

Effect of methanol-organosolv pretreatment on anaerobic digestion of lignocellulosic materials

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ARTICLE INFO

Article history:

Received 30 October 2020

Received in revised form

21 December 2020

Accepted 22 December 2020

Available online 28 December 2020

Keywords:

Biomethane

Organosolv

Methanol

Hazelnut skin

Spent coffee grounds

Almond shell

ABSTRACT

Lignocellulosic materials are the most abundant biomass on the planet, representing a great opportunity for energy valorisation. This work investigated the effect of methanol-organosolv pretreatment on the methane production from hazelnut skin (HS), spent coffee grounds (SCG), and almond shell (AS). The pretreatment on the three lignocellulosic materials was performed at 130, 160, and 200 °C for 60 min using a 50% (v/v) methanol solution, with and without the addition of sulfuric acid as a catalyst. The biomethane potential of raw and pretreated substrates was evaluated under wet-mesophilic conditions in batch reactors, achieving 17.3 (±32.3), 293.4 (±46.6), and 23.2 (±9.6) mL CH₄/g VS for HS, SCG, and AS, respectively. The methanol-organosolv pretreatment was particularly effective on HS, increasing its biomethane potential up to 310.6 (±22.2) CH₄/g VS. On the contrary, all pretreatment conditions were ineffective on SCG and AS in terms of cumulative methane production. Among the three substrates, only HS showed significant composition changes due to the pretreatment, with the lignin content decreasing from 39.66 to 34.73% and the amount of bioavailable sugars increasing. An energy assessment confirmed the pretreatment efficacy on HS, with a maximum net positive energy recovery of 1.35 kWh/kg VS.

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1. Introduction

Lignocellulosic materials (LMs) are the most abundant bio-resources on the planet, with approximately 200 billion tons of plant biomass produced every year and 5–10% of the primary biomass still accessible for biorefinery applications after the primary use [1,2]. The use of LMs for biofuel production does not compete with food production, since LMs are treated as wastes from agricultural, municipal, or industrial activities and generally have a low cost [3].

The energy valorization of LMs represents a great opportunity for the transition from a fossil fuel-based economy to a sustainable carbon-neutral bioeconomy, with anaerobic digestion (AD) being one of the most well-established technologies [4]. AD is an alternative to landfilling and combustion, with the advantages to avoid uncontrolled emissions and produce methane (CH₄) which, once combusted, generates a lower amount of carbon dioxide (CO₂) per unit of energy compared to other fossil fuels and few other atmospheric pollutants. The World Bioenergy Association reported a

domestic supply of biogas of approximately 1.33 EJ, with Europe accounting for half of the global supply [5]. The energy content of biogas, described by the lower calorific value, ranges from 20 to 36 MJ/Nm³ biogas depending on the methane content [6,7].

The use of LMs for AD is, nevertheless, still limited due to their complex and resistant structure, which mainly consists of cellulose, hemicellulose, lignin, and other non-structural components, called extractives [8]. The main reason for biomass recalcitrance seems to be the low accessibility of cellulose fibers, caused by the presence of lignin and hemicellulose, which prevents cellulase enzymes from reaching and attacking cellulose [9].

Pretreatments can be used to increase the hydrolysis of LMs and improve the accessibility to cellulose. The most commonly used classification categorizes the different pretreatments into physical, chemical, physico-chemical, and biological [10]. Chemical pretreatments improve the biodegradability of cellulose by removing lignin and, where appropriate, hemicelluloses, increasing the accessible surface area, and reducing the degree of polymerization and crystallinity of the cellulosic biomass components. The chemical agents can be classified into four main categories: acids, alkali, organic solvent, and salts [11].

Organosolv pretreatment has been reported as one of the most

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Abbreviations			
LMs	Lignocellulosic materials	RID	Refractive index detector
AD	Anaerobic digestion	Eq	Equation
HS	Hazelnut skin	H	Specific energy consumption
SCG	Spent coffee grounds	C_p	Specific heat capacity
AS	Almond shell	E_p	Specific energy production
BMP	Biochemical methane potential	E_R	Specific energy recovery
UASB	Upflow anaerobic sludge blanket	$E_{R,eff}$	Effective energy recovery
TS	Total solid	SMY	Specific methane yield
VS	Volatile solid	CHP	Combined heat and power
S/L	Solid to liquid ratio	ξ	Lower heating value of methane
rpm	Revolutions per minute	RSQ	Pearson product-moment correlation coefficient
WSC	Water swelling capacity	G_1, G_f, G_{m1}, G_{m2}	Methane production yields
SEM	Scanning electron microscope	R_{m1}, R_{m2}	Methane production rates
TCD	Thermal conductivity detector	λ_1, λ_2	Lag phases
VFAs	Volatile fatty acids	t_b	Crossover point
HPLC	High-performance liquid chromatography	ANOVA	Analysis of variance
		$r_{lign-CH4}$	Pearson's correlation between lignin content and cumulative methane production

efficient methods for lignin removal. In this pretreatment, the LMs are mixed with an aqueous organic solvent, and heated to dissolve the lignin and part of the hemicellulose, leaving the cellulose in the solid phase. The process temperature usually ranges from 120 to 200 °C, depending on the type of biomass, catalyst, and solvent. The duration varies between 0.5 and 3.0 h [12]. The organosolv pretreatment is well suited to be integrated into a biorefinery concept, combining the advantages of an easy solvent recycling and the recovery of a highly pure lignin fraction [13,14]. Several authors studied the effect of ethanol-organosolv pretreatment for ethanol and biogas production, as well as recovery of sugars and other valuable compounds [15–18]. Nevertheless, only a few studies investigated the use of other alternative solvents such as methanol, acetone, and butanol, which can result in a more efficient lignin removal and subsequent a higher methane production [19–21]. Methanol is considered an environmentally friendly solvent due to a low accumulation capacity in soils in case of accidental losses, and a high biodegradability under both aerobic and anaerobic conditions [22].

This study aims to investigate the effects of organosolv pretreatment on the biomethane yield obtained from the AD of three LMs materials, namely hazelnut skin, spent coffee grounds, and almond shell. In addition to this, the changes in lignocellulosic composition and physical structure were also studied. The organosolv pretreatment was carried out using methanol as the organic solvent at a 50% (v/v) water-methanol solution, with and without catalyst (sulfuric acid) addition. The pretreatment was conducted at 130, 160, and 200 °C for 1 h. The experimental methane production results were validated by fitting them with a modified Gompertz model. An energy balance was performed to assess the feasibility of the organosolv pretreatment.

