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Biological pre-hydrolysis and thermal pretreatment applied for anaerobic digestion improvement: Kinetic study and statistical variable selection

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ABSTRACT

In the present study, two pretreatment methods (thermal pretreatment and biological pre-hydrolysis) were suggested for food waste (FW) with the aim to enhance biomass conversion and biogas production by anaerobic. The effects of thermal pretreatment (TP), including TP at 60 °C and 80 °C for 60 min, and TP at 100 °C, 120 °C and 140 °C for 30 min, well as biological pre-hydrolysis (BPH) at 37 °C, 55 °C, 37 °C followed by 55 °C and 55 °C followed by 37 °C for 40 h on anaerobic digestion performance of FW were evaluated in batch tests. Results were compared with untreated FW. The BPH and TP caused an increase in the soluble chemical oxygen demand and hydrolysis efficiency. The methane yield (MY) increased from 371.17 mL CH4/g VS for untreated FW to 471.95 mL CH4/ g VS. The maximal MY was recorded for BPH at 37 °C for 20 h followed by 55 °C for 20 h. The pretreatments increased the biogas production rate and reduced the lag phase. The most influential variables on the methane yield were investigated using three statistical methods: Principal component analysis, Mutual Information and R-squared. The results allowed a good modeling of the methane yield and minimized the overfitting effect. For reproduction and solid contribution to the field, we have attached to our article all the necessary material to reproduce the same statistical work as in the paper body.

Introduction

The intensive growth of the urban population and living standards improvements result in an increasing amount of generated food waste (FW). In 2016, the amount of FW produced around the world reached 1.3 billion tons (FAO, 2016), which represents a major challenge for environmental protection and human health.

Municipal solid waste consists mainly of FW generated by restaurants, canteens, families, and hotels, and is predominantly sent to incineration or landfills. These technologies are not recommended in many countries due to the high organic material and water content of FW. Anaerobic digestion (AD) is an attractive treatment technology for FW. Besides its ability to treat diverse wastes, it offers the possibility of producing biogas as a renewable energy carrier rich in methane and, hence, limits greenhouse gas emissions, reduces waste volume and provides digestate as a by-product of anaerobic digestion, which can be used as a soil fertilizer.

The Characteristics of FW change according to the eating habits of each country. The moisture content of FW represent up to 70% (Li et al., 2021), which makes FW a good substrate for AD. Nevertheless, FW is often characterized by a high protein content, which causes an excess of ammonia release and can result in the accumulation of volatile compounds and process disturbance during the anaerobic process (Zeng et al., 2021). Likewise, lipids and large-molecular-weight-carbohydrates contained in FW, which are complex organic compounds to degrade, making the hydrolysis step a limiting step in the AD of FW (Ariunbaatar et al., 2014; Ding et al., 2017). Therefore, it is necessary to find effective approaches to optimize the hydrolysis stage during AD of FW.

In order to improve AD performances in terms of methane production, biodegradability and process stability, several pretreatment techniques have been developed, such as physical, chemical, and biological pretreatments (Carrèrea et al., 2010). The effects of these techniques on improving AD performance are highly different, depending on the nature of the substrate, the type of pre-treatment and operating conditions (Ariunbaatar et al., 2014). Among these pretreatments, thermal and biological pre-hydrolysis (mesophilic and thermophilic) have been widely studied as a means to accelerate the hydrolysis of complex

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components of numerous substrates (Liu et al., 2012; El Gnaoui et al., 2020).

Thermal pretreatment (TP) was initially applied to improve dewaterability of sludge at temperatures between 150 °C and 180 °C (Brooks, 1970; Sheerwood and Philips, 1970). The main aim of TP is to promote the hydrolysis process of organic materials by disintegration and liquefaction of the cytomembrane of the substrate (Ren et al., 2018), thus resulting in methane production enhancement and the reduction of retention time (Ariunbaatar et al., 2014). A previous study reported that the soluble chemical oxygen demand (COD_s) and temperature are directly correlated, a higher temperature increase solubilization at short durations, whereas a lower temperature can increases the soluble fraction at longer durations (Ariunbaatar et al., 2014). Ariunbaatar et al., (2014) investigated the AD of FW waste improved by thermal and ozonation pretreatment. Results showed that the specific biomethane production was 647.5 mL CH_4/ g VS approximately, 52% higher than untreated FW. This improvement was observed with TP at 80 °C for 1.5 h. In contrast, an excessive temperature (around 180 °C) might cause undesirable effects such as the formation of complex and inhibitory compounds due to the Maillard reaction (Tampio et al., 2014). Bougrier et al., (2006) suggested that exceeding temperature during thermal pretreatment (temperature > 170 °C) might cause the creation of chemical bonds, which would conduct to the agglomeration of particles.

In biological pre-hydrolysis (BPH) two crucial parameters, temperature and micro-organisms, are involved. During this type of pretreatment, the acidogenic bacteria cause extracellular depolymerization of macromolecules (proteins, lipids, and polysaccharides) into oligomers and monomers. This results in the release of dissolved compounds that are easily accessible to microorganisms during the following stages of anaerobic digestion, in which acetogenic bacteria ferment small soluble molecules such as amino acids, sugars, glycerol, and peptides, and provide substrates for methanogenic archaea (Guo et al., 2014; Mehari et al., 2018). The BPH is carried out at moderate temperatures (35 – 70 °C) (Kavitha et al., 2014). In order to evaluate the effects of enhancement of biological hydrolysis (BH) on anaerobic digestion, Ding et al., (2017) applied BH to municipal secondary sludge at 35, 42 and 55 °C. The results showed that the biochemical methane potential of pretreated secondary sludge at 15 days was similar to that of untreated secondary sludge at 30 day showing that the BH accelerates the biogas production. In addition, COD_s increased from 175.2 to 3314.5 mg/L. Likewise, the dominant VFA was acetic acid, and its concentration increased from 41.5 to 786 mg/L.

The aim of this study is to determine an appropriate pretreatment method to improve AD performances of FW, with focus on thermal pretreatment and biological pre-hydrolysis. Although a larger number of studies on pretreatment of FW already exists, further research and comparison of pretreatment methods is required to identify the most effective pretreatment techniques including consideration of net effects on energy yield and profitability. To the best of our knowledge, the comparison between BPH and conventional TP applied for AD of FW has been poorly studied. Therefore, detailed objectives of this study include:

- Assessment of the effects of TP and BPH on solubilization efficiency and methane production potential of FW.
- Optimization of TP and BPH conditions with regard to temperature and treatment time
- Sophisticated statistical methods for the selection of most influential variables in order to simplify any forecasting method.

Material and methods

Substrate

The food waste was collected from the kitchen of the company responsible for providing food for the ATB cafeteria. It was collected for a week each day according to the menu served. The major components were pasta, vegetable, fruits, and meat.

The received FW was mixed with a kitchen blender to reduce the particle size and then stored in the fridge at (4 °C).

Pre-treatments methods

Pre-treatments of FW were performed just before preparing the feeding for the reactors, and the substrates were stored at 4 °C for maximum 3 weeks during the batch experiments.

Thermal pre-treatment

To evaluate the effect of temperature on the improvement of anaerobic digestion of food waste, 1 kg of substrate was placed in an oven (Binder GmbH BF 400 Germany) for each temperature variant. Five different temperatures were used (60 °C, 80 °C, 100 °C, 120 °C and 140 °C) at different treatment durations, 1 h for 60 and 80 °C, and 30 min for 100, 120 and 140 °C.

Biological pre-hydrolysis treatment

BPH was carried out in 1 L glass vessels that were flushed for five minutes using nitrogen (N_2) and then placed in the incubator for 40 h at different temperatures (37 °C, 55 °C, 37 °C for 20 h and then 55 °C for 20 h, 55 °C for 20 h and then 37 °C for 20 h). The mixture of food waste and inoculum was 10:1 (w/w).

