

Article

Leveraging Potato Chip Industry Residues: Bioenergy Production and Greenhouse Gas Mitigation

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Abstract: Anaerobic digestion (AD) offers a sustainable solution by treating biodegradable waste while recovering bioenergy, enhancing the share of renewable energy. Thus, this study aims to investigate the AD for managing and valorizing residues from the potato chip industry: potato peel (PP), potato offcuts (OC), waste cooking oil (WCO), wastewater (WW), and sewage sludge (SS). In particular, the biochemical methane potential (BMP) of each residue, anaerobic co-digestion (AcoD), and greenhouse gas (GHG) emissions of an AD plant are assessed. WW, OC, and SS present a BMP of around 232–280 NmL_{CH₄}/kg of volatile solids (VS). PP and WCO reach a BMP slightly lower than the former substrates (174–202 NmL_{CH₄}/g_{VS}). AcoD results in methane yields between 150 and 250 NmL_{CH₄}/g_{VS}. An up-scaled anaerobic digester is designed to manage 1.60 Mg/d of PP. A residence time of 12 days and a digester with 165 m³ is estimated, yielding 14 Nm³_{CH₄}/Mg_{VS}/d. A simulated AD plant integrated with a combined heat and power unit results in a carbon footprint of 542 kg of CO₂-eq/Mg_{db} PP, primarily from biogenic GHG emissions. These findings highlight the potential of AD to generate renewable energy from potato industry residues while reducing fossil fuel-related GHG emissions and promoting resource circularity.

Keywords: biochemical methane potential; anaerobic co-digestion; potato residues; potato peel; energetic valorization; GHG emissions



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1. Introduction

About 40% of the energy produced in the European Union (EU) is from renewable sources [1], but only 23% of all the energy consumed comes from renewables [2]. Indeed, more than half of the energy consumed in the EU is imported, creating a high dependence on other regions. In addition, aiming to reduce greenhouse gas (GHG) emissions, energy imports, and fossil fuel dependency, the Renewable Energy Directive (Directive (EU) 2023/2413 of the European Parliament and of the Council of 18 October) established a minimum share of 42.5% for renewable energy sources in the overall energy mix of the EU by 2030. Many strategies and plans have been designed to accomplish this target. The REPowerEU plan claims a set of strategies to reduce the need for fossil fuels, save energy, and boost the use of renewable energy. The sustainable production of biomethane is one of the strategies proposed. Biomethane (also known as “renewable natural gas” or

“green gas”) is composed mainly of methane (85–99%), which is obtained by upgrading biogas (formerly composed of 45–80% of CH_4 and 20–55% of CO_2), aiming to replace a fraction of natural gas [3]. The biogas is produced through biological or thermochemical processes. Anaerobic digestion (AD) is a complex biological process suitable for converting biodegradable organic matter into biogas using efficient microbial consortia [4]. It will be the route explored in the present study. Gasification followed by methanation is a thermochemical route more suitable for organic matter with low moisture and high lignin content because it uses high temperatures (600–1000 °C) to degrade the biomass into syngas (H_2 , CO , CO_2 , CH_4) [5].

The feedstocks commonly used for methane production can be divided into three categories: agricultural, industrial, and municipal residues [4]. Indeed, the food industry generates large amounts of organic residues, typically with a high moisture content, which are suitable for methane production through AD. Fresh potatoes, potato chips, ready meals, French fries, and others are some of the most consumed foods worldwide [6]. In particular, about 980 Gg of potato chips are consumed in the EU [7]. Along with the potato chips, relevant waste streams are generated in the potato chip industry. Commonly, potato peel, defective potatoes, leftovers from the potato cut (OC), defective fried potatoes, cooking oil, and wastewater are rejected by the potato chip industries. Thus, the evaluation of AD for valorizing these industrial streams is relevant since waste management costs may be avoided and financial revenues related to biogas can be obtained.

The biochemical methane potential (BMP, $\text{mL}_{\text{CH}_4}/\text{g}$ volatile solids (VS)) is commonly used to assess the anaerobic digestion performance. Potato peel (PP) presented a BMP value in the range of 83 to 348 $\text{mL}_{\text{CH}_4}/\text{g}_{\text{VS}}$ [8–11]. Zhang et al. [10] and Kryvoruchko et al. [12] reported BMP values of 340 and 332 $\text{mL}_{\text{CH}_4}/\text{g}_{\text{VS}}$, respectively, for OC. The experimental determination of BMP is a time-consuming procedure, typically taking up to 30–60 days. Thus, theoretical and multivariate regression models have been developed to enable the rapid and cost-effective prediction of BMPs [13]. Commonly, substrate characteristics such as elemental composition, carbohydrate content, lignin, and near-infrared (NIR) spectroscopy data have been extensively employed in the literature as fast, economical, and reliable methods to estimate the BMPs of various substrates.

Anaerobic co-digestion (AcoD) is a relevant strategy to valorize multiple substrates at the same time and create positive synergies to enhance methane production [14]. Potato-processing waste has also been used in AcoD with sheep manure [8], cow manure [9], microalgae *Chlorella vulgaris* [10], and sugar beet waste [15]. To the best of the authors' knowledge, the AcoD of potato-processing residues has not been found in the literature to assess the possibility of implementing an AD plant coupled to the potato chip industry.

In this context, this work aims to investigate the management of key residues from the potato chip industry (potato peel—PP, potato offcuts—OC, waste cooking oil—WCO, wastewater—WW, and sewage sludge—SS) while recovering energy through anaerobic digestion. The BMP of each residue was assessed experimentally, as well as through theoretical and predictive models. Additionally, AcoD trials were conducted by combining multiple residues according to the potato chip company's priorities, aiming to optimize the composition mixture that maximizes the methane yield. An industrial-scale AD simulation was conducted to estimate GHG emissions. The main scientific contribution of this work lies in demonstrating the feasibility of simultaneously managing multiple potato chip industry residues through AD while quantifying its environmental benefits. Overall, this work offers valuable insights into methane yields from real industrial residues and different mixture compositions, supporting industries in evaluating the feasibility of implementing anaerobic digestion plants.

2. Materials and Methods

2.1. Substrate and Inoculum Collection

This study used several residues collected in a potato chip company from Portugal that generates a large quantity of residues throughout the production process—Table 1. PP, OC, WCO, WW, and SS were collected from the industry to assess the possibility of treating and valorizing them through anaerobic digestion. WW corresponds to the liquid effluent produced during the washing steps, while SS was collected from the aerobic-activated sludge treatment of WW.

Table 1. The amount of waste streams produced by the potato chip company in 2021.

Residues from the Potato Chip Process		WWTP	
Potato peel—PP (Mg)	535	Wastewater—WW (m ³)	120,861
Potato offcuts—OC (Mg)	641	Sewage Sludge—SS (Mg)	1858
Waste cooking oil—WCO (Mg)	113		

Except for WCO and WW, the solid samples (PP, OC, SS) were divided into two fractions: one part was frozen to be used in the anaerobic reactors, and the other part was dried at 50 °C until constant weight and milled to characterize the materials.