2. Materials and methods

2.1. Raw materials

Three raw materials were used as substrates: hazelnut skin (HS), spent coffee grounds (SCG), and almond shell (AS). The HS came from the industrial roasting of imported Turkish hazelnuts performed by a local food farming company in the Campania region (Italy). SCG were directly collected from a coffee bar in Galway (Ireland). The initial moisture content of SCG was 63.2 (± 0.3) wt%. Due to the high water content and to prevent spoilage due to

microbial formation during storage, the SCG was dehydrated at 60 °C for about 48 h before use [23]. Almonds were commercially purchased from a local market in the Lazio region (Italy), crushed manually, and separated from the edible kernel to obtain the AS. Both HS and AS were cut down and sieved to screen for a particle size ranging from 1.0 to 2.5 mm. The raw materials were stored at 4 °C when not used. The concentration of total (TS) and volatile (VS) solids of the raw materials, as well as the thermal ultimate analyses of the raw LMs, is reported in Table 1.

2.2. Inoculum

The inoculum used in this study was a granular sludge obtained from a full-scale upflow anaerobic sludge blanket (UASB) digester, operated at ambient temperature for the treatment of dairy wastewater and located in Kilconnell (Ireland). The TS and VS content of the inoculum was 6.0 (± 0.1) and 5.2 (± 0.1)%, respectively. The total and volatile suspended solid concentration of the sludge was reported by Castilla-Archilla et al. [24], who used the same sludge as an inoculum in their acidogenic experiments. The inoculum was stored at 4 °C while waiting to be used.

2.3. Organosolv pretreatment

The organosolv pretreatment was performed on HS, SCG, and AS using a 50% (v/v) water-methanol solution as the solvent, with and without the addition of sulfuric acid as the catalyst. As pretreatment temperature, 130, 160 and 200 °C were investigated. The pretreatment duration was 60 min. Table 2 summarizes the

Table 1

TS and VS concentration, as well as the ultimate analyses of the raw substrates employed in this study.

	HS	SCG	AS
TS ^a (%)	94.3 \pm 0.1	68.3 \pm 0.2	91.1 \pm 0.1
VS ^a (%)	91.6 \pm 0.1	67.0 \pm 0.5	89.9 \pm 0.1
C ^b (%)	59.72 \pm 0.04	55.08 \pm 0.10	50.91 \pm 0.06
H ^b (%)	6.38 \pm 0.04	7.09 \pm 0.02	5.98 \pm 0.04
N ^b (%)	0.98 \pm 0.01	2.41 \pm 0.00	0.27 \pm 0.01
S ^b (%)	0.10 \pm 0.00	0.12 \pm 0.01	0.07 \pm 0.01
O ^b _{diff} (%)	32.82 \pm 0.00	35.30 \pm 0.12	42.76 \pm 0.01

^a TS and VS are based on the wet matter (g/g).

^b Content of C, H, N, S, and O is reported on a dry ash-free basis.

pretreatment conditions applied on the three substrates.

The pretreatment was performed using a high-pressure stainless-steel vessel (Sigma-Aldrich, Germany) with a working volume of 300 mL [25]. First, 20 g (dry weight) of the LMs were mixed with 200 g of 50% (v/v) methanol solution, keeping a solid to liquid ratio (S/L) of 1:10 [13]. In the case of catalyst addition, sulfuric acid was added to the solution to obtain a sulfuric acid concentration of 0.1% (w/v). The procedure was identically repeated to pretreat all three LMs.

The vessel was then sealed, placed in a convective oven (UN110, Memmert, Germany), and heated to the desired temperature, which was kept for 60 min. After the pretreatment, the vessel was cooled in an ice bath. The pretreated LMs were removed from the vessel, washed with 100 mL fresh 50% (v/v) methanol, and rinsed with abundant distilled water until obtaining a clear liquor with neutral pH. The pretreated LMs were dehydrated at 60 °C for about 2 days and stored in plastic bags at 4 °C until use.

2.4. Biochemical methane potential tests

Batch biochemical methane potential (BMP) tests were carried out under mesophilic (~37 °C) conditions in 250 mL serum glass bottles (OCHS, Germany) (Fig. S1). Temperature was kept using an orbital water bath (OLS26, Grant, UK), which continuously maintained the bottles at 100 rpm. Each bottle was filled with the inoculum and the raw or pretreated LMs (Table S1). The inoculum to substrate ratio was kept at 1.5 in terms of g VS. Distilled water was added to adjust the final volume to 150 mL in all bottles, leaving 100 mL as headspace volume for the biogas accumulation. The final solid content was 1.8% TS in order to operate AD under wet conditions [26]. To ensure anaerobic conditions, each bottle was flushed with nitrogen gas (N₂) and then vented to reach atmospheric pressure. Control biochemical tests, containing only inoculum and distilled water, were simultaneously carried out to evaluate the methane production obtained from the inoculum alone. Results are all reported as net cumulative methane production obtained after subtracting the amount of methane produced with the substrate-free controls. All experiments were performed in triplicate and methane production was recorded for 45 days.

2.5. Analytical methods

TS and VS of the inoculum, raw and pretreated materials were determined according to Sluiter et al. [27,28] by using a convective oven (UN110, Memmert, Germany) incubated overnight at 105 °C and a muffle furnace (BWF 11/13, Carbolite, UK) at 575 °C for 4 h, respectively.

Water swelling capacity (WSC) or water-holding capacity was evaluated as an indicator of porosity before and after the pretreatment following the protocols described by Jeihanipour et al. [29]. The external surface of raw and pretreated substrates was

Table 2

Methanol-organosolv pretreatment conditions applied on hazelnut skin, spent coffee grounds, and almond shell used as substrates for anaerobic digestion in this study.

Pretreatment condition	Solvent	Catalyst	T (°C)	t (min)
A	Untreated	—	—	—
B	50% MeOH	none	130	60
C	50% MeOH	none	160	60
D	50% MeOH	none	200	60
E	50% MeOH	0.01M H ₂ SO ₄	130	60
F	50% MeOH	0.01M H ₂ SO ₄	160	60
G	50% MeOH	0.01M H ₂ SO ₄	200	60

observed using a scanning electron microscope (SEM) (S2600N, Hitachi, Japan) at an acceleration voltage of 15 kV. All LMs were preliminarily made conductive by gold coating [30] with a sputter coater (K550, Emitech, UK).

The ultimate analysis of raw LMs, as well as full characterization of raw and pretreated LMs, were carried out by Celnignis Limited (Limerick, Ireland). The ultimate analysis was done following the procedure outlined in European Standard EN 15104:2011 using an elemental analyser (Vario MACRO cube, Elementar, Germany) to determine the carbon, hydrogen, nitrogen, and sulfur content of the raw samples, with the oxygen content obtained by subtraction from 100 of the values of the other elements. The full characterization of raw and pretreated LMs in terms of full extractives, lignocellulosic sugars, lignin, and ash was performed in duplicate according to the procedure described by Sluiter et al. [31,32].