Chemical analyses

Samples of FW untreated and treated were stored at − 18 °C prior to chemical analyses and analyses of methane production. Total solids (TS) were measured by oven drying at 105 °C, and volatile solids (VS) were determined by subsequent ashing of the samples in a muffle furnace at 550 °C (Ding et al., 2017). Due to losses of organic compounds, all analytical analyses expressed in TS were corrected in accordance of the suggestion proposed by Weißbach and Strubelt (2008). The degree of hydrolysis was calculated by subtracting the SCOD after pretreatment from the SCOD before pretreatment, compared to the initial SCOD. Furthermore, the soluble proteins were determined by analyzing the Kjeldahl-Nitrogen of the soluble fraction and then multiplied the values by 6.25 for each pretreatments conditions.

To determine the neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) the samples were dried at 60 °C for 48 h and ground to a particle size < 1 mm. NDF, ADF and ADL content were analyzed as described by Carrèrea et al., (2010). Samples of Food waste untreated and treated taken prior to drying were analyzed for pH, ammonium–nitrogen, organic acids and alcohols. pH values and NH4-N content of FW were measured as described by Carrèrea et al., (2010). Organic acids and alcohols were determined in cold water extracts of FW. Lactic acid was analyzed using a high performance liquid chromatograph (Dionex, Sunnyvale, USA) equipped with an Eurokat H column (Knauer, Berlin, Germany) and refractive index detector. Volatile fatty acids content (acetic, propionic, butyric, isobutyric, valeric, iso-valeric and caproic acid) and alcohols (ethanol, propanol, bithanol) were analyzed by gas chromatography (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a PERMABOND® FFAP capillary column (Machery-Nagel GmbH & Co KG, Düren, Germany) and a flame ionization detector.

Batch test

A series of batch tests were carried out in order to evaluate the effects of BPH and TP on enhancement of AD. In batch anaerobic digestion tests biogas production characteristics, including specific methane

yields of food waste treated, untreated and the composition of the produced biogas, were analyzed. Batch tests were performed in 2 L glass vessels filled with 1.5 L of inoculum. The inoculum consisted of digestate from previously completed batch digestion tests. A ratio of VS Substrate to VS Inoculum (*ai*) of 0.5 ± 0.2 was met for the tests. Vessels were placed in an oven maintained at a temperature of 37 °C and were incubated for 23 days. In order to dissolve scum layers, vessels were shaken manually once a day.

The biogas produced is measured by a data acquisition system that calculates the volume of biogas each hour, and then collected it in bags. The biogas composition including the content of methane and carbon dioxide, was measured with a portable gas analyzer equipped with infrared sensors (GEM 5000, Geotech, UK). Specific methane yields are calculated as the sum of methane produced during the test period, referring to the VS of substrate added to the test. The methane content equates to the total methane volume produced during the test period divided by the total biogas volume.

Kinetic study

In order to determine the kinetic parameters, the Modified Gompertz model was used according to the following equation:

$$C = P\exp\left\{-\exp\left[\frac{Rm.\ e}{P}(\lambda - t) + 1\right]\right\}$$

Where:

C is the cumulative biogas yield production (mL/g VS), P is the ultimate biogas production potential (mL/g VS), Rm is the maximal biogas production rate (mL.g VS^{-1}. h^{-1}), $\lambda$is the lag phase time in hour.

Statistical study

In this section, we proposed a new method for variable selection that mostly influences the methane yield.

We used the principal component analysis (PCA) to explain the variance in the data. To extract the statistical dependence between variables, we utilized a robust indicator in the statistical literature which is the Mutual Information (MI). Also, the R-square indicator is used to explain the linear relationship between variables.

To select influential variables, we took into account shared variables between all indicators which are greater than 10% of the maximum value returned for each calculated score.

Results and discussion

Characteristics of FW and inoculum

The characteristics of the substrate and inoculum used during these experiments are shown in Table 2. As shown, the VS (%TS) of the inoculum was 58.2%, while, for FW the ratio was 94% indicating the high content of organic matter contained in FW, which is suitable for anaerobic digestion. It is important to determine the elemental composition of feedstocks, especially the carbon to nitrogen (C/N) ratio since the AD process requires an appropriate nutrient balance for optimal bacteria growth. As summarized in Table 1, the C/N ratio of FW was 24.6. This value is in the range of 20–30 suggested as the optimum condition for AD (Lahboubi et al., 2022). Furthermore, the NH_4-N is another important parameter to be evaluated. After proteins decomposition, the ammonia ions release and form with bicarbonate ions the ammonium bicarbonate NH_4HCO_3, which is benefic for buffer capacity of the AD process. The concentration of NH_4-N based on FM was 72 mg/kg FM for FW and 1625 mg/kg FM for inoculum which is beneficial for AD because nitrogen is the major nutrient for microbe's growth.

Table 2
Characteristics of food waste and inoculum.

Parameters	Unite	FW	Inoculum
TS	% FM	19	1.8
VS (%TS)	%	94	58.2
pH	–	3.9	7.9
COD_T	g/kg FM	231.13	15.31
SCOD	g/kg FM	67.03	11.96
C	% TS	46.2	–
N	% TS	1.9	–
C/N	–	24.6	–
TKN	g/kg FM	3.45	–
NH_4-N	mg/kg FM	72	1625
Crude fat	% TS	5.9	–
Crude protein	% TS	11.7	–
Lactic acid	g/kg	3.75	0

*FM = fresh matter.

Effects of pretreatments on the physico-chemical characterization

Soluble chemical oxygen demand

Due to the effect of TP and BPH, organic compounds and microbial cells disintegrate, leading to an increase in the concentration of SCOD, which makes SCOD monitoring a key parameter for evaluating the performance of the pre-treatments applied (Bakraoui et al., 2021). The Fig. 1 shows the variation of SCOD for all reactors. As can be seen, the two pretreatments, TP and BPH affected positively the degradation of organic matter. During the TP, the concentration of SCOD increased from 67.03 ± 6.90 mg/ Kg FM to 67.85 ± 3.50, 68.42 ± 2.31, 71.47 ± 2.23, 80.40 ± 2.10 and 84 ± 11 g/kg FM, while the hydrolysis efficiency showed the values of 0.35%, 0.60%, 2.07%, 5.78% and 7.33% for the reactors R_1 R_2 R_3 R_4 R_5 respectively. This increase in SCOD was due to the increase in temperature and duration of TP. The elevated temperature causes a breakdown of chemical bonds which results in the degradation of many organic compounds such as polysaccharides, proteins and carbohydrates in FW (El Gnaoui et al., 2020). Some authors explain this increase by the degradation of insoluble polymers in substrates into monomers that are transferred into the

Table 1
Reactors configuration, substrate and inoculum portion and pretreatment conditions.

Reactor	Substrate (g)	Inoculum (g)	Sub/Ino	Pretreatment applied	Pretreatment conditions
R_0	98.25	1500	0.5	–	Control
R_1	98.10	1500	0.5	TP	60 °C – 1 h
R_2	96.16	1500	0.5	TP	80 °C – 1 h
R_3	94.94	1500	0.5	TP	100 °C – 30 min
R_4	96.09	1500	0.5	TP	120 °C – 30 min
R_5	95.97	1500	0.5	TP	140 °C – 30 min
R_6	166.67	1500	0.5	BPH	37 °C – 40 h
R_7	166.67	1500	0.5	BPH	55 °C – 40 h
R_8	166.67	1500	0.5	BPH	37 °C (20 h) - 55 °C (20 h)
R_9	166.67	1500	0.5	BPH	55 °C (20 h) - 37 °C (20 h)

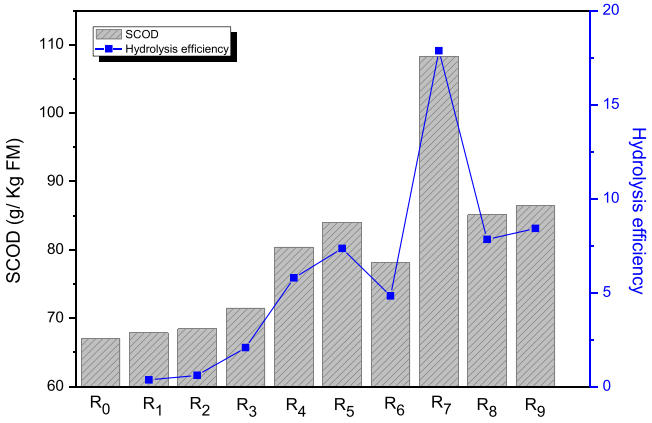


Fig. 1. Variation of SCOD for all reactors.