The inoculum for the anaerobic digestion tests was collected from an anaerobic digester from a WWTP that treats urban wastewater from the central region of Portugal. The collected anaerobic sludge contained 24–49 g/L of total solids (TS), about 40% of volatile solids, and an alkalinity of around 3014 mgCaCO₃/L. Although no microbial characterization was performed, sourcing inoculum from an active anaerobic digester ensures the presence of a suitable microbial community for digestion. The inoculum was used without any pre-treatment and stored at room temperature in a 25 L container. For each experimental batch, fresh inoculum was collected and stored for no longer than one month.

2.2. Anaerobic Digestion and Co-Digestion

Anaerobic mono-digestions were carried out for all the substrates selected according to the conditions described in Section 2.2.1 to determine the individual BMP. Since PP and OC are the most pressing residues for the company to manage, mixtures with varying compositions of these two substrates (on a volatile solid basis) were tested initially. One of the tested mixtures reflected the actual proportions produced by the industry (35 wt.% PP and 65 wt.% OC), corresponding to 48 and 93 Mg on a volatile solid, respectively. Subsequently, additional experiments were conducted using mixtures of PP, OC, WCO, and WW to assess the feasibility of managing these streams via anaerobic digestion and potentially enhancing methane production. Two different blends were tested, both respecting the original PP-to-OC production ratio. In all cases, it was ensured that PP and OC together represented at least 50% of the total mixture, as their treatment was a primary objective of the industrial plant. Given that food waste mixtures containing more than 35 wt.% of WCO have been associated with prolonged lag phases [16], this study limited the WCO content to 25 wt.% of WCO. Accordingly, two mixtures were tested: a ternary blend composed of 25 wt.% PP, 50 wt.% OC, and 25 wt.% WCO; and a quaternary blend consisting of 17.5 wt.% PP, 32.5 wt.% OC, 25 wt.% WCO, and 25 wt.% WW.

The AcoD performance index (CPI) was estimated to assess the synergetic interactions of the different mixtures tested:

$$\text{CPI} = \frac{\text{BMP}_{i,n}}{\sum_i^n x_i \text{BMP}_i} \quad (1)$$

where $BMP_{i,n}$ corresponds to the experimental methane yield for AcoD, and x_i and BMP_i refer to the volatile solid fraction and the biochemical methane potential of the substrate i in mono-digestion [14,17]. Antagonistic, additive, and synergistic interactions in AcoD are characterized by CPI below, equal to, and above 1, respectively.

2.2.1. BMP Experimental Procedure

BMP was performed in glass bottles of 500 mL sealed with rubber stoppers, using a working volume of 40%. An inoculum-to-substrate ratio (ISR) of 2 (in terms of VS) was selected for the tests to avoid acidification through volatile fatty acid accumulation [14,18]. A total concentration of volatile solids (including inoculum and substrate(s)) was set at 20 g/L within the range recommended by Holliger et al. [18]. Micro- and macronutrients were added to the reaction mixture at the start of the batch experiment. The BMP tests occurred in an incubator at 37.5 °C until no production of biogas was observed (about 30 days). The bottles were agitated once a day, and the biogas formation was analyzed periodically. The volume of biogas was estimated through manometric pressure in the headspace of the reactors [14]. The composition of the biogas was measured with portable equipment GAS DATA (GMF406), with sensors for methane, carbon dioxide, oxygen, and hydrogen sulfide. Figure S1 in the Supplementary Materials represents how the measurements were made. Blank assays without substrate were also considered to discount the methane production from the inoculum. The experiments were carried out at least in triplicate, and the results are reported in normalized gas volume (at STP conditions—273 K and 1 atm)— NmL_{CH_4}/g_{VS} .

AD performance using the PP substrate was also evaluated in 5 L reactors to assess the behavior of batch operation. The same operating conditions used in the smaller bottles were assured. However, the biogas volume was measured with a MilliGascounter (RITTER) and accumulated in biogas bags as presented in Figure S2 (Supplementary Material). Its composition was determined with the same portable equipment GAS DATA (GMF406), using a sample of gas stored in the bag. The methane production rate was evaluated using the first-order kinetic model with and without a lag phase (Equations (2) and (3), respectively).

The experimental data were adjusted with the first-order kinetic model with and without any lag phase (Equations (2) and (3), respectively),

$$SMP(NmL_{CH_4}/g_{VS}) = BMP_{\infty} \left(1 - e^{-k(t-t_{lp})} \right) \quad (2)$$

$$SMP(NmL_{CH_4}/g_{VS}) = BMP_{\infty} \left(1 - e^{-kt} \right) \quad (3)$$

where SMP is the specific methane potential at time t (d), BMP_{∞} (NmL_{CH_4}/g_{VS}) corresponds to the methane production when time tends to infinity, k (1/d) is the rate constant of the first-order kinetic model, and t_{lp} is the time of the lag phase.

2.2.2. Predictive Models

The experimental BMP obtained for the solid substrates (PP, OC, and SS) was compared to the one determined through predictive models (Table 2), aiming to evaluate the accuracy of the models. Met_I and Met_II are theoretical models based on elemental composition and chemical oxygen demand (COD), respectively. Chandler et al. [19] reported a correlation between the organic matter and biodegradability (BD) of the substrates used for methane production ($BD_f = 0.83 - 0.028 \times LG$ (%VS)). Indeed, only part of the organic matter is biodegradable. Met_Ic and Met_IIC correspond to Met_I and Met_II corrected with the correlation reported by Chandler et al. [19]. This correction can only be used for substrates with concentrations of lignin lower than 20% in terms of VS.

Mod_I, Mod_II, Mod_III, and Mod_IV are multivariate regression models from the literature [20,21]. BMP_{NIR} uses the near-infrared (NIR) spectra of each substrate to estimate the BMP value in mL_{CH₄}/g_{VS}. The procedure for its determination was described by Almeida et al. [13]. Briefly, a FlashBMP[®] calibration developed by Ondalys (Chemo-metrics–Data Analytics, Clapiers, France) and commercialized by Buchi (Flawil, Switzerland) was used.

Table 2. Mathematical models used to predict the BMPs of residues.

Model	Equation	RMSE	Ref.
Theoretical models			
Met_I	$\text{BMP} = \frac{22400 \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8} \right)}{12n + a + 16b + 14c}$	nd	[22]
Met_II	$\text{BMP} = 350 \times \text{COD}_{\text{solids}}$	nd	[13]
Met_Ic	$\text{BMP} = \text{BMP}_{\text{Met_I}} \times BD_f$		
Met_IIC	$\text{BMP} = \text{BMP}_{\text{Met_II}} \times BD_f$		
Multivariate regression models			
Mod_I	$\text{BMP} = 3160.439 - 19.293\text{N} + 1.834\text{C} - 40.199\text{H} - 9.566\text{O} + 0.1993\text{N} \times \text{H} + 0.01897\text{N} \times \text{O} + 0.1157\text{H} \times \text{O} - 0.001482\text{C}^2$	193.6	[20]
Mod_II	$\text{BMP} = 378x_{\text{CL}} + 354x_{\text{HC}} - 194x_{\text{LG}} + 313 \times (1 - x_{\text{CL}} - x_{\text{HC}} - x_{\text{LG}})$	51.7	[21]
Mod_III	$\text{BMP} = -42.849 - 182.814\text{tCOD} + 0.5432\text{VS} \times \text{tCOD} - 41.544\text{tCOD}^2$	80.9	[20]
Mod_IV	$\text{BMP} = 115.302 + 9.371 \times 10^{-1}\text{PT} + 2.379 \times 10^{-1}\text{CRB} + 5.706 \times 10^{-4}\text{LP}^2 - 1.505 \times 10^{-3}\text{PT} \times \text{CRB}$	78.1	[20]
Computational model			
BMPNIR	Computational software based on NIR spectra	28	[13]

