1:1 was only 298 mL CH₄ g^{−1} VS. The increases in biochar presence were explained by the adsorption of inhibitors, as well as provided the high surface area that promoted the adhesion and growth of micro-organisms.

3.4. Kinetic Evaluation

According to Kainthola et al. [56], to analyse the results of a kinetic study, the percentage error between the experimental and predicted values should not exceed 25%. As was shown in Table 4, this condition has been fulfilled for all the applied models. Moreover, the results indicated that the best fitted model for selected substrates were the modified Gompertz, cone and logistic growth models; this fact was also confirmed by high R² values as well as a low value of RMSE. Previous studies indicated that the modified Gompertz showed the best fit for anaerobic co-digestion systems [57,58]. In turn, the cone and logistic growth models have been frequently applied for various food wastes [58–61].

In both the hyperbolic and cone models, the *k* constant was improved in almost all of the anaerobic co-digestion series as compared to control, indicating enhanced rates of degradation in the presence of co-substrates [58,62]. The highest *k* values were found in the presence of both doses of orange peels and sewage sludge (R4 and R5), corresponding to increased biogas production. However, in R8, supplied by 5 g of orange pulp and 1.5 g of brewery spent grain, a comparable result to the control was found. This fact might be related to both the introduction of hardly biodegradable brewery spent grain with a significant lignin content and the increased dose of orange pulp [59,63]. A similar trend, indicating a drop in *k* during the anaerobic digestion of fruit residues with significant lignin content, was also observed by Zhao et al. [59].

In R2, fed by sewage sludge and the lowest dose of orange pulp, a decreased *k* was observed. This seems to confirm to the process inhibition caused by toxic compounds. It should be pointed out that the obtained *k* constants were higher than for those from other studies [64,65]. This is probably due to the fact that the value of *k* is directly related to the feedstock characteristic, as well as to the adopted process conditions (mono- or co-digestion, temperature, substrate doses and type of inoculum). It typically varies between a wide range of 0.02–0.49 d^{−1} [66]. Moreover, the higher *k* values were found in the cone model, though the same observation was found in the study performed by Zhao et al. [59].

While considering R8, there was no concordance between the tendency observed for the experimental data (MPR) and the *k* constant from the models listed above. It was shown that in the experiment an increased MPR value was found as compared to control. This seems to indicate some inadequacy in using such models for a complex, three-component feedstock of sewage sludge, orange pulp and brewery spent grain. It is commonly known that models are usually well verified for mono-substrates with strictly defined composition,

although they might be inadequate for describing the complexity of the co-digestion of sewage sludge with other waste.

Regarding the maximum methane production rate, the increased values were found in the presence of both doses of orange peels (R4 and R5), as well as for orange pulp and brewery spent grain (R7 and R8) in the two- and three-component systems, respectively. Importantly, as compared to control, the decrease in this parameter occurred for both doses of pulp (R2 and R3) and for orange peels and brewery spent grain (R6), which is consistent with the trend observed for MPR (Table 4).

Lag phase describes the microbial adaptation to the substrates. In both modified Gompertz and logistic growth models, this parameter reached values below zero, indicating a sufficient acclimatization of micro-organisms to degrade the substrates and a rapid start to the reaction. The results also indicated the absence of the lag phase. Similar findings were reported by Zhao et al. [59] and Liew et al. [66]. The lowest values of λ corresponded to the highest dose of easily biodegradable orange pulp (R3). In contrast, the increased λ was obtained in the presence of co-substrates with a complex structure, such as brewery spent grain.

The values of the shape factor in the cone model were comparable to the results reported in literature (1.3–3.6) [58,60,64,67]. The increased values occurred in the presence of both the pulp and brewery spent grain co-substrates.

3.5. FT-IR/PAS Analysis

The FT-IR/PAS analysis was used to evaluate both the feed and digestate quality and provided insight into the transformations of organic matter resulting from anaerobic co-digestion.