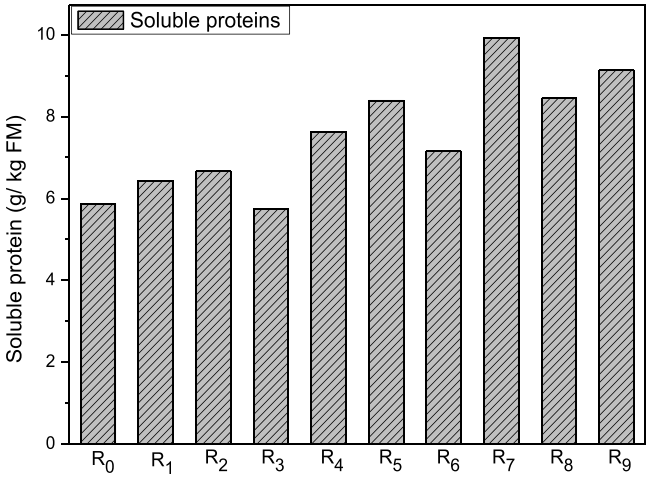


Fig. 2. soluble proteins for all reactors.

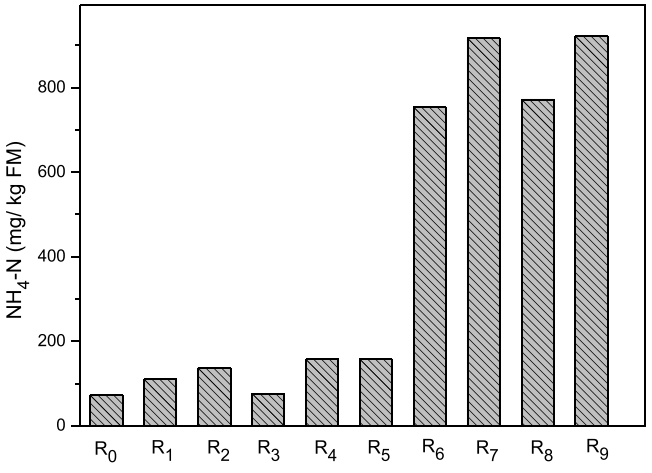


Fig. 3. variation of ammonia for all reactors.

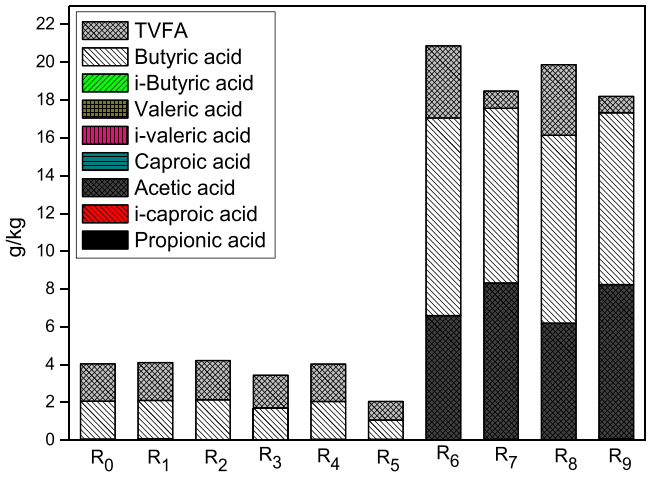


Fig. 4. Concentration and composition of TVFAs for all reactors.

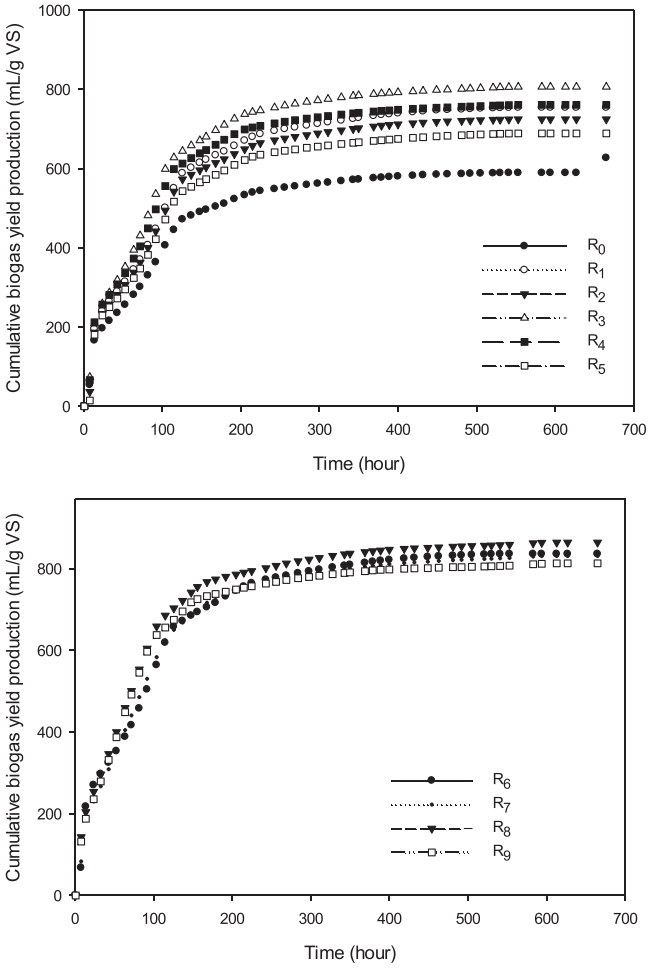


Fig. 5. Variation of biogas yield throughout of time for all reactors.

liquid phase and increase the concentration of SCOD (Raso et al., 1999). For BPH, the SCOD increased but not progressively and had a wavy trend. The SCOD concentrations were 78.17 ± 6.90, 108.30 ± 5.52, 85.12 ± 1.60, 86.46 ± 3.40 g/kg FM for the reactors R_6 R_7 R_8 R_9 respectively. Therefore, it is clear that the BPH enhanced the solubilization of FW better than TP, which can also be seen in hydrolysis efficiency. The highest hydrolysis efficiency of 17.85% was recorded when the raw material was pretreated by BPH at 55 °C for 40 h.

Soluble proteins

It was reported in literature that the soluble fraction of substrate is mainly composed of VFAs, soluble proteins and soluble carbohydrates when a pretreatment was applied (Han et al., 2017). Therefore, this study focused on the interpretation of soluble proteins and VFAs. Fig. 2 shows the results of soluble proteins for all reactors. The soluble protein concentrations increased for all pretreatments and conditions in relation to the untreated FW except for reactor R_3. The TP caused a

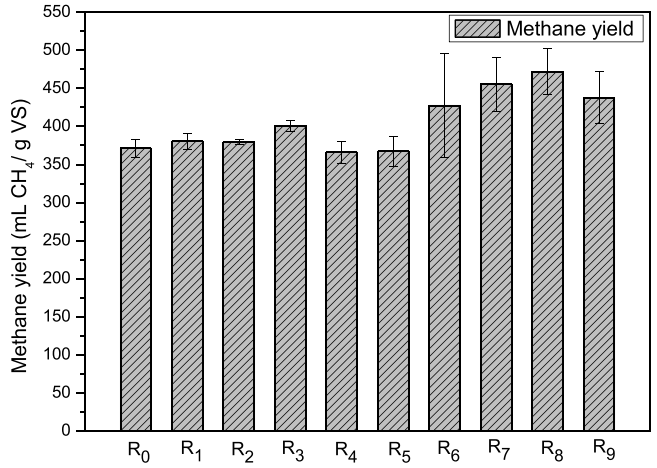


Fig. 6. Methane yield for all reactors.

significant increase in the quantity of the soluble proteins only at higher temperatures (120 °C and 140 °C). The concentration of soluble proteins increased from 5.87 ± 0.02 g/kg FM to 7.62 ± 0.10 and 8.39 ± 0.28 g/kg FM at 120 °C and 140 °C respectively. Whereas, when the FW was treated at moderate temperatures (60 and 80 °C), the concentration of soluble proteins was not enhanced significantly and showed the values of 6.42 ± 0.43 and 6.66 ± 0.14 g/kg FM respectively. Paradoxically, at 100 °C the trend of the soluble proteins released was not like the other temperatures, it decreased to 5.74 ± 0.24 g/kg FM compared to the control. Moreover, for the BPH the evolution of soluble proteins had a growing increase compared to the FW untreated. Therefore, it exhibited values of 7.14 ± 0.01, 9.92 ± 0.05, 8.44 ± 0.03, 9.12 ± 0.04 g/kg FM for the reactors R_6 R_7 R_8 R_9 respectively, which indicate that with BPH the proteins are more solubilized than TP. These results could be explained by the location of proteins.During TP the proteins were inside the cells and the temperature had no effect on them. With the increase of temperature (> 100 °C), the cell walls were lyse, which make proteins not protected and easy to degrade (Bougrier et al., 2008). Furthermore, some author reported that the hydration of water molecules and the side chains of amino acids and peptide can be affected by the TP by forming bounds and multilayer of water (Yinying et al., 2016).