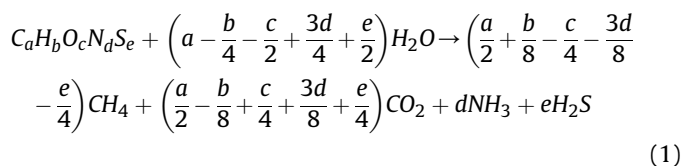
Biogas accumulation in the headspace volume was monitored with a pressure-meter (Leo 1, Keller, Switzerland) and calculated as pressure difference using the ideal gas law, according to Li et al. [33]. The gas composition was evaluated with a gas chromatograph (7890B, Agilent, USA), equipped with a thermal conductivity detector (TCD) heated at 250 °C, able to detect CH₄, CO₂, N₂, O₂, and H₂. Helium was used as the carrier gas with a flow rate of 10 mL/min. The headspace was regularly sampled and then restored at atmospheric pressure.

The volatile fatty acids (VFAs) accumulation during the AD process was monitored by using a high-performance liquid chromatograph (HPLC) (1260 Infinity II, Agilent, USA) equipped with a Hi-Plex H (300 × 7.7 mm) column, heated at 60 °C and a refractive index detector (RID) set at 55 °C. A 0.005M H₂SO₄ solution was used as the mobile phase at a flow rate of 0.7 mL/min. For analysis of VFAs, 2.5 mL of the liquid phase was sampled from each bottle during the first 20 days of the experiment, following the same timing of the gaseous samples. Before being analysed, the samples for VFAs analysis were centrifuged for 10 min at 14,500 rpm and filtered with 0.2 µm polyethersulfone membranes (Filtropur S 0.2, Sarstedt, Germany). The pH of liquid samples was measured with a pH meter (300 pH/ORP, Cole Parmer, USA).

3. Calculations

3.1. Theoretical methane potential

The theoretical BMP of raw substrates was estimated considering their elemental composition (C, H, O, N) according to Peller and Gidaracos [34]. The following Boswell-Boyle's Eq. (1) and Eq. (2) describe the stoichiometry of the degradation reaction and the theoretical BMP (NmL/g VS), respectively:



$$BMP_{th} = 22.4 \cdot \frac{\left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{12a + b + 16c + 14d + 32e} \cdot 1000 \quad (2)$$

The elemental composition enables a fast estimation of the maximum BMP. However, this equation does not consider the presence of non-biodegradable matter, including lignin. It is also based on the assumption of perfect mixing, constant temperature, ideal conditions for the microbial activity, and no ashes accumulation. Despite that the theoretical BMP is never achieved, it gives

an estimation of the maximum accessible methane production of a substrate [35,36].

3.2. Model fitting

Methane production was modelled by fitting the experimental data with a modified Gompertz model, in two stages, using the Origin2018 software (OriginLab Corporation, USA). The end of the first stage was defined as the last steady-state point observed followed by an exponential increase in methane production, assigned as the start of the second stage. The precision of fitting was evaluated with the Excel 2016 RSQ (Pearson product-moment correlation coefficient) function (Microsoft Corporation, USA).

The Gompertz model, used by several authors [34,37,38] to evaluate methane production through AD, is described by Eq. (3) when t is less or equal to t_b , and by Eq. (4) when t is higher than t_b , respectively.

$$G_1 = G_{m1} \cdot \exp \left\{ - \exp \left[\frac{R_{m1} \cdot e}{G_{m1}} \cdot (\lambda_1 - t) + 1 \right] \right\} \quad (3)$$

$$G_f = G_1 + G_{m2} \cdot \exp \left\{ - \exp \left[\frac{R_{m2} \cdot e}{G_{m2}} \cdot (\lambda_2 - t) + 1 \right] \right\} \quad (4)$$

where t (d) is time, the independent variable of the model, and t_b (d) is the crossover point between the two stages, observed experimentally. G_1 and G_f (mL CH₄/g VS) are the cumulative methane productions during the first stage and at the end of the process, respectively. G_{m1} and G_{m2} (mL CH₄/g VS) are the maximum methane production yields estimated for the two stages. R_{m1} and R_{m2} (mL CH₄/g VS·d) are the maximum methane production rates. λ_1 and λ_2 are the lag phases (d)

3.3. Energy balance

The energy balance of the organosolv pretreatment on HS, SCG, and AS was roughly estimated. The specific energy consumption H (kWh/kg VS) required for the pretreatment was calculated according to Mancini et al. [39] using Eq. (5):

$$H = \frac{m \cdot C_p \cdot \Delta T}{3600} \quad (5)$$

where m (kg) is the mass of aqueous-organic solvent required to treat 1 kg VS of the raw substrate, C_p (2.83 kJ/(kg·°C) [40]) is the solvent specific heat capacity, ΔT is the difference between ambient (25 °C) and pretreatment temperature, and 3600 is the conversion factor between kJ and kWh.

The specific energy production E_p (kWh/kg VS) from the methane produced was obtained using Eq. (6), as reported by Bianco et al. [41]:

$$E_p = (SMY_{treated} - SMY_{raw}) \cdot \xi \cdot 0.5 \quad (6)$$

where $SMY_{treated}$ and SMY_{raw} (kg CH₄/kg VS) are the specific methane yields from pretreated and raw substrates, ξ is the lower heating value of methane (13.9 kWh/kg CH₄), and 0.5 represents the efficiency of a combined heat and power unit (CHP), equal to 50%. The specific energy recovery E_R was obtained by subtracting H from E_p .

3.4. Statistical analysis

Statistical comparison of the cumulative methane production data from the control and each substrate under the different

pretreatment conditions were compared by one-way analysis of variance (ANOVA) followed by the Tukey post hoc test [42]. The same statistical analysis was performed for the porosity index of raw and pretreated LMs. The correlation between lignin content and cumulative methane production ($r_{\text{lign-CH}_4}$) was evaluated using the Pearson product-moment correlation. All analyses were performed with Minitab 17 Statistical Software (Minitab LCC, USA), where a difference marked with a p -value lower than 0.05 was considered statistically significant.

4. Results

4.1. Methane production and energy balance assessment

Table 3 shows the methane production after 45 days of AD from AS, SCG, and HS. The theoretical BMP calculation showed a maximum achievable methane production of 613.8, 573.0, and 490.0 mL/g VS, respectively for raw HS, SCG, and AS.

The organosolv pretreatment significantly increased the methane production from HS ($p < 0.05$) (Table S2) under all the pretreatment conditions (Fig. 1a and b). The methane yield increased from 17.3 up to 310.6 mL CH₄/g VS. The energy balance assessment showed a positive energy gain for the methanol-organosolv pretreated HS, with the net energy production (E_R) ranging from 0.08 to 0.75 kWh/kg VS (Table S3), depending on the pretreatment condition used.