RMSD—root-mean-square deviation of the models; nd—non-defined; n, a, b, and c correspond to the elemental coefficients of the material (C_nH_aO_bN_c); N, C, H, and O correspond to the elemental composition of nitrogen, carbon, hydrogen, and oxygen, respectively, in g/kg_{VS}; PT, LP, and CRB correspond to proteins, lipids, and carbohydrates, respectively, in g/kg_{VS}; CRB was calculated by subtracting the PT, LP, and ash content from the TS of each material. COD_{solids} is expressed in g/g_{VS}; VS is expressed in g/kg_{TS}; x_{CL} , x_{HC} , and x_{LG} correspond to cellulose, hemicellulose, and lignin fractions.

2.3. Anaerobic Reactor Design

Scaling up an anaerobic digester can be a complex process that includes multiple relevant factors (microbial community stability, efficient mixing, reactor configurations, loading rate, hydraulic retention time, and others). Although incremental increases in the reactor size can help bridge the gap between laboratory and industrial scales, models based on lab-scale data can be a first approach for scaling up. A simplified anaerobic digestion plant was designed considering the kinetic data. A continuous stirred-tank reactor (CSTR) model following first-order kinetics with a lag phase was assumed to manage the PP produced by the company in one year (535 Mg/year). It was assumed that the company operated 335 days per year, considering 30 days for maintenance. The assumptions and the detailed procedure for the reactor volume determination are described in the Supplementary Material.

2.4. Greenhouse Gas Emissions

SuperPro Designer[®] (Scotch Plains, NJ, USA) was used to simulate an anaerobic digestion plant for managing 535 Mg of PP/year. The plant incorporated a combined heat and power (CHP) unit for energy generation from biogas. The software performed the mass and energy balances, estimating the amount of emissions and energy required for the process. The simulation was based on lab results, considering a continuous and large-scale unit. The GHG emissions of the processing facility were estimated considering several factors: CO₂ emissions from biogas and CH₄ combustion; electricity consumption for pumping various streams and mixing the reaction mixture; the energy needed for keeping the reactor at 37 °C; and electricity generation in the CHP unit. For the calculations, the emission factor of the electricity mix in Portugal was used (0.242 kg of CO₂-eq/kWh, as reported by APA, 2024 [23]). This factor accounted for CO₂, CH₄, and N₂O gases, each

with their respective global warming potentials (GWPs) outlined in the 5th report of the IPCC (AR5) over 100 years. Additionally, the electricity emission factor did not include the CO₂ emissions from renewable energy sources (e.g., biomass and biogas). The factor emission for hot water and steam (66.33 kg of CO₂/mmBTU) was used to estimate the GHG emissions of heating the reactor (EPA). This factor assumed that natural gas was used as fuel to generate steam or heat, with a thermal efficiency of 80%. The carbon footprint of the feed and the digestate formed was not considered since other works have demonstrated low GHG emissions associated with these streams when compared to the energy consumption and anaerobic digestion process [24].

2.5. Analytical Procedures for Characterization of Samples

A suspension of 20 mL/g was prepared and left in agitation for 2 h to measure (Consort C1020) the natural pH of PP, OC, and SS. Total solids (TS) and volatile solids (VS) were determined by drying the samples at 105 °C overnight and 550 °C for 2 h, respectively [25]. The total dissolved solids (TDS) and total suspended solids (TSS) of WW were assessed through vacuum filtration, and then, the masses of the samples (dried at 105 °C) in the filtrate and retained in the filter correspond to the TDS and TSS, respectively. Elemental Analyzer NA 2500 equipment was used to determine the elemental analysis (C, N, H, S). The oxygen content was calculated by subtracting the sum of CHNS from VS. Lignin (LG), cellulose (CL), and hemicellulose (HC) content were analyzed through the National Renewable Energy Laboratory (NREL) method, as described elsewhere [26]. Megaenzyme kits for total starch determination were used to obtain the starch content present in PP. Rapid total starch for samples containing resistant starch methodology was followed. Total Kjeldahl Nitrogen was assessed through the digestion (DKL Fully Automatic Digestion Unit from VELP Scientifica, Usmate, Italy) of 0.5 g of a sample, followed by distillation (UDK Distillation Unit from VELP Scientifica, Usmate, Italy), and titration [13]. The protein content was calculated by multiplying the Total Kjeldahl Nitrogen by 6.25 [13]. The lipid determination followed the Official Methods of Analysis of AOAC, No. 950.54. Briefly, a Soxhlet extraction with hexane was performed at a liquid–solid ratio of 67 mL/g for 6 h. The chemical oxygen demand was determined for solid samples (COD_{solids}) and liquid samples (COD_{total} and COD_{soluble} for the WW). It was determined according to standard methods [27]. Briefly, the samples were digested with dichromate in an ECO25 Thermoreactor (Velp Scientifica, Usmate, Italy) for 2 h at 150 °C, and the absorbance at 605 nm was measured using a photometer PhotoLab S6 (WTW). The determinations were made in triplicate, and the results are reported as mean ± standard deviation.

2.6. Statistical Analysis

Statistical analysis at a significance level (α) of 0.05 was performed, aiming at the comparison of the BMPs of different substrates. A non-linear regression was applied to the experimental data to determine the parameters of the kinetic models (Equations (1) and (2)) using the SigmaPlot 11.0 software. In addition to data visualization, the coefficient of determination (R^2) and the root-mean-square error (RMSE) were used to evaluate the fitting quality.

3. Results and Discussion

3.1. Characterization of Potato Peel Residues

The main physical and chemical characteristics of the residues studied are summarized in Table 3. Since the pH of the materials ranges between 5.9 and 8.8 and the inoculum commonly presents a high buffering capacity (2500–5000 mg CaCO₃/L), the introduction of these flows in the reactional mixture may not affect the pH. Regarding the solid materials, PP and OC show a low concentration of TS, with a high moisture content (around 90 wt.%). Except for SS,

the solid fraction of materials is mainly composed of organic matter (quantified as volatile solids), with concentrations higher than 65%. In particular, PP and OC present VS content of around 90 wt.% as reported in the literature [9,10,12,28,29]. This is a good indicator of their suitability for anaerobic digestion, especially if the volatile solids are biodegradable. However, about 20 wt.% of lignin concentration was measured for PP and SS, which may hinder methane production since lignin is hardly biodegradable. Starch is more degradable than lignin. However, PP presents a low starch content, contrasting with the literature results (which reported values of around 25 wt.%) [6,30,31]. The abrasion mechanism used by the company to remove the peel may justify the difference because only the very thin peel is removed. The higher value of COD_{solids} for OC indicates that it may present more potential for methane production than PP and SS. WW presents a COD_{soluble} and COD_{total} higher than the amount permissible for discharge (150 mg O₂/L), meaning it needs treatment to reduce the organic load. At the industrial level, this WW is currently treated by aerobic-activated sludge treatment. The comparison of SS and WW with the literature is difficult and may not be realistic because their characteristics depend on the process and treatment used.