Ammonia nitrogen

The release of ammonia (NH_4-N) during the two pretreatments applied was due to the decomposition of nitrogen-containing organics such as (protein, urea, amino-acids, etc.). The concentration of NH_4-N after pretreatments is shown in the Fig. 3. The results showed that when the BPH was applied, the concentration of NH_4-N was 10–12 times higher than untreated. The NH_4-N concentration significantly increased from 72 ± 4.15 g/kg for untreated FW to 754 ± 3.20, 917 ± 25.62, 772 ± 4.02, and 922 ± 15.31 g/kg for R_6 R_7 R_8 and R_9 respectively. The increase in NH_4-N concentration was first due to the decomposition of nitrogenous components, and secondly due to a source of nitrogen

Table 4
variable used in the statistical study.

Variable	unit
Lactic acid	g/kg
Methanol	g/kg
Ethanol	g/kg
Propanol	g/kg
Acetic acid	g/kg
Butanol	g/kg
Propionic acid	g/kg
n-butyric acid	g/kg
organic acids	g/kg Aceq
NH_4-N	mg/ kg FM
pH	–
TS	% FM
VS	% TS
COD	mg/ kg FM
SCOD	mg/ kg FM
Crude fat	% TS
Carbon	% TS
Nitrogen	% TS
Kjeldahl-Nitrogen	mg/ kg FM
Kjeldahl-N soluble	mg/ kg FM
NDF	% TS
ADF	% TS
Lignin	% TS
C/N	–

like the inoculum used during BPH. However, for TP the concentration of NH_4-N increased 1–2 times compared with untreated FW, to 110 ± 17, 137 ± 23, 76 ± 6, 157 ± 24, 158 ± 32 g/kg.

VFAs concentration

It was reported that the VFAs are an intermediate product in AD and are generated from the degradation of substrate. In this study, the VFAs were evaluated through the sum of acetic, propionic, n-butyric, i-butyric, n-valeric, i-valeric, n-caproic, and i-caproic acids, and the results are exhibited in Fig. 4. As can be seen, the most present acids were butyric and acetic acids. Acetic acid is the preferred precursor for methane production (Srisowmeya et al., 2020). For the TP, it was observed that there was only the production of acetic acid. Its concentration did not change compared to FW without pretreatment and varied between (1.97 ± 0.10 and 2.07 ± 0.12 g/kg), while it was decreased for R_3 and R_5 and exhibited the values of 1.72 ± 0.30 g/kg and 0.99 ± 0.21 g/kg respectively. This decrease in acetic acid could be due to the loss of acetic acid by volatilization at higher temperatures. Contrariwise, at BPH we observed the production of two VFAs (acetic and butyric), in which butyric acid concentrations were 6.59 ± 0.16, 8.27 ± 0.55, 6.16 ± 0.32 and 8.16 ± 0.90 g/kg and acetic acid were 3.83 ± 0.06, 0.91 ± 0.06, 3.73 ± 0.27, and 0.86 ± 0.01 g/kg for R_6 R_7 R_8 and R_9 respectively. This change in TVFA composition could be due to the temperature, it was reported that the composition of VFA changes with the operating temperature. While mesophilic conditions favor the production of ethanol and acetic acids, at thermophilic conditions, the main component of VFAs is butyrate, which was discovered during this experiments (International, 2004). When the BPH was

Table 3
Kinetic study results using Modified Gompertz Model.

Parameters	unite	R_0	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
Experimental biogas yield	mL biogas /g VS	657.70	753.76	724,57	806.1	760.66	688.66	835.63	812.86	831.17	760.28
Predicted biogas yield	mL biogas /g VS	652.16	745.22	734.16	795.73	751.25	678.38	825.83	796.2	812.40	743.3
R_b	mL biogas / g VS^{-1}. h^{-1}	3.21	4.19	4.24	4.92	4.95	4.90	5.07	5.12	6.20	6.37
λ	h	25.90	26.83	24.88	21.95	23.87	24.87	23.51	19.21	18.13	14.21
R^2		0.9874	0.9882	0.9879	0.9889	0.9877	0.9866	0.9881	0.9910	0.9898	0.9912

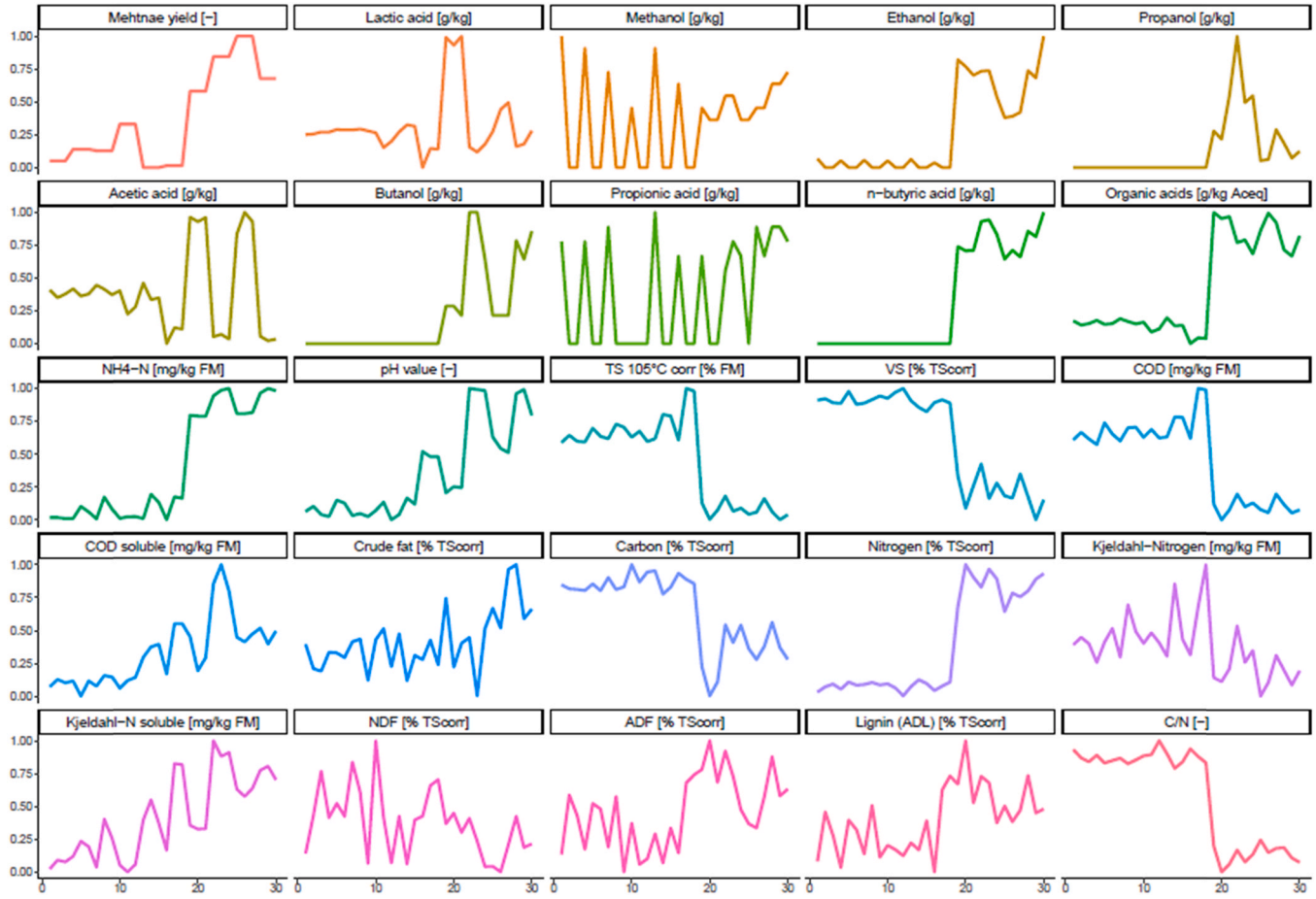


Fig. 7. Graphical illustration of variables used in the statistical study.

applied for FW, we observed an increase in concentration of acetic and butyric acids, as well as an increase in ethanol concentration. The formation of these components is favorable for methane production.