The FT-IR/PAS spectra of both the raw and digested sewage sludge, as well as the spectra of the sewage sludge with the addition of pulp, orange pulp and brewery spent grain (both raw and digested) are shown in Figure 3a. The intensities of the IR bands are lower in the spectra of the digested samples than in the raw ones. The smallest differences were observed in the raw and digested sewage sludge spectra without an added co-substrate (Figure 3a). The bands indicating the presence of nitrile $\text{C}=\text{N}$ and isonitrile $\text{N}=\text{C}$ bands (2135 and 2062 cm^{-1} , respectively) almost completely disappeared for the digested samples. The intensity changes of bands within $2956\text{--}2852\text{ cm}^{-1}$ (C-H stretching) also indicate the decomposition processes of organic components and can be used to evaluate the anaerobic digestion efficiency [68].

The addition of orange pulp and orange peels causes the appearance of new bands in the FT-IR/PAS spectra (Figure 3, R2-F–R8-F) and increases the intensity of other bands. Broad bands with maxima at 3400 and $\sim 3340\text{ cm}^{-1}$ are typical of the alcohol hydroxyl. The band at 1733 cm^{-1} ($\text{C}=\text{O}$ stretching) is more intense and sharper than in the spectrum of sewage sludge (Figure 3, R1-F). A similar situation occurs in the case of vibration of the C–H groups ($2956\text{--}2852\text{ cm}^{-1}$). The band at $\sim 1572\text{ cm}^{-1}$ is due to the presence of a $\text{C}=\text{O}$ stretching vibration in flavonoids [69], aromatic $\text{C}=\text{C}$ [70], COO^- and/or amide II. This band may also indicate the presence of $\text{C}=\text{C}$ vibration in the terminal methylene group of limonene, which may be confirmed by the presence of the band at 898 cm^{-1} (out-of-plane bending of the terminal methylene group) [71]. The band at 1460 cm^{-1} , as well as the band at 1412 cm^{-1} , may have contributions from more than one group vibration: aliphatic C–H, aromatic $\text{C}=\text{C}$ and C–O in alcohols. The first of the mentioned bands is characteristic for limonene and p-cymene [72,73]. The band at 1373 cm^{-1} is probably due to the combination of the O–H deformation vibration and C–O stretching vibration in the phenolic compounds. The band at 1203 cm^{-1} is due to C–O stretching vibration in alcohols, as well as the bands at 1105 and 1052 cm^{-1} [69]. The band at 1052 cm^{-1} may also correspond to C–O–H or C–O–R in alcohols or esters [74].