On the other hand, no significant difference ($p > 0.05$) in methane production was observed with the pretreated SCG compared to the raw material (Fig. 1c and d), with the methane content in the biogas steadily ranging from 62.7 to 68.8% and the net methane production between 175.8 and 322.9 mL CH₄/g VS. All the applied pretreatment conditions on AS were ineffective in terms of increased cumulative methane production (Fig. 1e and f). Nevertheless, by treating AS at 200 °C without catalyst addition, the methane content in biogas rose from 57.1 to 77.4%.

No significant VFAs accumulation was observed for both raw and pretreated materials (Fig. S2), with pH always ranging from 6.3 to 7.5 during the AD process.

4.2. Effect of pretreatments on the chemical composition of lignocellulosic materials

The compositional analysis revealed the remarkable recalcitrant nature of the three raw substrates (Table 4). The total lignin content was 39.66 (± 0.09), 20.31 (± 0.29), and 30.58 (± 0.13) g/g TS, respectively for HS, SCG, and AS. On the other hand, the sugar content and composition were significantly different between the three LMs. Raw HS resulted in a significantly lower sugar content (13.72%), mainly consisting of glucan (10.15%), mostly associated with the total cellulose content (Table 4). On the contrary, raw SCG showed a high content of six-carbon hemicellulose sugars, such as mannan (23.14%) and galactan (8.79%), with cellulose being only 8.77% of the dry mass composition (Table 4). Lastly, the compositional analysis of raw AS resulted in a more balanced composition between cellulose, hemicellulose, and total lignin, with glucan (23.35%) and xylan (19.74%) being the most abundant sugars (Table 4). The lignocellulosic compositional analysis also revealed the presence of extractives, especially in HS and SCG.

Organosolv pretreatment reduced the lignin content of HS by 7–12%, with total sugars increasing from 13.72 up to 17.34%. The SCG glucan and mannan content increased to 8.86–10.05 and 24.25–26.24%, depending on the pretreatment condition, with a maximum lignin reduction of 10%, associated with the highest pretreatment temperature with no catalyst addition. On the other hand, the pretreatment has not reduced the lignin content of AS,

Table 3
Cumulative specific net methane production and methane percentage in biogas from untreated and methanol-organosolv pretreated LMs after 45 days of anaerobic digestion.

Pretreatment condition ^a	HS		SCG		AS	
	(mL CH ₄ /g VS)	(% CH ₄) ^b	(mL CH ₄ /g VS)	(% CH ₄) ^b	(mL CH ₄ /g VS)	(% CH ₄) ^b
A	17.3 ± 32.3	36.3	293.4 ± 46.6	62.7	23.2 ± 9.6	57.1
B	259.7 ± 1.5	72.4	175.8 ± 28.6	68.8	8.8 ± 3.9	65.1
C	253.5 ± 9.8	72.8	243.2 ± 14.5	64.8	3.7 ± 3.4	55.2
D	272.9 ± 1.6	72.9	302.4 ± 41.4	64.2	24.8 ± 2.6	77.4
E	310.6 ± 22.2	69.1	273.5 ± 20.9	62.6	17.1 ± 3.8	56.3
F	297.9 ± 6.9	69.7	321.3 ± 43.4	62.0	12.0 ± 1.6	48.4
G	296.9 ± 12.5	69.0	322.9 ± 19.5	62.1	10.9 ± 5.8	48.7

^a The pretreatment conditions are defined in Table 2.

^b Calculated as cumulative methane to cumulative biogas ratio.

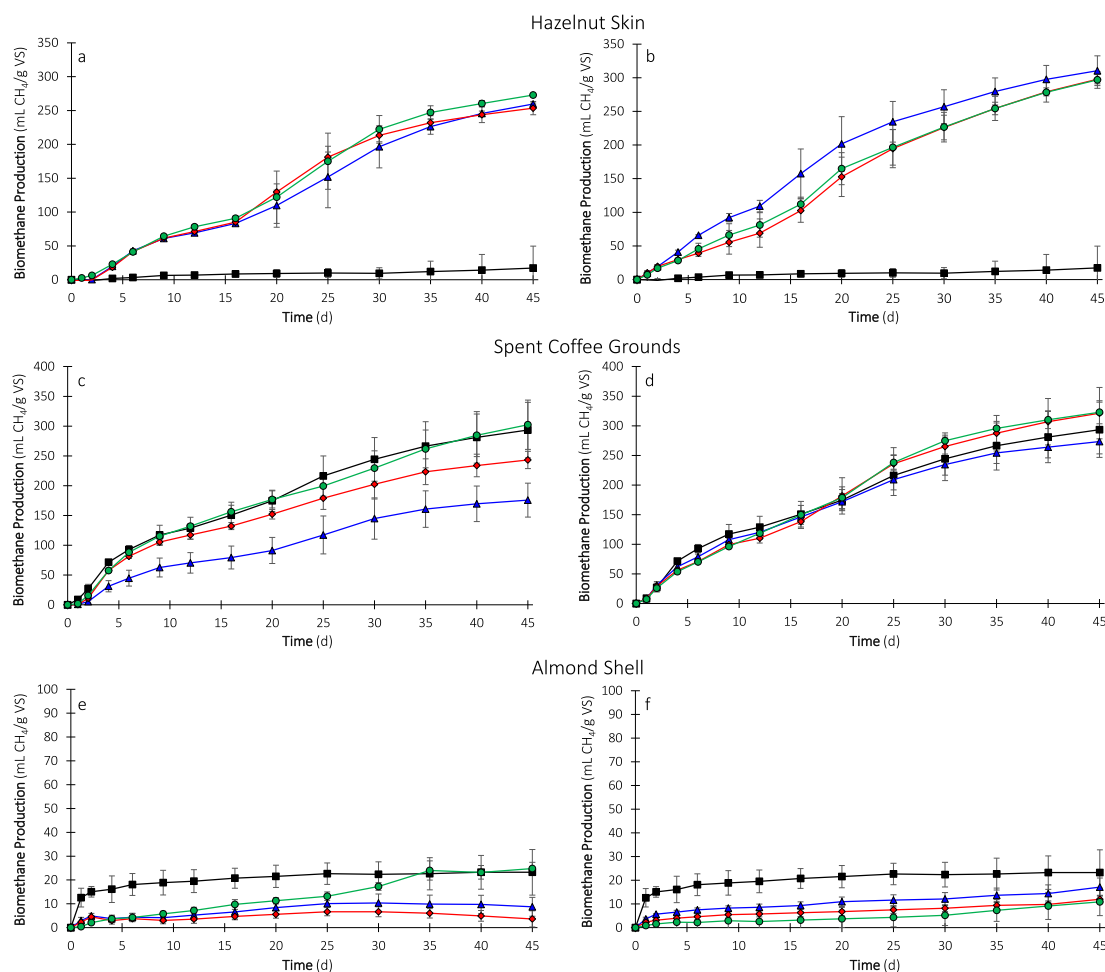


Fig. 1. Cumulative methane production from AD of HS, SCG and AS: untreated (■); organosolv at 130 °C (▲), 160 °C (◆), and 200 °C (●) without (a, c, e) and with (b, d, f) catalyst addition.

with a slight increase in the total sugars content. Besides, all pretreatment conditions removed part of the extractives from the three LMs.