Effects of pretreatments on biogas and methane production in batch tests

Biogas yield production

The batch tests were carried out for 28 days in order to evaluate the biogas yield and methane yield through anaerobic digestion of food waste pretreated by TP and BPH at different pretreatment conditions. The evolution of cumulative biogas yield production as a function of time is represented in Fig. 5. The results show that the FW untreated could produce 657.70 mL biogas/g VS. When the pretreatments were applied, we observed a significant increase in the amount of biogas produced. For TP, the maximum biogas yield was recorded in R3 when the substrate was pretreated thermally at 100 °C for 30 min, exhibiting a value of 806.1 mL biogas/g VS, followed by R4 (760.66 mL biogas/g VS), R1 (753.76 mL biogas/g VS), R2 (724,57 mL biogas/g VS) and R5 (688.66 mL biogas/g VS) respectively. The biogas yield for TP was 33.57% and 53.51% higher than without pretreatment. Therefore, these results indicate that the temperature had a positive impact on biogas production, when the temperature was increased from 60 °C to 140 °C the biogas production increased. With the effect of temperature, the insoluble fraction structure is altered, which makes it easier for degradation and results in an improvement of biogas production. As well as the TP having a positive impact on biogas production, the BPH resulted in an enhancement of biogas yield. However, the BPH improved the biogas yield more than TP. The maximum biogas yield was recorded for R6 (835.63 mL g/VS), followed by R8 (831.17 mL/ gVS), R7 (812.86 mL/g VS) and R9 (760.28 mL /gVS). The biogas yield of BPH was 50.56% and 63.61% higher than untreated. This enhancement of biogas production could be attributed to the depolymerization of microbial cell walls and sludge cells network, which results in small dissolved compounds that are easily degradable by microorganisms during anaerobic digestion (Guo et al., 2014).

Methane yield

In order to assess the effect of pretreatments applied to FW, the methane yield of each pretreatment condition was evaluated, and the results are shown in Fig. 6. In addition to the pretreatments had a positive impact on biogas production, they also improve the methane production. As can be seen in Fig. 6, the methane yield of the untreated substrate was 371.17 ± 12.06 mL CH_4/ g VS. For TP and at moderate temperatures (60–100 °C), the methane was enhanced compared to untreated and exhibited the following values (380.65 ± 10.61, 379.45 ± 3.57, and 400.89 ± 6.84 mL CH_4/ g VS) for the temperatures 60, 80, and 100 °C respectively, which were 2.23 – 8% higher than untreated. The enhancement of methane yield was due to the breakdown of the cell membrane and the dissolution of recalcitrant organic compounds, which resulted in the promotion of hydrolysis of macromolecules. In contrast, when the temperatures reached 120 and 140 °C, we observed a decrease in methane yield that was 365.87 ± 19.38 and 367.33 ± 14.62 mL CH_4 / g VS for 120 and 140 °C, respectively. This decrease might be due to the formation of undesirable compounds such as melanoidins that result from the Maillard reaction, a reaction between sugars and amino acids. Consequently, the production is negatively affected, and the methane yield of untreated FW was higher than

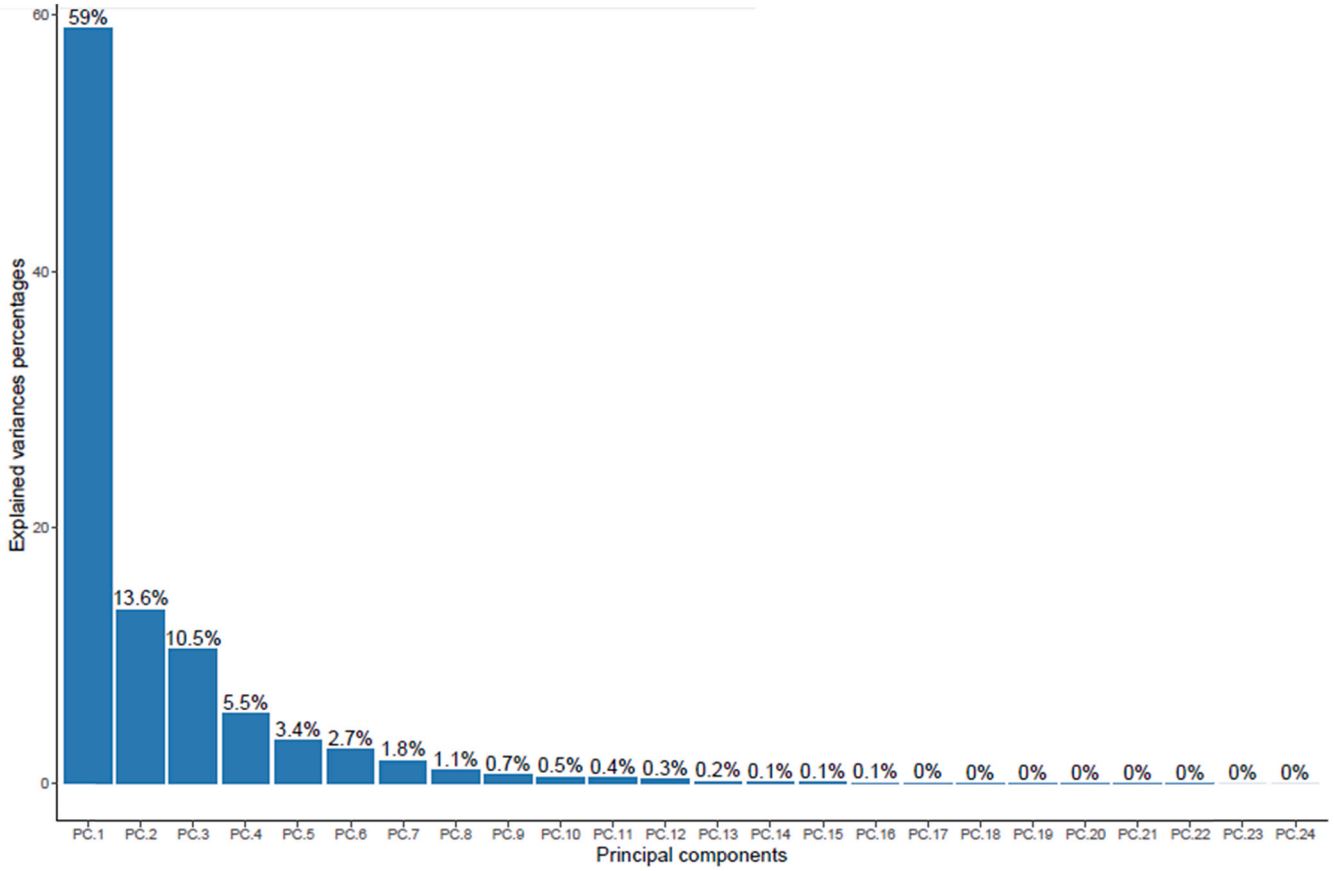


Fig. 8. Contribution of all variables using PCA.