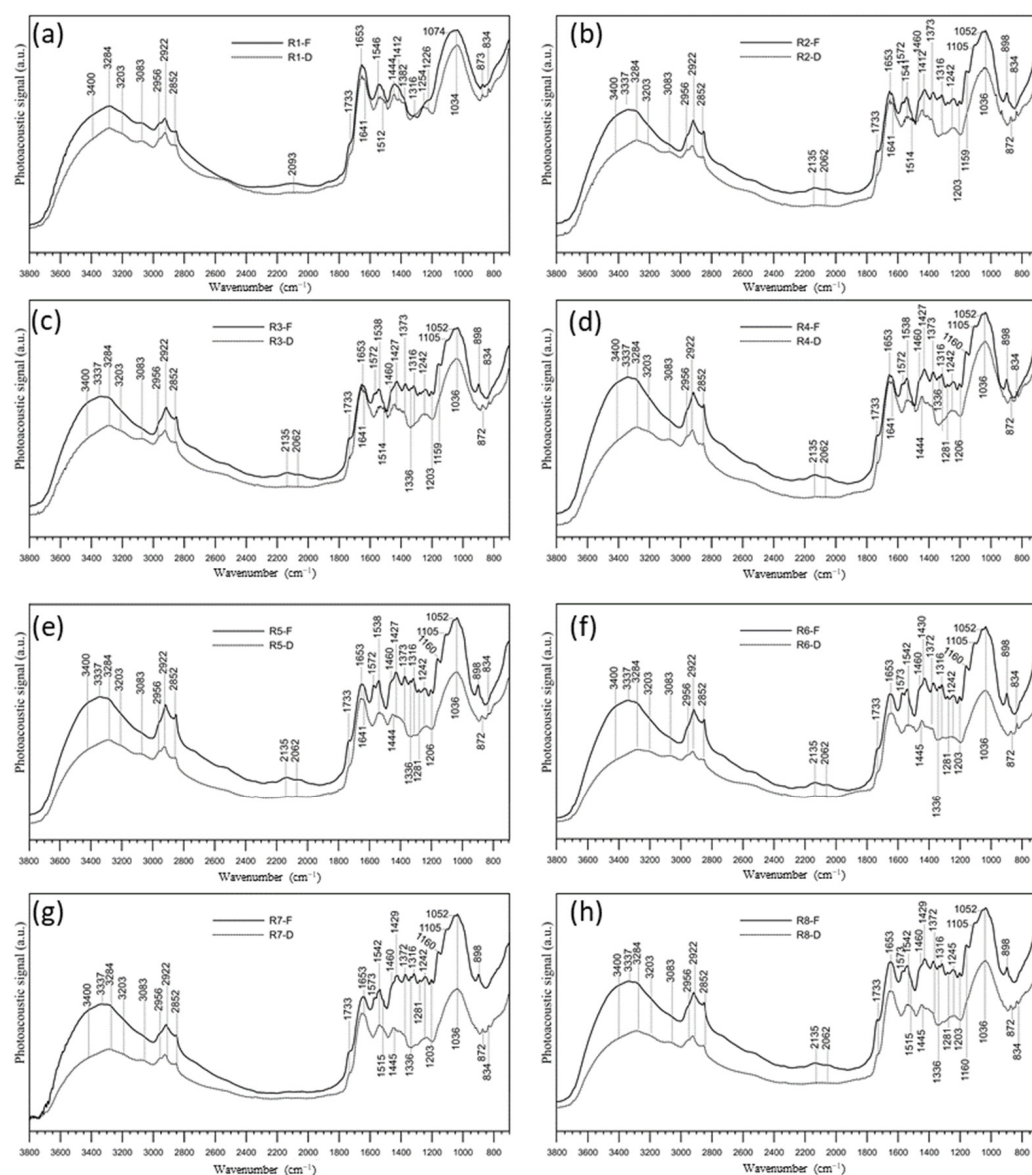


Figure 3. FT-IR/PAS spectra before (F) and after digestion (D) in the series (a) R1, (b) R2, (c) R3, (d) R4, (e) R5, (f) R6, (g) R7, (h) R8.

The decrease in intensity of the bands in the FT-IR/PAS spectra may be evidence of the reduction of organic compounds in the digestate. In the case of the R1-F and R1-D samples (sewage sludge without co-addition before and after anaerobic digestion, respectively), these changes are not as significant as in the cases of the subsequent samples, although the decrease in peak intensities is observable for O–H stretching of hydroxyl and =C–H in aromatic structures groups ($3600\text{--}3080\text{ cm}^{-1}$), C–H and –OH of COOH in hydroxyl or amine compounds (1412 cm^{-1}), C=C in aromatic rings, C–H and C–O–C in ethers ($1254\text{--}1226\text{ cm}^{-1}$) and C–O–C ($1074\text{--}1034\text{ cm}^{-1}$). As mentioned before, the addition of co-substrates changes the spectral characteristics. The additional bands visible in the spectrum of the R2-F–R8-F samples disappear completely for digested ones (R2-D–R8-D). Additionally, the intensities of the other bands also decrease. In the R5-F and R6-F spectra, the flavonoids, limonene and p-cymene bands ($1572, 1538, 1460, 898\text{ cm}^{-1}$) are the most intense, which suggests that their highest contents are in these samples. These bands, but of lower intensity, are also visible in the spectra of other samples with the pulp and orange peels and with brewery spent grain co-additions. However, the addition of the latter does not significantly affect the shape of the IR spectrum. The absence of the mentioned bands

in the spectra of the samples after digestion (R3-D–R8-D) suggests the decomposition of flavonoids, p-cymene and limonene during the AD process. The band at 1572 cm^{-1} and 898 cm^{-1} disappear completely, same as the bands of the hydrogen-bonded –OH groups in alcohols (3400 , 3340 , 1203 , 1105 and 1052 cm^{-1}), while the bands of O–H deformation vibration and C–O stretching vibration in phenolic compounds (1373 cm^{-1}) have much lower intensity. In the spectra of all digested samples, except R1 (Figure 3a), a decrease in the intensity of the aliphatic C–H groups bands can be observed within the 2956 – 2852 cm^{-1} range.