Table 3. Physical and chemical properties of residues from a potato chip company.

Parameter	Solid Residues			Liquid Flows	
	PP	OC	SS	WCO	WW (*)
pH	7.2 ± 0.1	5.9 ± 0.1	8.4 ± 0.2	8.8 ± 0.1	5.96
TS (%)	10.6 ± 0.5	15.6 ± 0.1	22.3 ± 0.1	44.7 ± 0.4	0.55 ± 0.10
VS (%TS)	89.3 ± 0.5	93.5 ± 0.2	51.7 ± 0.5	99.1 ± 0.2	66.13 ± 0.65
C (%TS)	48.9 ± 0.1	38.3 ± 0.1	27.0 ± 0.2	-	-
H (%TS)	6.56 ± 0.51	6.06 ± 0.20	3.94 ± 0.39	-	-
N (%TS)	2.00 ± 0.07	0.509 ± 0.265	3.63 ± 0.01	-	-
O (%TS)	30.9 ± 0.6	48.7 ± 0.5	17.2 ± 0.6	-	-
S (%TS)	<dl	<dl	<dl	-	-
LG _{total} (%TS)	23.4 ± 0.84	<dl	18.9 ± 3.7	-	-
CL (%TS)	18.4 ± 1.9	32.3 ± 1.4	3.4 ± 0.4	-	-
HC (%TS)	8.6 ± 0.9	4.7 ± 0.1	1.9 ± 0.16	-	-
Starch (%TS)	3.87 ± 0.21	-	-	-	-
Proteins (%TS)	11.20 ± 0.30	5.84 ± 0.17	28.4 ± 0.2	-	-
Lipids (%TS)	2.54 ± 0.35	0.31 ± 0.06	3.31 ± 0.4	-	-
COD _{solids} (mg O ₂ /g TS)	1339 ± 127	1524 ± 80	1367 ± 70	-	-
BMP _{NIR} (mL _{CH4} /g _{VS})	228 ± 28	386 ± 28	320 ± 28	-	-
Empirical formula	C ₂₉ H ₄₆ O ₁₄ N	C ₈₈ H ₁₆₇ O ₈₄ N	C ₉ H ₁₅ O ₄ N		

(*) TS = 5.16 ± 0.93 g/L; TSS = 4.09 ± 0.10 g/L; TSD = 1.15 ± 0.12 g/L; COD_{total} = 4645 ± 339 mg O₂/L; COD_{soluble} = 3692 ± 353 mg O₂/L.

3.2. BMP Determination of Potato Industrial Residues

The experimental biochemical methane potential of the main residues from a potato chip company ranges from 174 to 280 NmL_{CH4}/g_{VS} (Figure 1A). Although SS presents a low content of VS, it is highly biodegradable with a BMP statistically similar ($\alpha < 0.05$) to WW and OC. A high methane yield (232 NmL_{CH4}/g_{VS}) is expected for OC since it is mainly composed of starch, which presents high biodegradability (85%) and a BMP of around 350 ± 33 NmL_{CH4}/g_{VS} [32]. PP and WCO present slightly lower methane yields: 174 and 202 NmL_{CH4}/g_{VS}, respectively. The anaerobic biodegradation of PP could be impaired by its low starch content (Table 3) compared to other potato peel samples, mostly obtained through manual peeling. Regardless of the residue treated, the biogas formed through AD presents statistically similar methane concentrations ($\approx 60\%$) (Figure 1B). The remaining biogas is mainly composed of CO₂, while H₂S is present at a maximum concentration of 12 ppm for OC and WW. This low H₂S content in biogas is a positive aspect since this gas is corrosive and toxic in low concentrations. Moreover, the pH of the reactional AD mixture remains neutral (6.91–7.23), meaning that the methanogenic inhibition through acidification does not occur. Overall, the potato chip residues present a high potential to be managed and valorized through anaerobic digestion.

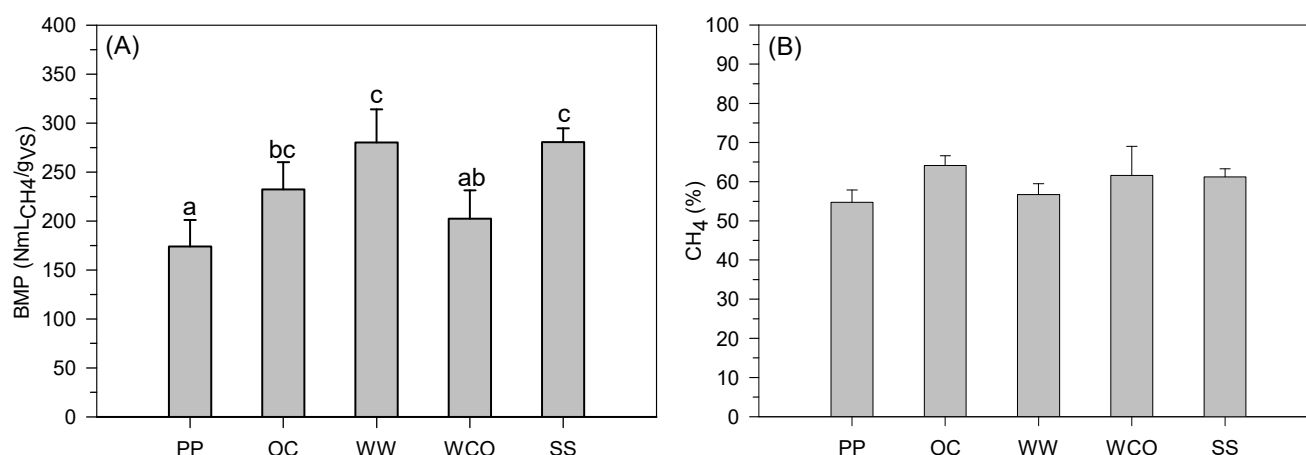


Figure 1. BMP results (A) and methane concentration (B) of the biogas formed during the anaerobic digestion of the main residues collected from a potato chip company. (Different letters mean statistically different results for $p < 0.05$. The absence of letters in (B) corresponds to statistically similar results).

The experimental results obtained in this study and the ones found in the literature are compared in Figure 2. Indeed, for SS, WW, and WCO, the comparison is hard because, to the best of our knowledge, these kinds of effluents are not evaluated by other authors considering the potato-processing industry. While the PP and OC analyzed in this work present proximate and ultimate analyses close to the literature, WW, WCO, and SS streams may show many different characteristics according to their origin [33,34]. The BMPs found in the literature for primary sludge and activated sludge are collected to compare with WW and SS, respectively [33–39]. Fat, oil, grease (FOG), and lipid effluents are used as a reference for WCO [16,40,41].