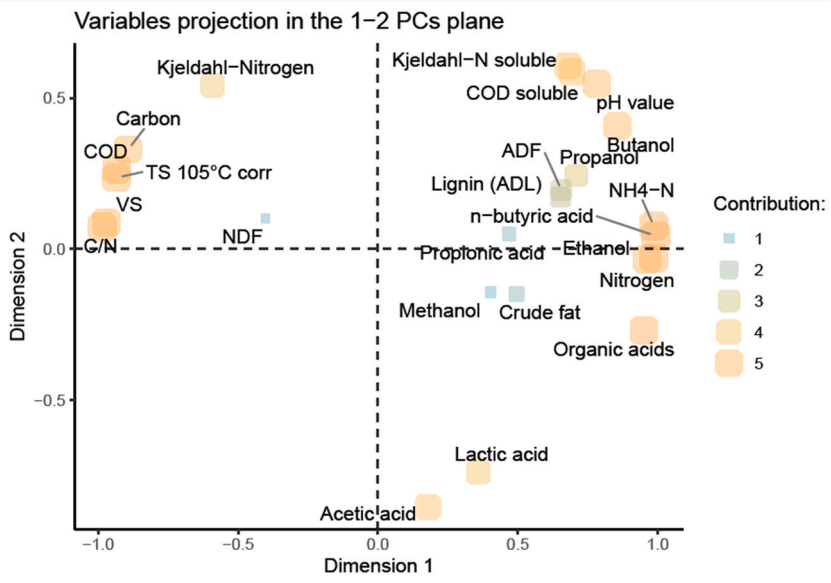


Fig. 9. Variables projection in the 1–2 plane.

after TP at 120 and 140 °C for 30 min. Furthermore, the batch test for BPH revealed that this pretreatment improved methane yield significantly. The methane yield for the reactors R_6 R_7 R_8 and R_9 was 427.42 ± 68.70, 455.43 ± 35.30, 471.95 ± 30.37 and 437.80 ± 34.37 mL CH_4 / g VS respectively. This increase in methane production was probably due to the concentration of VFA and alcohols especially ethanol. The VFAs are substrates that mainly consist of carbon atoms, essential for biogas production. In acetogenesis and methanogenesis phases, the VFA are gradually degraded which results in production of acetic acid, and then converted into methane by the acetyl-CoA pathway (Huihuang et al., 2017).

Kinetic study

A kinetic study was carried out on the biogas yield of all reactors using the Modified Gompertz Model. As can be seen from Table 4, the maximum biogas production rate increased using the TP and BPH for untreated FW. It was 3.21 mL/ g VS. h and increased to 4.19, 4.24, 4.92,

Table 5
The contribution of each variable in the first 5 PCs.

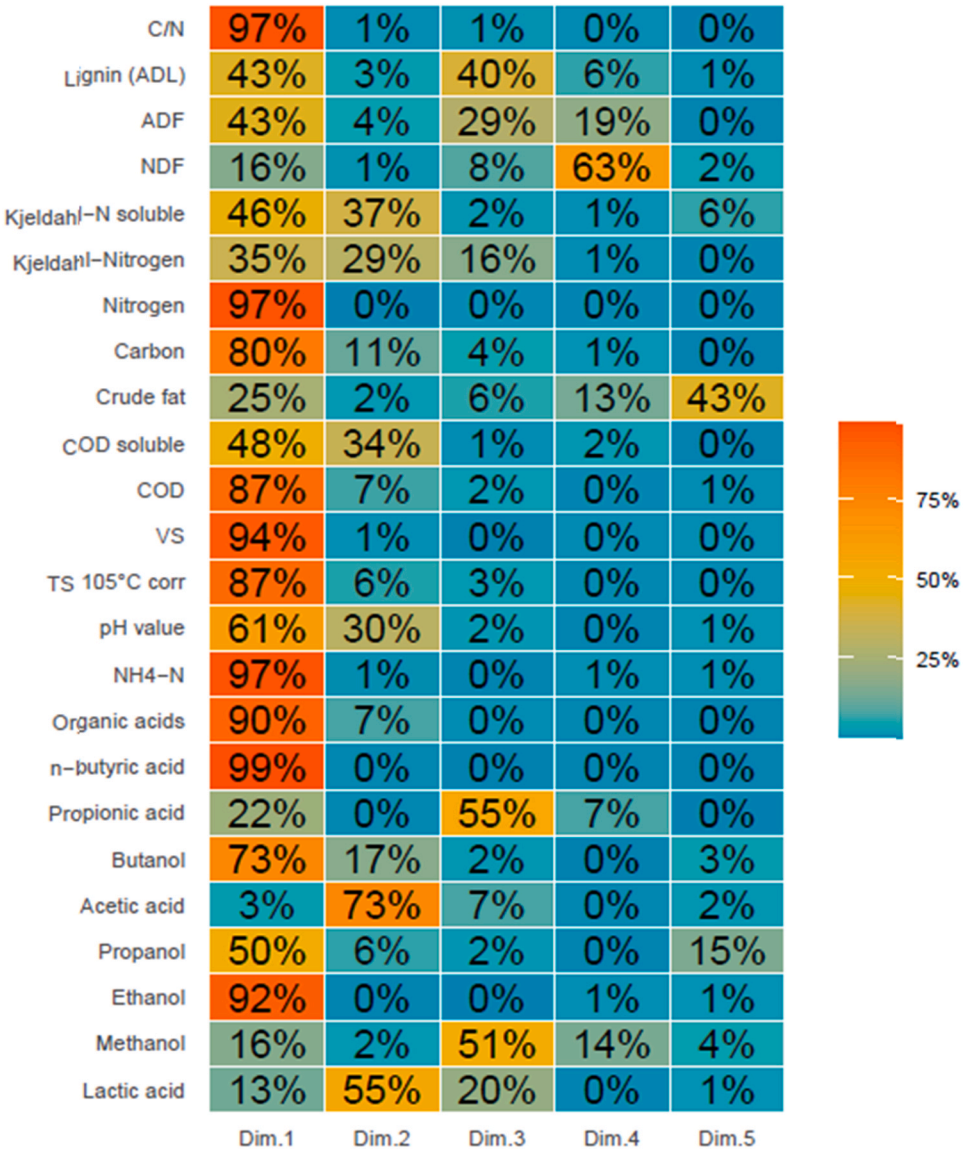


Table 6
Selected variables using PCA method.

Variable	Contribution
Ethanol	5.315551
Butanol	5.151267
n-butyric acid	5.674781
organic acids	5.603223
NH_4-N	5.612550
pH	5.238313
TS	5.337864
VS	5.453926
COD	5.395852
Carbon	5.202927
Nitrogen	5.595059
C/N	5.606004

4.95 and 4.90 mL biogas /g VS/h for the reactors R_1 R_2 R_3 R_4 and R_5 respectively when the TP was applied. For the BPH, the maximum biogas production rates were 5.07 5.12 6.20 and 6.37 mL biogas /g VS for R_6 R_7 R_8 and R_9 respectively. The values of the lag phase λ are also shown in Table 3. Results indicate that the pretreatments enhanced the biogas production rate and reduced the lag phase during the batch tests compared to the untreated substrate.

Statistical variable selection

In this section, we present a method for variable selection candidate for modeling the methane yield in a robust way and which helps minimize the known problem of model overfitting for possible methods of prediction.

We used three indicators to measure the statistical dependence between variables. The PCA which explains the variance in the data, the mutual information which measures the probabilistic non-linear dependence between variables, and finally the linear correlation R-squared.

For each indicator, we select 10% of the most influential variables and lastly, we select shared variables returned by all the used indicators.

The data used in the statistical study is the chemical analysis of the substrate after each pretreatment type and conditions.