The Pearson's test showed a strong inverse correlation between the lignin content and cumulative methane production from HS ($r_{\text{lign-CH}_4} = -0.927$) with a p-value of 0.003. In contrast, no significant correlation was observed between the lignin content and the cumulative methane production for AS and SCG ($p > 0.05$).

4.3. Effect of pretreatments on porosity and external surface area of lignocellulosic materials

WSC was measured as a representative parameter of the LMs porosity, showing a significant difference among the three substrates (Table 5). HS resulted in the higher WSC, ranging from 4.80 to 6.20 g/g depending on the pretreatment conditions. Opposite, SCG and AS showed WSC values ranging from 2.76 to 3.41 g/g and from 1.07 to 1.45 g/g, respectively. Among the pretreatment

Table 4
Chemical composition of raw and pretreated substrates expressed as ashes, full extractives, total lignin and structural sugars content.

Substrate	Pretreatment condition ^a	Lignocellulosic materials characterization				Total sugars composition					
		Ashes ^b (%)	Full extractives ^b (%)	Total lignin ^{b,c} (%)	Total sugars ^{b,d} (%)	Glucan ^b (%)	Xylan ^b (%)	Mannan ^b (%)	Arabinan ^b (%)	Galactan ^b (%)	Rhamnan ^b (%)
HS	A	2.71 ± 0.06	35.02 ± 0.02	39.66 ± 0.09	13.72 ± 0.08	10.15 ± 0.05	0.98 ± 0.01	0.29 ± 0.02	0.70 ± 0.01	0.91 ± 0.02	0.69 ± 0.00
	B	2.37 ± 0.10	29.87 ± 0.65	36.90 ± 0.38	14.80 ± 0.04	10.78 ± 0.01	1.06 ± 0.02	0.29 ± 0.02	0.82 ± 0.01	1.06 ± 0.01	0.79 ± 0.00
	C	2.35 ± 0.20	30.07 ± 0.65	35.95 ± 0.21	16.74 ± 0.04	12.23 ± 0.05	1.18 ± 0.07	0.32 ± 0.02	0.92 ± 0.02	1.22 ± 0.01	0.87 ± 0.06
	D	1.89 ± 0.07	31.03 ± 0.69	36.30 ± 0.72	14.04 ± 0.01	10.57 ± 0.07	1.00 ± 0.01	0.26 ± 0.02	0.66 ± 0.02	0.94 ± 0.02	0.61 ± 0.02
	E	1.51 ± 0.13	32.91 ± 0.17	36.04 ± 0.06	15.64 ± 0.12	11.80 ± 0.01	0.98 ± 0.04	0.28 ± 0.03	0.69 ± 0.00	1.07 ± 0.01	0.83 ± 0.05
	F	1.74 ± 0.06	29.44 ± 0.07	35.04 ± 0.39	15.79 ± 0.11	11.68 ± 0.03	1.14 ± 0.01	0.29 ± 0.00	0.76 ± 0.02	1.07 ± 0.03	0.85 ± 0.03
	G	1.98 ± 0.10	32.38 ± 0.59	34.73 ± 0.16	17.34 ± 0.03	13.06 ± 0.01	1.38 ± 0.02	0.39 ± 0.00	0.70 ± 0.02	1.05 ± 0.01	0.76 ± 0.01
SCG	A	1.69 ± 0.10	30.47 ± 0.83	20.31 ± 0.29	42.38 ± 0.04	8.77 ± 0.06	0.15 ± 0.01	23.14 ± 0.00	1.53 ± 0.01	8.79 ± 0.04	nd ^e
	B	0.98 ± 0.15	25.67 ± 0.18	20.52 ± 0.11	45.68 ± 0.28	9.25 ± 0.04	0.14 ± 0.01	25.14 ± 0.12	1.64 ± 0.03	9.51 ± 0.10	nd ^e
	C	0.96 ± 0.09	25.74 ± 0.07	19.22 ± 0.15	43.76 ± 0.08	8.86 ± 0.02	0.14 ± 0.00	24.25 ± 0.04	1.56 ± 0.00	8.94 ± 0.02	nd ^e
	D	1.07 ± 0.19	26.34 ± 0.13	18.33 ± 0.38	46.81 ± 0.40	10.01 ± 0.04	0.16 ± 0.01	26.24 ± 0.25	1.46 ± 0.01	8.92 ± 0.09	nd ^e
	E	0.65 ± 0.08	25.75 ± 0.45	19.30 ± 0.26	45.88 ± 0.15	9.36 ± 0.03	0.15 ± 0.03	24.96 ± 0.09	1.66 ± 0.01	9.74 ± 0.04	nd ^e
	F	0.39 ± 0.01	24.55 ± 0.46	19.85 ± 0.17	46.83 ± 0.21	9.58 ± 0.01	0.15 ± 0.01	25.42 ± 0.23	1.70 ± 0.06	9.99 ± 0.03	nd ^e
	G	0.70 ± 0.08	26.04 ± 0.87	20.38 ± 0.23	47.68 ± 0.15	10.05 ± 0.19	0.14 ± 0.02	25.81 ± 0.31	1.62 ± 0.01	10.07 ± 0.02	nd ^e
AS	A	1.45 ± 0.04	7.78 ± 0.63	30.58 ± 0.13	45.20 ± 0.07	23.35 ± 0.18	19.74 ± 0.16	0.08 ± 0.01	0.66 ± 0.01	1.08 ± 0.03	0.30 ± 0.00
	B	0.48 ± 0.01	4.14 ± 0.15	33.67 ± 0.28	46.77 ± 0.36	24.63 ± 0.13	19.82 ± 0.14	0.09 ± 0.03	0.77 ± 0.03	1.19 ± 0.02	0.27 ± 0.01
	C	0.73 ± 0.05	4.26 ± 0.50	32.60 ± 0.36	46.46 ± 0.56	24.35 ± 0.19	19.72 ± 0.44	0.09 ± 0.00	0.80 ± 0.04	1.17 ± 0.02	0.32 ± 0.00
	D	0.48 ± 0.02	2.68 ± 0.18	31.80 ± 0.33	49.39 ± 0.12	25.69 ± 0.16	21.34 ± 0.19	0.10 ± 0.04	0.77 ± 0.05	1.18 ± 0.07	0.30 ± 0.00
	E	0.33 ± 0.00	3.96 ± 0.61	31.64 ± 0.12	49.48 ± 0.75	25.61 ± 0.24	21.67 ± 0.53	0.09 ± 0.01	0.66 ± 0.01	1.14 ± 0.01	0.31 ± 0.00
	F	0.47 ± 0.08	4.80 ± 0.20	33.56 ± 0.22	47.55 ± 0.44	25.05 ± 0.13	20.37 ± 0.60	0.17 ± 0.05	0.59 ± 0.01	1.08 ± 0.03	0.29 ± 0.01
	G	0.43 ± 0.12	3.78 ± 0.79	33.01 ± 0.46	47.84 ± 0.49	24.98 ± 0.09	21.02 ± 0.37	0.08 ± 0.01	0.49 ± 0.00	1.01 ± 0.02	0.26 ± 0.00

^a The pretreatment conditions are defined in Table 2.