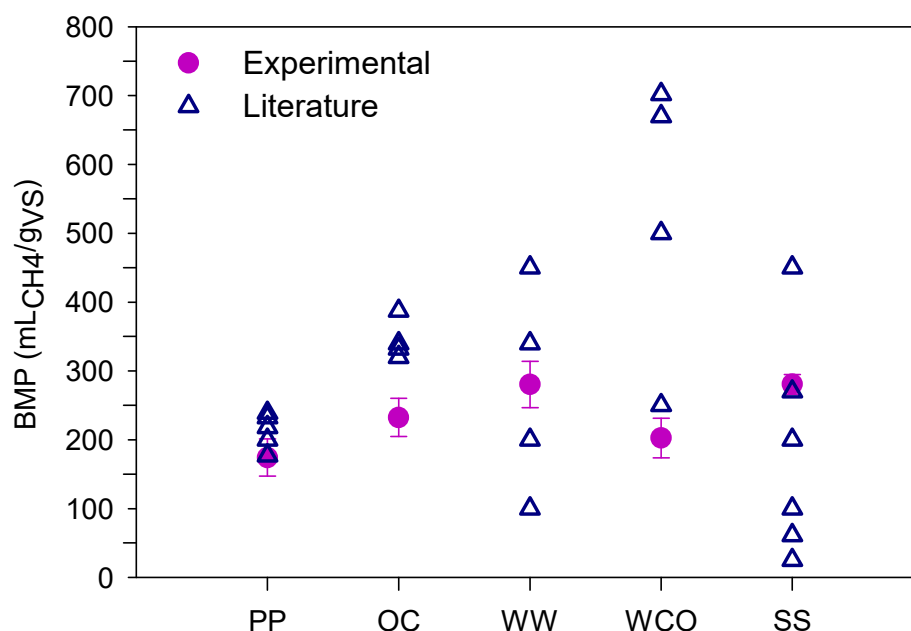


Figure 2. Comparison between the BMP results obtained in this work (experimental) and found in the literature for PP [8–11], OC [10,12,42], WW [33,35,36], WCO [16,40,41], and SS [33,34,37,39].

Despite variations in experimental conditions and material compositions, the BMPs of PP, WW, and SS are within the range found in the literature (Figure 2). OC presents a slightly lower methane yield than similar residues treated by other authors (320–387 mLCH₄/gVS) [10,15,42]. Discrepancies are likely due to variations in experi-

mental conditions, particularly the inoculum-to-substrate ratio (ISR) and particle size. In particular, the ISR is a critical parameter influencing both the stability and kinetics of AD. A higher ISR generally leads to increased degradation rates, but a lower quantity of substrate is treated. Conversely, a lower ISR can result in the rapid accumulation of volatile fatty acids due to substrate overload, which changes the medium pH and hinders the growth rate of methanogenic bacteria. For example, Achinas et al. [9] reported a methane yield of 218 mLCH₄/gVS for PP at an ISR of 2, whereas a significantly lower yield of 83 mLCH₄/gVS was observed at an ISR of 0.25. Particle size also plays an important role in the degradability of the substrate. Smaller particles provide a higher surface area, improving the interactions between enzymes, bacteria, and substrate particles [18]. Therefore, using substrates with a particle size < 10 mm is recommended for AD [18].

Although the anaerobic digestion of FOG or lipids presents a high theoretical biochemical methane potential of 1000 mLCH₄/gVS, its hydrolysis produces low-chain fatty acids (LCFAs) and glycerol that compromise methane production due to mass transfer limitations [43]. For that reason, high residence times (to overcome the lag phase) are needed, which may explain the lower BMP result obtained in this work compared to the literature (250–700 mLCH₄/gVS) [16,40,41]. On the other hand, long lag phases are disadvantageous from an industrial point of view; thus, AcoD has been studied to manage FOG and enhance the methane production of other substrates [16,43].

The experimental determination of the BMP is a time-consuming procedure. Thus, theoretical and multivariate regression models have been studied to predict the BMP rapidly and economically [13]. Since the prediction capacity of the models depends on the substrates included in the calibration set, the validation of the models for the materials tested in this study is relevant before using them. The comparison between the BMP predicted by these methods and models with the experimental results is presented in Figure 3. The theoretical methods using the elemental analysis and the COD parameter (Met_I and Met_II) overestimate the BMP because both ignore the biodegradability of the materials (Figure 3A,B). However, if a biodegradability correction is applied to these methods, the results come close to the experimental values. Indeed, the decrease in the RMSE calculated in this work proves it. This trend is also noted by other researchers [13,20]. Among the multivariate regression models studied, Mod_II, Mod_IV, and BMP_{NIR} (Figure 3D,F,G) reveal the best prediction capacity with a calculated RMSE of 90, 86, and 97 mLCH₄/gVS, respectively. Indeed, the marks corresponding to PP, OC, and SS are close to the diagonal. Almeida et al. [13] performed a similar analysis and reported similar outcomes. The prediction capacity of the models for a mixture of substrates (anaerobic co-digestion) is discussed in Section 3.3.

3.3. Assessment of Co-Digestion

The anaerobic co-digestion of PP, OC, WW, and WCO is presented in Figure 4. The mixtures of PP and OC achieve methane yields higher than 150 NmLCH₄/gVS (Figure 4A). Mixtures with higher concentrations of OC (>65 wt.% VS) reveal methane production of around 230 NmLCH₄/gVS. Even so, AD with PP or a 50 wt.% PP mixture does not show a statistically significant decrease in the BMP results. Indeed, the CPI for all the mixtures is around 1. This means that the residues can be simultaneously managed without compromising the process performance. Moreover, if the potato chip processing industry produces different proportions of PP and OC, there is no need to change the operating conditions of the AcoD. To the best of the authors' knowledge, this analysis has never been addressed in the literature.