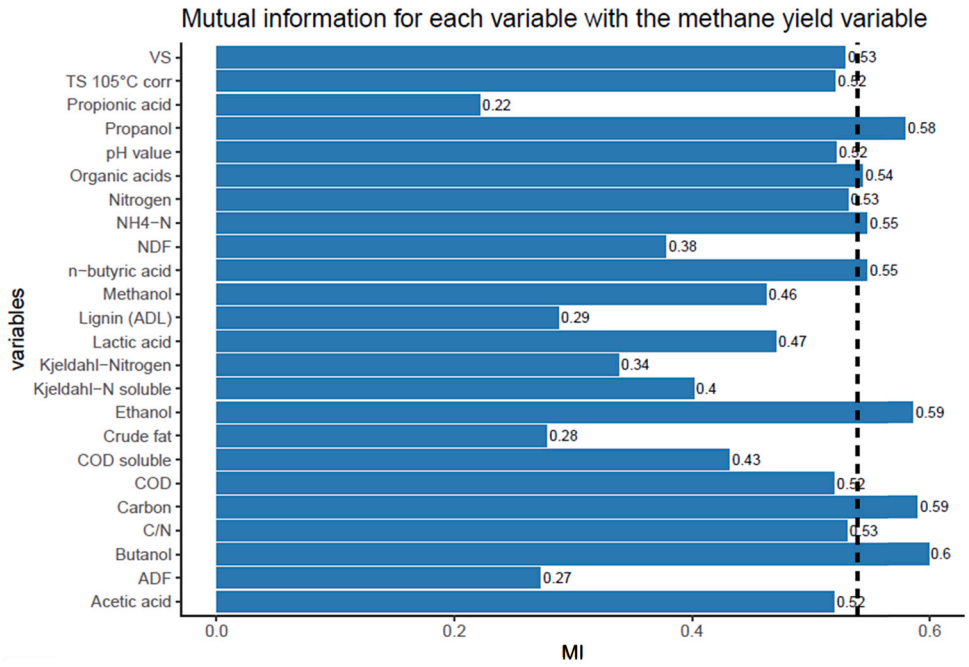


Fig. 10. Mutual information for each variable with the methane yield.

Table 7
Selected variables using MI method.

Variable	MI
Ethanol	0.60
Propanol	0.60
Butanol	0.60
n-butyric acid	0.55
Organic acids	0.55
NH_4-N	0.55
Carbon	0.60

Table 8
Selected variables using R-squared method.

Variable	Entropy
n-butyric acid	0.81
Organic acids	0.81
NH_4-N	0.80
TS	0.80
VS	0.76
COD	0.80
Nitrogen	0.80
C/N	0.80

Data summarization

The following table summarizes the most commonly used variables for methane yield modeling. Some of them are needed, and others are not. It is our task to remove non-needed variables.

Fig. 7 shows the graphical representation of all measured variables and the methane yield. A good correlation can be easily observed between for example the methane yield and the ethanol.

Variables selection

Three indicators are used to select the IMPORTANTE variables that most influence the methane yield, each one is explained in a separate subsection.

Principal components analysis

Fig. 8 illustrates the percentage of the explained variance for each PC direction, the first PC explains 59% of variance and the second PC explains 13.6%.

The contribution of each variable in the 1–2 PCs plane (1–2 stands for first and second PC axis) is calculated with the following formula:

$$Contribution = \frac{C_1 \times E_1 + C_2 \times E_2}{E_1 + E_2},$$

where C1 and C2 are the contributions of the variable in each of the axes PC1 and PC2; it is calculated as the square value of the variable coordinate in each axis. E1 and E2 are the eigenvalues for PC1 and PC2 respectively. Fig. 8 shows calculated contributions of all variables and the selection limit of 10%.

In order to have more information about contribution of variables, a projection of the variables was conducted, and Fig. 9 demonstrates the projection of the variables in the 1–2 PCs plane. The contribution of each variable is highlighted with the shape and color of each point (scale from 1 to 5):

Table 5 highlights the contribution of each variable in the first 5 PCs:

Finally, the selected variables with PCA method are given in the Table 6.

Table 9
Physico-chemical data used for methane yield prediction.

Parameter	unite	R_0	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
n-butiric	g/kg	0	0	0	0	0	0	6.60	8.27	6.16	8.16
organic acid	g/kg AC_{eq}	2.00	2.02	2.10	1.72	2.01	1.01	10.44	9.24	9.94	9.10
Nitrogen	mg/kg FM	72.4	110.3	136.6	75.6	157.0	158.0	754.0	916.3	771.7	922.4

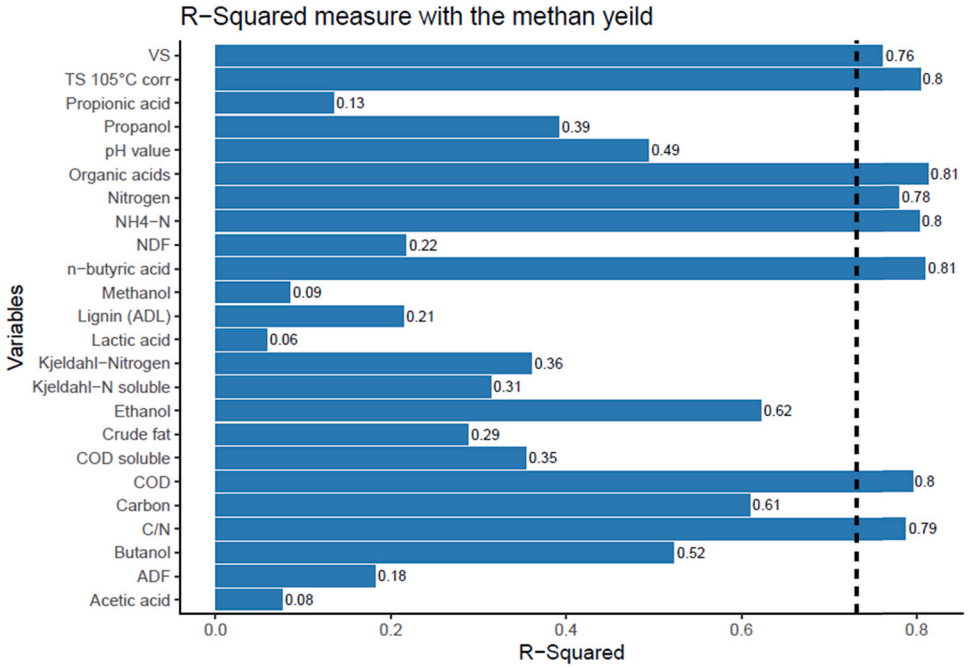


Fig. 11. Measured R-squared for all variables.