The decrease in the intensity of all bands, and thus the highest degree of decomposition, can be observed for the three-component systems (R6–R8, Figure 3f–h). These observations were consistent with the results presented and discussed in the previous sections.

3.6. Energy Balance

To estimate the potential energy profits in full-scale facilities, the energy balance for the most favourable two- and three-component series (R5 and R8) was performed. This evaluation was performed on the basis of the procedure described by Szaja and Montusiewicz [32]. The detailed calculations are presented in Table 5.

Table 5. The energy balance evaluation of selected reactors.

Parameter	Unit	R1 Control	R5	R8
Characterisation data				
VS	g kg^{-1}	35.13	38.47	40.77
Feedstock density	kg m^{-3}	947.8	949.7	952.4
VS load	kg d^{-1}	4162	4567	4854
Methane yield	$\text{mL CH}_4\text{ g}^{-1}\text{ VS}$	353	341	395
Daily methane production	$\text{m}^3\text{ CH}_4\text{ d}^{-1}$	1471	1555	1918
Feedstock temperature	$^{\circ}\text{C}$	8	8	8
Feedstock flow rate	$\text{m}^3\text{ d}^{-1}$	125	125	125
Energy terms				
Theoretical thermal energy	MJ d^{-1}	52,648	55,680	68,675
Thermal energy needed for heating the feedstock	MJ d^{-1}	14,175	14,175	14,175
Thermal energy needed for covering the heat loss	MJ d^{-1}	3766.0	3766.0	3766.0
Thermal energy demand	MJ d^{-1}	19,735	19,735	19,735
Profit of thermal energy	%	166.8	182.1	248.0
Net thermal energy profits	%	—	15.4	81.2
Daily energy production	kWh d^{-1}	14,706	15,553	19,183
Energy production	kWh t^{-1}	117.6	124.4	153.5
Power terms				
Theoretical thermal power production	kW	263.5	278.7	343.7
Theoretical electric power production	kW	232.8	246.3	303.7
Profit of both theoretic thermal and electric power productions	%	—	5.4	23.3

The evaluation was made for an existing digester with a volume of 2500 m^3 , operating at an HRT of 20 days under mesophilic conditions ($35\text{ }^{\circ}\text{C}$) (located at the WWTP in Lublin, Poland).

In co-digestion series R5 and R8, the obtained thermal energy would completely cover the digester energetic demand necessary for heating the feedstock as well as the heat losses. Importantly, in both cases, an additional energy surplus was found. As compared to the control, the energy profit was improved by 15.4 and 81.2% in R5 and R8, respectively. Moreover, the related thermal/electric power production was enhanced by 5.4 and 23.3%. The beneficial results for R8 were attributed to the synergistic effect of the substrates used; thus, significantly higher methane production accompanied the increased VS load in the feedstock.

The results in terms of energy balance, regarding the implementation of this technology in an existing digester, are particularly important. Such a solution might provide energy neutrality to WWTPs. However, consideration should be taken regarding the seasonality of these wastes or, eventually, the necessity of their storage, as well as their transport cost.

4. Conclusions

The conducted research has investigated the effectiveness of the co-digestion of selected beverage wastes and municipal sewage sludge in two and tertiary mixtures. As compared to the control, the increased methane production was achieved only in three-component co-digestion in the presence of the highest dose of orange pulp and brewery spent grain (R8). This was accompanied by an increased VSR, comparable kinetics and a lower accumulation of p-cymene. Importantly, therein was the essential improvement of energy balance by 81.2% as compared to control also observed. These were achieved despite the increased limonene and phenol content in the feedstock, confirming that a synergistic effect occurred in this case. Moreover, the FT-IR/PAS analysis also seems to indicate such a three-component anaerobic co-digestion as a beneficial choice.

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