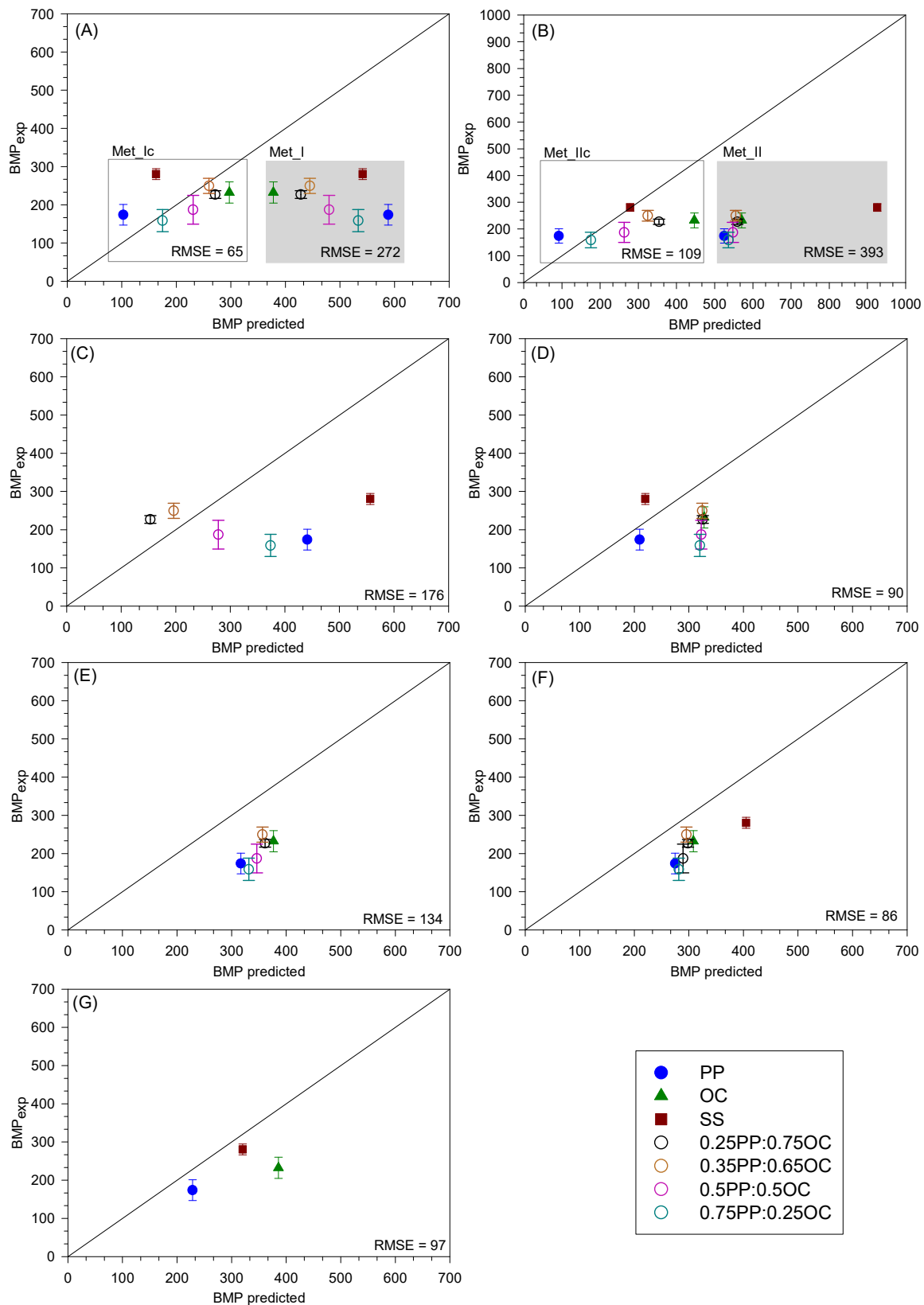


Figure 3. Prediction capacity of the models: Met_I (A), Met_II (B), Mod_I (C), Mod_II (D), Mod_III (E), Mod_IV (F), and BMP_{NIR} (G) for potato peel, potato offcuts, sewage sludge, and mixtures of potato peel and offcuts. BMP_{exp} and $BMP_{predicted}$ are presented in mL_{CH_4}/g_{VS} .

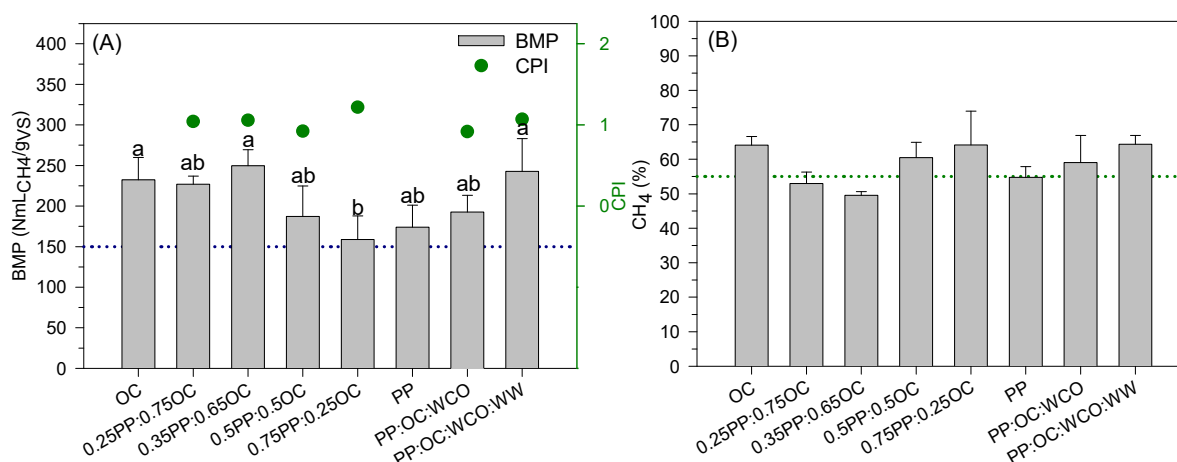


Figure 4. BMP results (A) and methane concentration (B) of the biogas formed during the anaerobic co-digestion of PP, OC, WCO, and WW. (Different letters mean statistically different results for $p < 0.05$; The absence of letters in (B) corresponds to statistically similar results).

The addition of WCO is evaluated with a mixture that respects the proportion of PP and OC produced by the company to evaluate the possibility of enhancing methane production. Since mixtures of food waste with more than 35 wt.% of WCO revealed large lag phases [16], in this work, mixtures with 25 wt.% of WCO are tested. The ternary mixture (0.25 PP: 0.50 OC: 0.25 WCO) shows a BMP result of 193 NmL_{CH₄}/g_{VS}. The methane yield does not increase as expected, but it also does not decrease when compared to mono-digestion or the mixtures of PP and OC.

Lastly, a mixture with 17.5 wt.% PP, 32.5 wt.% OC, 25 wt.% WCO, and 25 wt.% WW is evaluated to understand if the process performance could be improved. However, a statistically similar BMP (243 NmL_{CH₄}/g_{VS}) is attained, which means that (if needed) the residues can be managed simultaneously at an industrial level without compromising the methane production.

In all the assays, the biogas produced reveals statistically similar methane concentrations (around 55%). The remaining biogas composition is mainly CO₂, and the formation of H₂S is not detected in these mixtures. The reactional mixtures present a pH around neutrality (6.95–7.23) at the end of the experiment. Overall, the potato residues can be managed through AcoD with a medium methane yield of around 208 ± 34 NmL_{CH₄}/g_{VS} regardless of the mixture composition.

Although the microbial community analysis is beyond the scope of this study, the similar BMP values observed across the tested mixtures suggest that the underlying microbial communities are also similar. The stable pH values observed at the end of the assays further confirm process stability, indicating the absence of microbial inhibition and that bioaugmentation is unnecessary. The inoculum used (sourced from a municipal anaerobic digester) contains a diverse and metabolically active microbial community that readily adapts to the tested substrates. This community is likely enriched with the most effective microorganisms for degrading carbohydrates, proteins, and lipids. The rapid methane production observed supports this effective adaptation. According to the literature, the main hydrolytic bacteria in the AD of food residues belong to Firmicutes and Bacteroidetes, which play key roles in the breakdown of complex organics such as starch and proteins [44]. The methanogenic phase is typically carried out by archaea such as *Methanosaeta*, *Methanosarcina*, *Methanobacterium*, and *Methanolinea* [44].

The compositions of the mixtures were estimated using the characterization of the raw material in the proportion used in the mixture, aiming at the evaluation of the predictive capacity of the methods and models summarized in Table 2. The comparison between

the BMP predicted with the experimental results of the PP and OC mixtures is presented in Figure 3. This assessment shows that Mod_II and BMP_{NIR} can be used to predict the methane yield of different mixtures using the characterization of raw materials. Thus, multivariate regression models are a reliable, affordable, and fast way of optimizing the AcoD of potato industrial residues.