^b Based on dry matter (g/g TS).

^c Total lignin is reported as the sum of Klason lignin and acid soluble lignin according to Sluiter et al. [32].

^d Total sugars are obtained as the sum of glucan, xylan, mannan, arabinan, galactan, and rhamnan.

^e nd: not detected.

conditions, no significant positive effect on WSC was observed for HS and AS ($p > 0.05$), while organosolv pretreatment under all conditions significantly increased the swelling capacity of SCG ($p < 0.05$) from 2.76 (± 0.06) up to 3.41 (± 0.08) g/g.

Fig. 2 shows the structure of the external surface area of raw (panel a, b and c) and pretreated LMs at 130 °C with catalyst addition (panel d, e and f) using SEM images. The breakdown of cell walls was evident for HS when comparing the SEM images before (Fig. 2a) and after (Fig. 2d) the pretreatment, showing a major exposure of cellulose fibers after pretreatment. Raw AS (Fig. 2c) presented a series of vascular bundles, while pretreatment destroyed the original structure showing a craggy surface, with deep fissures (Fig. 2f). On the other hand, organosolv pretreatment slightly affected the external surface of SCG (Fig. 2b and e), but mainly kept the original thick structure.

4.4. Modified Gompertz model fitting of the experimental data

The modified Gompertz model was applied to fit the experimental methane production obtained from raw and pretreated SCG and HS (Fig. 3), which achieved a significantly higher biogas production than that observed in the substrate-free controls. On the contrary, no fitting was achieved when AS was used as a substrate for AD, due to the low and fluctuating methane production.

Two stages of methane production were identified, with 12 days (t_b) being the crossover point for all the substrates except for raw HS, where t_b was 20 days. Table 6 shows that all pretreatment conditions considerably increased the rate of methane production (R_m) from HS for both the first and second stages. Besides, the catalyst addition reduced the lag phase λ_1 from 2 to 3 days to less than 1 day, as well as λ_2 , with the distinction of the two stages being less noticeable with the increase in pretreatment temperature and the use of catalyst.

With regards to SCG, the pretreatments at 160 and 200 °C with catalyst addition showed a reduction of the rate R_{m1} in the first

stage and an increase of R_{m2} , compared to the raw SCG. In any case, the catalyst addition had a positive effect on the lag phase λ .

5. Discussion

5.1. Effect of organosolv pretreatment on the AD process of the three LMs

This study showed for the first time the effect of methanol as an organic solvent for the pretreatment of HS, SCG, and AS. Several studies investigated the efficiency of organosolv pretreatment to enhance biogas production, with BMP improvement being associated with lignin removal and an increase in the availability of polysaccharides (Table 7). Most of the previous studies on organosolv used ethanol as a solvent [43–45]. However, to the best of the authors' knowledge, only Kabir et al. [46] investigated the methanol-organosolv pretreatment to enhance methane production from LMs. That study compared the effects of the most employed organic solvents on forestry residues, with and without catalyst addition, showing that catalysed-methanol pretreatment was the most performing and cost-effective alternative, with a recovery rate of the solvent up to 98.2% [46].

The BMP tests clearly showed the effectiveness of methanol-organosolv pretreatment on HS (Table 3). On the contrary, no remarkable positive effect of pretreatment on cumulative biogas production was observed for SCG and AS (Table 3). In particular, the highest methane yield from HS (310.6 mL CH₄/g VS) was obtained with the HS pretreated with the catalyst at the lowest temperature, achieving 50.6% of the theoretical methane yield calculated from the elemental composition of the raw substrate. On the other hand, the BMP of raw HS only represents 2.8% of the theoretical methane yield. The catalyst addition during the pretreatment at 130 °C resulted in a significant benefit for the AD of HS by increasing the biomethane production of 20% compared with the catalyst-free pretreated HS. The benefit of catalyst addition is reduced by

Table 5
Water swelling capacity and statistical comparison of raw and pretreated LMs.

Substrate	Pretreatment condition ^a	Water swelling capacity (g/g)	Statistical information ^b
HS	A	5.53 ± 0.49	ab
	B	5.34 ± 0.65	ab
	C	5.31 ± 0.25	ab
	D	6.20 ± 0.69	a
	E	5.28 ± 0.44	ab
	F	4.81 ± 0.30	ab
	G	4.80 ± 0.52	b
SCG	A	2.76 ± 0.06	d
	B	3.07 ± 0.06	b
	C	3.41 ± 0.08	a
	D	3.04 ± 0.04	b
	E	2.87 ± 0.03	cd
	F	2.96 ± 0.09	bc
	G	3.05 ± 0.01	b
AS	A	1.40 ± 0.10	a
	B	1.45 ± 0.07	a
	C	1.14 ± 0.08	bc
	D	1.07 ± 0.06	c
	E	1.30 ± 0.02	ab
	F	1.13 ± 0.03	bc
	G	1.30 ± 0.14	abc

^a The pretreatment conditions are defined in Table 2.

^b The same letter represents no significant differences ($p > 0.05$) with the compared condition.

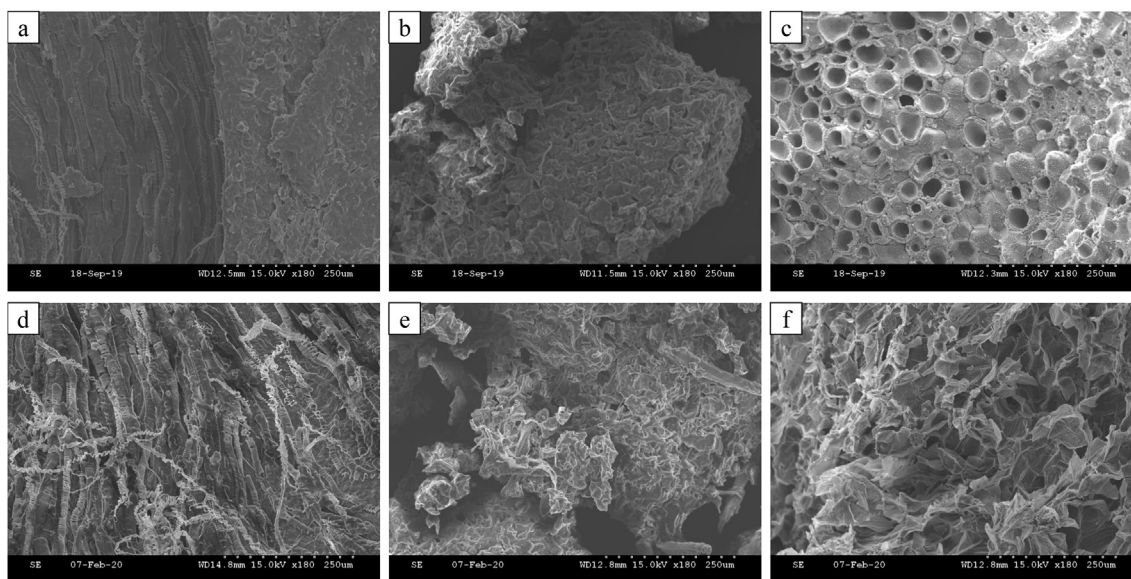


Fig. 2. SEM images of untreated and pretreated materials at 130 °C with catalyst addition: (a) raw AS, (b) raw SCG, (c) raw HS, (d) treated AS, (e) treated SCG, and (f) treated HS.