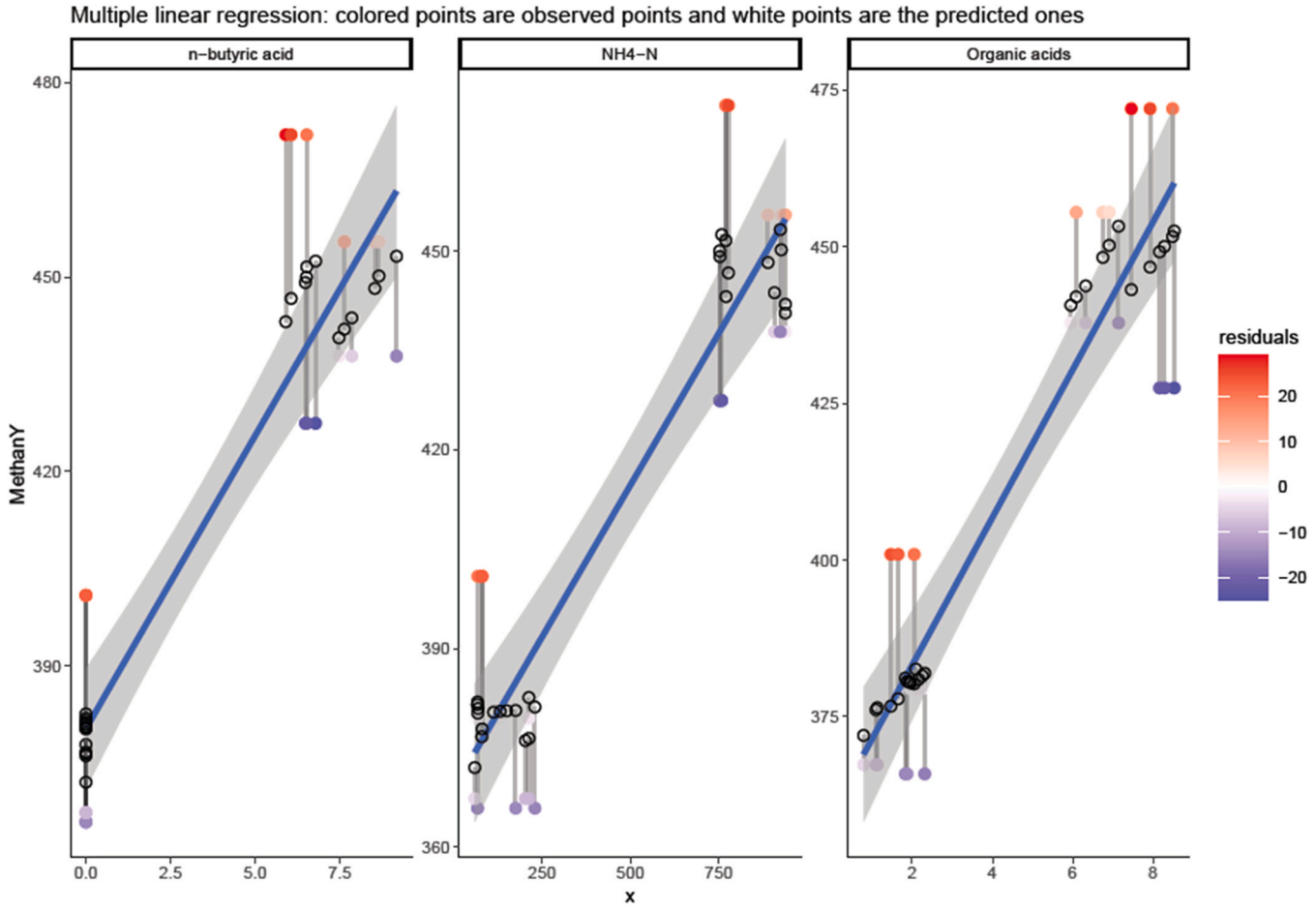


Fig. 12. Multiple linear regression: colored points are observed points and white points are the predicted ones.

Table 10
Comparison between experimental and predicted methane yield.

Parameter	R_0	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
Experimental methane yield	371.17	380.65	379.45	400.89	365.87	367.33	427.42	455.43	471.95	437.80
Predicted methane yield	379.95	380.61	381.49	378.19	381.20	374.79	529.73	546.06	521.03	543.82

Mutual information

Mutual information is the theoretic measure of dependency between two random variables X and Y. It is calculated by the following formula:

$$MI\left(X, Y\right) = \sum_{x \in X} \sum_{y \in Y} p\left(x, y\right) \times \log_2\left(\frac{p(x, y)}{p(x)p(y)}\right),$$

Where p(x) is the empirical distribution of X and p(y) is the empirical distribution of Y. p(x, y) is the joint empirical distribution of X and Y. Independence occurs if and only if p(x, y) = p(x)p(y) otherwise I(X, Y) is a positive quantity.

The following graph is the calculated mutual information for each variable with the methane yield variable. Note that we use here a normalized version of the mutual information by using the following non-linear transformation:

$$MI_n = 1 - \exp(-MI)$$

Fig. 10 shows the measured MI for all variables with the methane yield and the limit 10%. Tables 7–9.

The selected variables with the MI method are:

R-squared

To help extract more information about dependence of variables with the methane yield, we used also the R-Squared measure.

Fig. 11 shows the measured R-squared for all variables with the methane yield and the limit 10%.

The selected variables in this case of the R-squared are:

Shared variables selection

Finally, we select the variables which contribute more to the variation of the methane yield by selecting the shared variables between all indicators which have: MI greater than 90% of the maximum mutual information, PC contribution greater than 90% of the maximum contribution and an R-square greater than 90% of the maximum R-square value.

Selected variables
n-butyric acid
Organic acids
NH_4-N

Multiple linear regression model

After selecting important variables which contribute to the variation of the methane yield, the formula of the multiple linear regression is given by:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + .+\beta_i X_i$$

where Y is the dependent variable (Methane yield), X's the independent variables (predictors) and β's are the regression weights of the model (each β is interpreted as the mean effect on the dependent variable by its corresponding independent variable and holding as others fixed).

To test the model, we ignore the 'food waste untreated' sample at a first stage and fit the linear regression model on all other samples, then predict the methane yield based on the ignored sample using the resulting regression equation (Fig. 12).

Therefore, the methane yield can be explained by the following multi-linear equation:

$$Methaneyield_{predicted} = 366.094 + 13.036 \times C_{n-butyric} + 6.422 \times C_{organicacid} + 0.014 \times C_{Nitrogen}$$

Where $C_{Ethanol}$ is the concentration of Ethanol in substrate, $C_{n\text{-butyric}}$ is the concentration of n-butyric acid, $C_{organic\ acid}$ is the concentration of the total organic acid and C_{carbon} is the content of carbon in the substrate.

The reason for the positive relationship between n-butyric acid and methane yield in the plot when it has a negative coefficient in the equation is that when we calculated the predicted values, we used the whole dataset, i.e. all independent variables contributed in the calculation. So there are some variables highly positively correlated with the methane yield that submerge/remove the negative effect of the n-butyric acid which were the ethanol and the intercept constant.

In other words, each coefficient in the equation is calculated for each variable by holding all other variables constant, but when predicting new values, the effects of all other variables are taken into account, which may result in dominating the effect of the current independent variable — for the carbon, for example, the negative slope is preserved, which means that all the other variables did not dominate the negative effect of the carbon.

To evaluate the reliability of this equation, it was applied for all batch tests using the data of the physical-chemical characteristics of the substrates after each type and pre-treatment conditions. The results are illustrated in the Table 10.

As can be seen from the Table 10, the predicted values are close to the values obtained experimentally, which validate the model of multiple linear regression and the selected variables.

Conclusion

This study evaluated the influence of two different pretreatment techniques thermal and biological pre-hydrolysis. The results showed that the application of these two pre-treatments resulted in a change in the physico-chemical properties, including soluble COD, soluble protein faction, ammoniacal nitrogen, and volatile fatty acid concentration.

Biogas production was improved by the pre-treatments and the maximum biogas yield value was recorded when the BPH was applied, starting at 37 °C for 20 h and ending at 55 °C for 20 h. The maximum methane yield increased from 382.21 mL CH_4/ g VS to 674.49 mL CH_4/ g VS by BPH at 37 °C for 40 h. This increase in methane production was probably due to the concentration of VFA and alcohols especially ethanol. The VFA are a substrate contained mainly by carbon atoms, essential for biogas production.

A kinetic study was conducted and revealed that the TP and BPH enhanced the biogas production rate and reduced the lag phase during batch test.

The statistical study allowed us to determine four essential variables for modeling the methane yield in a robust way and minimize the known problem of model overfitting for possible methods of prediction.

The resulting variables from the selecting variables method are used to predict the methane yield using a multiple linear regression. Good results were obtained, and predicted values were in the line of the measured ones.

For reproduction and a solid contribution to the field, we have attached to our article the code source to reproduce the same statistical work as in the paper body.

Acknowledgments

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Update

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Erratum regarding previously published articles

Owing to a Publisher error Declaration/Conflict of Interest statements were not included in the published versions of the following articles, that appeared in previous issues of Cleaner Waste Systems.

The authors for the below mentioned articles declared that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in their articles.

1. Biological pre-hydrolysis and thermal pretreatment applied for anaerobic digestion improvement: Kinetic study and statistical variable selection, Volume 2, July 2022, 100005. https://doi.org/10.1016/j.clwas.2022.100005
2. Methane production from date seed cake (Phoenix dactylifera L.) using mesophilic fed-batch anaerobic digestion, Volume 2, July 2022, 100009. https://doi.org/10.1016/j.clwas.2022.100009
3. Possibilities for sustainable household waste management: A case study from Guanajuato, Mexico, Volume 2, July 2022, 100016. https://doi.org/10.1016/j.clwas.2022.100016
4. Recycling of organic residues to produce insulation composites: A review, Volume 3, December 2022, 100023. https://doi.org/10.1016/j.clwas.2022.100023
5. Predictive comparison and assessment of ANFIS and ANN, as efficient tools in modeling degradation of total petroleum hydrocarbon (TPH), Volume 3, December 2022, 100052. https://doi.org/10.1016/j.clwas.2022.100052

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