3.4. Scale-Up

The anaerobic digestion of PP in a batch reactor of 5 L is also evaluated, and the experimental data are used to assess the kinetics of the methane production—Figure 5. According to the experimental data, a production of $188 \pm 11 \text{ NmL}_{CH_4}/g_{VS}$ is achieved after 10 d of operation (Figure 5A), while biogas gradually becomes more enriched in methane, reaching 60% (Figure 5B). This result is statistically similar ($\alpha < 0.05$) to the one obtained before (Section 3.2), validating the experimental assessment of the BMP. The methane production kinetics is well described by a first-order model with a lag phase (Equation (3)), evidenced by the lowest RMSE ($8.3 \text{ NmL}_{CH_4}/g_{VS}$). This model considers 0.87 days of lag phase and results in the following parameters: a first-order rate constant of 0.745 d^{-1} and a maximum SMP (BMP_{∞}) of $184 \text{ NmL}_{CH_4}/g_{VS}$. The methane production rate is highly dependent on the operating conditions, making comparisons with the literature difficult. Even so, a lower first-order rate constant has been reported by other authors (around $0.198\text{--}0.273 \text{ d}^{-1}$) [8,11], probably because a lag phase is not considered.

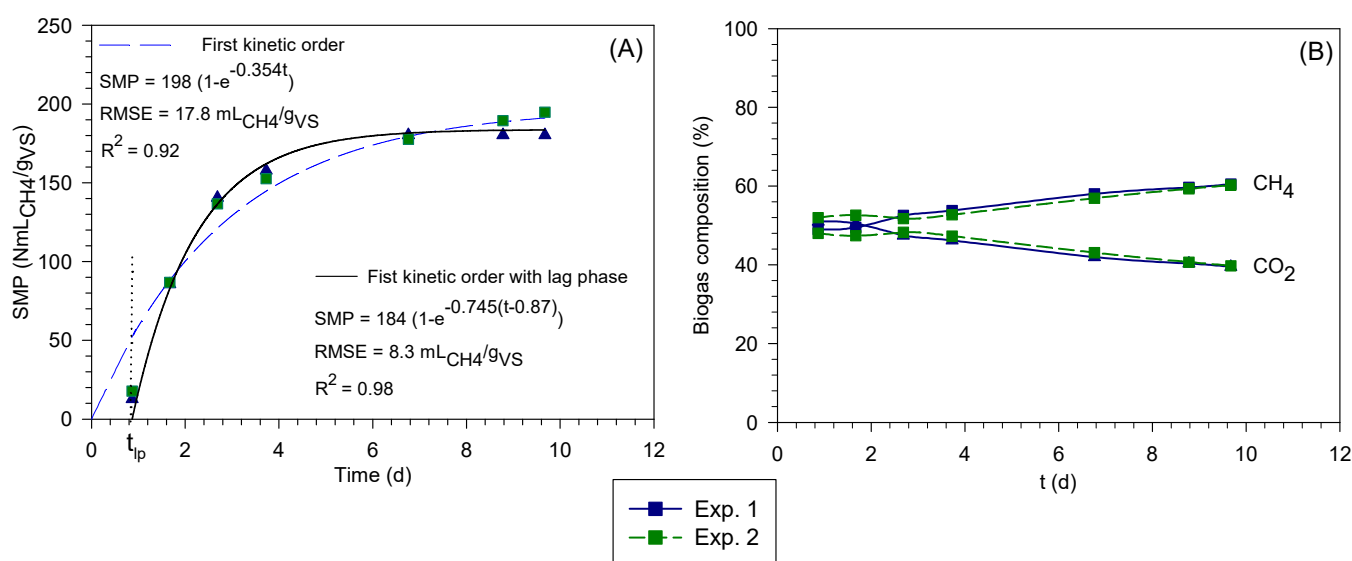


Figure 5. Kinetics of methane production through the anaerobic digestion of PP in reactors of 5 L (A) and the composition of the biogas formed over time (B).

A first estimation of the volume of an anaerobic digester to manage the PP produced by the company in one year (535 Mg_{wb}) can be obtained from the kinetic data—Table 4. Considering the assumptions mentioned in the Supplementary Material, the HRT of the AD plant must be 12 days. Thus, to manage 1.60 Mg/d of PP, a reactor with 165 m^3 is needed, considering a working volume of 0.8. In future work, a semi-continuous or continuous operation at the lab scale should be evaluated to validate the HRT and the OLR.

Table 4. Design of a continuous anaerobic digester to manage PP from a potato chip company, considering the performance of the batch experiment.

Feed flow rate of PP— F_{PP} (Mg _{wb} /d)	1.60	
Feed flow rate— Q_{in} (m ³ /d)	11.3	
Methane yield— Y (Nm ³ CH ₄ /Mg _{VS})	165	
Hydraulic residence time—HRT (d)	12	
Working volume (fraction)	0.8	
Reactor volume— V (m ³)	165	
Organic load rate—OLR (kg _{VS} /m ³ /d)	1.1	

wb—wet base.

3.5. Greenhouse Gas Emissions Analysis

Global warming and climate change have boosted the relevance of measuring and reducing greenhouse gas (GHG) emissions in industrial activities. Indeed, standards and protocols were created by the Greenhouse Gas Protocol to facilitate the GHG calculation. The estimation of GHG emissions from an anaerobic digestion plant for managing PP and electricity generation was based on Figure 6, which indicates the system boundary for that assessment. The calculations consider the conversion of the PP produced annually through AD into electricity with a CHP unit. An input of electric energy from the grid is accounted for in the electricity consumption (e.g., in pumps and agitators), and heat from a boiler is included to keep the reactor at 37 °C. Indeed, the heat dissipated by the CHP unit was used to preheat the feed, but it was not enough to keep the reactor at the desired temperature. Figure 7 summarizes the data obtained regarding the Mg CO₂eq/y and kgCO₂eq/Mg_{db} of PP. Methane combustion for electricity generation accounts for most GHG emissions (16.0 tCO₂eq/y), while about 10.9 Mg CO₂eq/y are derived from CO₂ in the biogas. However, GHG emissions associated with energy generation through renewable sources (PP in this case) are considered biogenic CO₂ emissions [45]. It should be mentioned that biogenic CO₂ is considered part of the natural carbon cycle because the carbon released during combustion or decomposition was recently absorbed from the atmosphere by living organisms through photosynthesis. Thus, in this AD plant, only the external electricity and heat usage represent GHG emissions from fossil fuels (about 3.8 Mg CO₂eq/y). Two different scenarios are proposed (Figure S4, in the Supplementary Material): one where the energy generated by the processing plant is all exported to the electric grid (Figure S4A) or part of it is internally consumed (Figure S4B). Although the same amount of biogenic equivalents of CO₂ are emitted in both scenarios, in the second, a reduction of 74% of the fossil fuel emissions is identified by avoiding the use of electrical energy from the grid. The electricity generated has an emission factor of 1.4 kgCO₂eq/kWh if the input electricity is from the grid (Scenario A) or 2.8 kgCO₂eq/kWh if self-consumption is assumed (Scenario B). The higher emission factor of the second scenario is associated with the smaller amount of energy (10 MWh/y) that goes out to the electrical grid, as shown in Figure S4B. Thus, the second scenario seems promising for reducing the GHG emissions from fossil fuels. It is important to highlight that biogenic CO₂ emissions should always be calculated and considered, but priority should be given to reducing CO₂ emissions from non-renewable sources.