increasing the pretreatment temperature. Previous studies showed a similar synergy between catalyst and pretreatment temperature, regardless of the organic solvent employed [44,47]. At high temperatures, LMs self-catalyse the pretreatment by releasing acids [48]. Instead, when a lower temperature pretreatment is performed, external catalyst addition is required to optimize the cost-benefit balance and reduce the energy consumption during pretreatment [48]. Moreover, the catalyst addition during the pretreatment is reported to be particularly beneficial in terms of methane production when methanol and isopropanol are used as organic solvents, being less advantageous in combination with ethanol and acetic acid [44,46,47].

Fig. 3 shows the evolution of the methane production for both raw and pretreated SCG and HS according to the modified Gompertz model, by which the biogas production rate is proportional to the microbial activity [49]. Two stages of digestion can be

identified: the first stage within the first 12 days, in which the easily degradable materials are digested, and a second phase, where the less readily and more recalcitrant materials start to be degraded. This was particularly observed in catalyst-free conditions, where the double “S” shape methane production profile is more evident (Fig. 3). A similar pattern was previously observed by Rincon et al. [50] during the AD of two-phase olive mill solid waste and by Pelleria and Gidaracos [34] for different agroindustrial wastes. In the present study, the crossover point was less noticeable when sulfuric acid was used as a catalyst during the pretreatment, resulting in a reduction of the lag phases, especially in the case of treated HS. The catalyst addition is reported to be the most important factor for both lignin fractionation and hemicellulose hydrolysis during pretreatment [13]. With regards to SCG, the pretreatment lowered the methane production rate of the first stage but enabled a more efficient use of the more recalcitrant

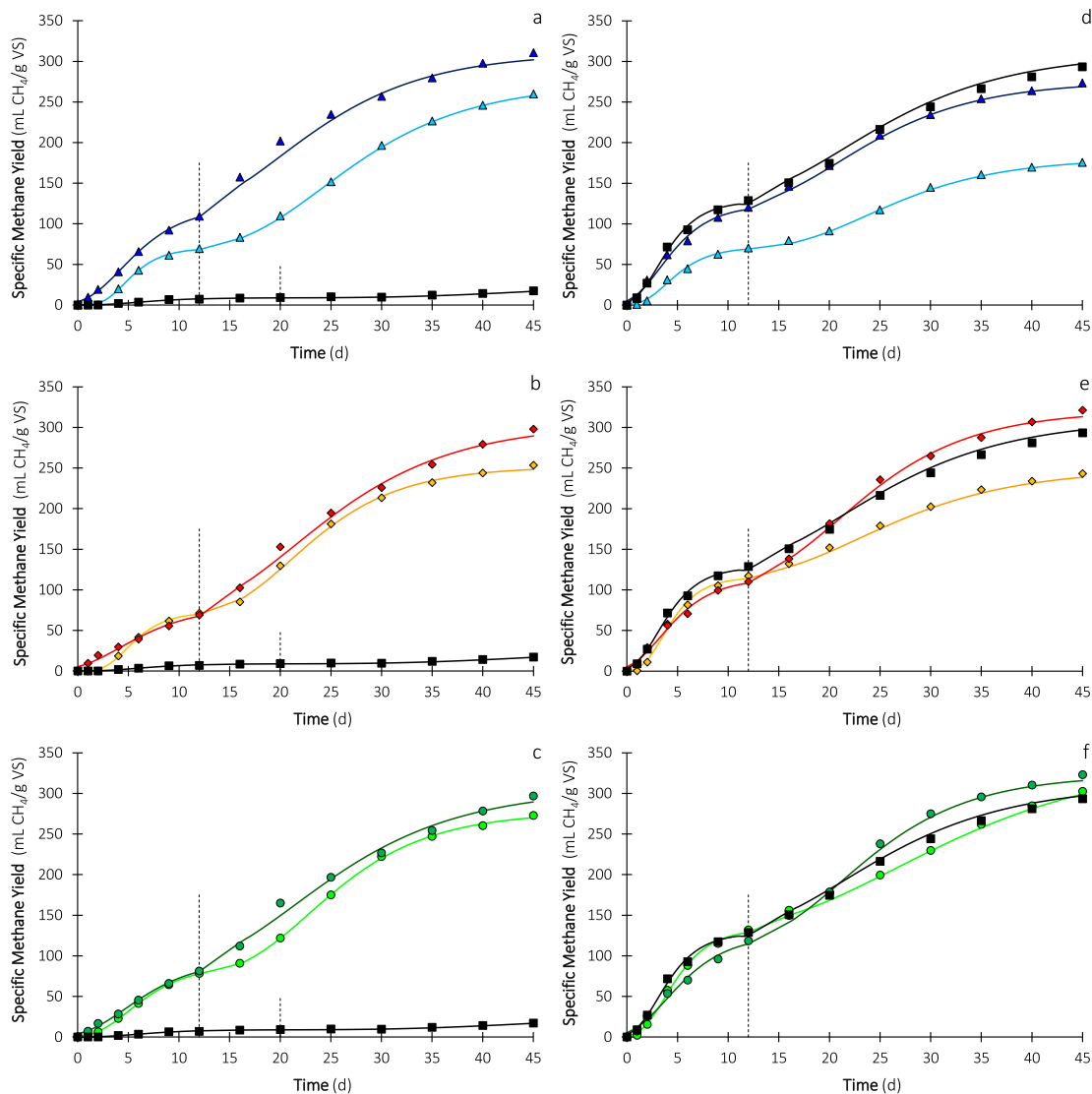


Fig. 3. Fitting of the experimental methane production values from hazelnut skin (a, b, c) and spent coffee grounds (d, e, f), raw (■) and treated at 130 °C (▲), 130 °C with the catalyst (◆), 160 °C (◇), 160 °C with the catalyst (◆), 200 °C (●), and 200 °C with the catalyst (●), by a modified Gompertz model. The dashed line identifies the crossover point t_c between the two stages of methane production. No fitting was achieved when AS was used as a substrate for AD.

materials, resulting in a higher rate of methane production in the second stage, when SCG was pretreated at 160 and 200 °C with the catalyst (Table 6).