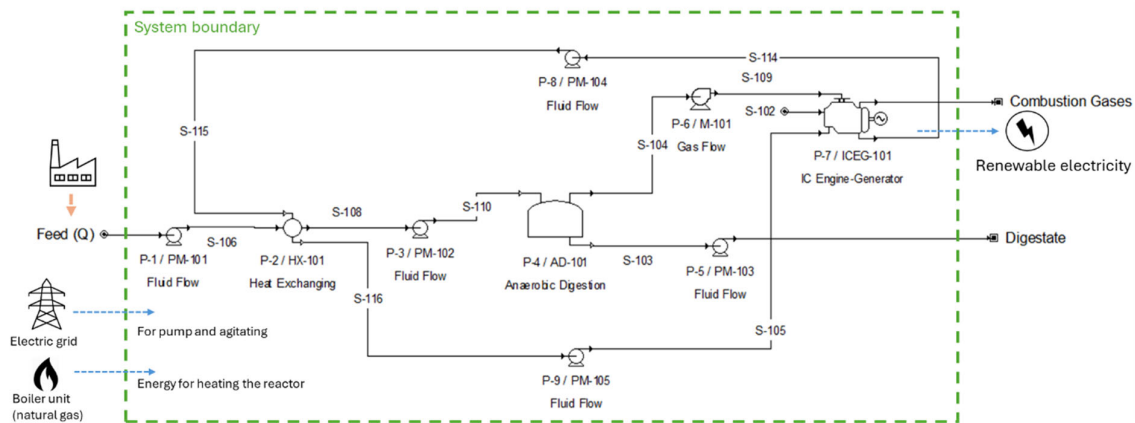


Figure 6. Anaerobic digestion plant with a CHP unit for managing PP from industrial potato residues.

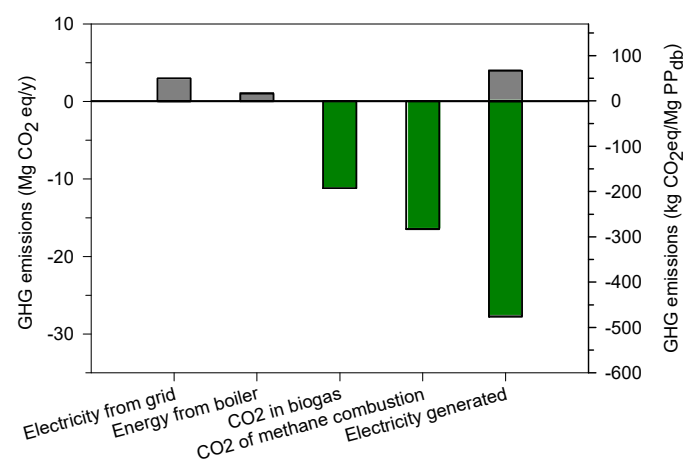


Figure 7. GHG emissions per year and GHG emissions per mass of residue of the AD plant. (Gray bars correspond to fossil fuel emissions, and green bars represent biogenic CO₂ emissions).

The comparison with the literature is challenging because multiple system boundaries and layouts have been established. In addition, the calculation of GHG emissions is influenced by the different processing efficiencies and processing capacity. Even so, AD has been reported as an important strategy for mitigating the emissions related to the management of vinasse [46], cow manure [47], sewage sludge [48], and municipal solid waste [49]. According to Pilli et al. [24], Niu et al. [48], and Liu et al. [49] the GHG emissions associated with the energy recovery from biogas range between 200 and 750 kg of CO₂-eq/Mg_{db}.

Overall, adding an AD installation into the potato-processing industry would contribute to carbon neutralization. About 2.8 MgCO₂eq/y from fossil fuel sources are avoided if PP is managed through AD, generating 22 MWh/y of renewable energy. In the future, a life cycle assessment (LCA) and economic analysis of a system with larger boundaries must be performed to validate and strengthen the possibility of using anaerobic digestion as a management strategy for the potato residues.

4. Conclusions

Anaerobic digestion proves to be an important strategy for valorizing and managing the potato residues studied: potato peel (PP), potato offcuts (OC), waste cooking oil (WCO), wastewater (WW), and sewage sludge (SS). WW, OC, and SS present statistically similar BMPs of around 232–280 NmL_{CH₄}/kg of volatile solids (VS). PP and WCO achieve a BMP slightly lower than the former substrates, reaching a value around 174–202 NmL_{CH₄}/g_{VS}. In practice, BMP estimations of PP, OC, and SS can be obtained through multivariate

regression models using NIR spectra, lignin, cellulose, and hemicellulose content, or carbohydrates, lipids, and protein content. This procedure saves the time and resources needed for the BMP assays.

Although PP presents a lower methane yield, its mixture with OC does not compromise the anaerobic co-digestion performance. Indeed, the results of the different mixtures of PP and OC prove to be statistically similar. WW and WCO are added in 25 wt.% (in terms of volatile solids) each to a mixture of PP and OC, yielding 243 NmL_{CH₄}/g_{VS}. This presents an AcoD performance index of 1, meaning that these residues can be managed simultaneously without compromising methane production compared to mono-digestion.

A simulation of an anaerobic digestion plant that manages 1.60 Mg/d of PP yields 14 NmL_{CH₄}/g_{VS}/d with a reactor of 165 m³ and a hydraulic residence time of 12 d. This design allows for the reduction of greenhouse gas emissions of fossil fuels since the process is energetically self-sufficient. About 5.4 MgCO₂eq/y of GHG emissions from fossil fuels are avoided by replacing the 22 MWh/y from the electrical grid with the energy generated by the biogas produced in the AD plant.

Overall, this work proves that AD is a relevant strategy for recovering energy from residues from an agro-industry and meeting the European Goals regarding the use of renewable energies and attaining carbon neutrality.

Future work should assess the feasibility of anaerobic digestion at a regional scale to enhance methane production while optimizing the investment and operational costs of biogas plants. Co-digestion studies using residues representative of a specific region should be conducted to support locally adapted solutions. Moreover, understanding microbial dynamics in anaerobic digestion is relevant, as the efficiency and stability of the process rely on the activity and interactions of diverse microbial populations responsible for the breakdown of complex substrates and methane production. Pilot-scale continuous experiments are also necessary to validate the process stability and scalability of the proposed approach under real-world conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su17115023/s1>, Figure S1: Schematic representation of BMP determination in batch anaerobic reactors (500 mL). Figure S2: Experimental setup of anaerobic digestion in 5 L reactors. Figure S3: Schematic representation of the continuous anaerobic digester for managing PP produced in the potato chip industrial plant. Figure S4: Mass and energy balance for the calculation of carbon footprint (CF) and emissions factor (EF) related to the electricity generated considering two different scenarios: the use of the electric grid (A) or self-consumption (B).

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