Interestingly, the methane production from raw HS obtained in the present study was considerably different to that reported by Mancini et al. [25], who observed a much higher methane yield (261 mL CH₄/g VS) for raw HS, with organosolv pretreatment being only slightly effective on HS. The different effectiveness of pretreatment on HS can be ascribed to the use of a different organic solvent. Methanol is reported to be a better solvent for lignin, compared to ethanol [51]. On the other hand, the difference in biogas production from raw HS is most likely attributed to the use of a different inoculum, which was a digestate from buffalo manure and dairy factory in the work of Mancini et al. [25]. This hypothesis is supported by the study of Gu et al. [52], in which a digestate from dairy manure was significantly more efficient than

anaerobic granular sludge to promote the AD of untreated rice straw. The use of granular sludge, together with the limited mixing, likely led to a scarce contact between the solid substrates and the methanogenic population [53]. The intimate contact between the cellulose and cellulase enzymes is one of the most critical factors affecting the enzymatic hydrolysis yield and rate, with particle size being responsible for the external accessible surface area [54]. This may explain the low BMP observed for AS and raw HS. On the other hand, although pretreatment was not effective, the AD of raw SCG allowed a high cumulative methane yield (293.4 mL CH₄/g VS) in line with previous studies [55,56] and corresponding to the 51.2% of the maximum theoretical methane yield.

5.2. Change of LMs composition by methanol pretreatment

HS, SCG, and AS largely differ in their composition (Table 4). HS

Table 6

Parameters obtained by modelling the experimental data of HS and SCG from Fig. 1 with the modified Gompertz model. No fitting was achieved when AS was used as a substrate for AD.

Substrate	Pretreatment condition ^a	t _b ^b (d)	Stage 1		Stage 2		RSQ ^e
			R _{m1} ^c (mL CH ₄ /g VS·d)	λ ₁ ^d (d)	R _{m2} ^c (mL CH ₄ /g VS·d)	λ ₂ ^d (d)	
HS	A	20	0.98	2.4	0.65	12.6	0.9951
	B	12	12.51	2.5	9.22	3.9	0.9999
	C	12	12.26	2.6	11.04	3.0	0.9994
	D	12	9.82	1.8	11.01	4.1	0.9999
	E	12	12.80	0.8	9.34	0.0	0.9972
	F	12	6.90	0.0	10.04	0.8	0.9977
	G	12	8.60	0.7	9.16	0.5	0.9973
SCG	A	12	20.70	0.8	7.54	0.5	0.9991
	B	12	11.17	1.6	5.54	4.2	0.9991
	C	12	20.98	1.5	5.75	2.3	0.9989
	D	12	20.47	1.4	6.30	2.0	0.9991
	E	12	16.30	0.5	7.61	1.3	0.9986
	F	12	14.43	0.4	10.72	1.6	0.9984
	G	12	13.65	0.5	10.74	2.0	0.9986

^a The pretreatment conditions are defined in Table 2.

^b t_b identifies the crossover point between the two stages of the AD process.

^c R_{m1} and R_{m2} are the maximum methane production rates of the two stages.

^d λ₁ and λ₂ are the lag phases of stage 1 and stage 2, respectively.

^e RSQ is the Excel function used to measure the correlation between experimental and model data.

Table 7

Comparison of methane yield enhancement by organosolv pretreatment on different LMs reported by various studies^b.

Substrate	Raw – pretreated composition			Organosolv pretreatment	Optimal conditions				Methane production (mL CH ₄ /g VS)		Reference
	Cellulose ^a (%)	Hemicellulose ^a (%)	Lignin ^a (%)		S/L ^b (g/g)	T (°C)	Solvent (%)	t (h)	Raw – pretreated	Increase (%)	
Sugarcane bagasse	47.6–60.9	22.6–28.9	27.6–14.0	Ethanol-Ammonia	1:14	70	25–10	12	106–249	135	[57]
Rice straw	28.6–32.0	19.5–16.0	17.3–14.1	Ethanol	1:10	180	50	1	235–332	41	[25]
Hazelnut skin	11.4–12.5	5.9–4.7	34.4–32.5	Ethanol	1:10	180	50	1	261–288	10	[25]
Cocoa bean shell	13.5–15.0	7.0–5.8	29.9–26.3	Ethanol	1:10	180	50	1	231–219	–5	[25]
Wheat straw	31–36.3	18.4–9.4	18.3–15.8	Ethanol	1:10	180	50	1	274–316	15	[58]
Elm hardwood	46.4–58.1	26.3–21.3	26.2–19.1	Ethanol (Catalyst)	1:8	180	75	1	54 ^c – 94 ^c	73	[43]
Pine softwood	44.5–51.3	28.0–20.2	26.8–27.8	Ethanol (Catalyst)	1:8	150	75	0.5	39 ^c – 71 ^c	84	[43]
Rice straw	21.5–28.7	50.1–45.3	17.1–13.4	Ethanol (Catalyst)	1:8	150	75	1	116 ^c – 153 ^c	32	[43]
Forest residues	22.3–43.1	20.0–11.5	44.7–40.7	Ethanol (Catalyst)	1:10	190	50	1	50–190	280	[46]
Forest residues	22.3–35.2	20.0–17.2	44.7–43.0	Methanol (Catalyst)	1:10	190	50	1	50–210	320	[46]
Forest residues	22.3–31.2	20.0–15.5	44.7–42.1	Acetic Acid	1:10	190	50	1	50–200	300	[46]
Sunflower stalks	34.1–59.6	26.2–17.6	26.8–21.2	Isopropanol (Catalyst)	1:10	160	50	0.5	124–278	124	[47]
Sorghum stalks	35.5–40.2	17.3–14.9	15.5–11.6	Ethanol	1:10	160	50	0.5	75–155	106	[44]
Rubberwood waste	43.6–68.1	8.3–5.2	31.0–8.1	Ethanol	1:10	210	75	N/A ^d	59–166	179	[45]
Hazelnut skin	10.2–11.8	3.6–3.8	39.7–36.0	Methanol	1:10	200	50	1	17–311	1729	This study
Spent coffee grounds	8.8–10.1	33.6–37.6	20.3–20.4	Methanol (Catalyst)	1:10	200	50	1	293–323	10	This study
Almond shell	23.4–25.7	21.9–23.7	30.6–31.8	Methanol (Catalyst)	1:10	130	50	1	23–25	9	This study

^a Based on dry matter (g/g TS).

^b S/L stands for solid to liquid ratio.

^c Mirmohamadsadeghi et al. [43] reported the biomethane potential as mL CH₄/g carbohydrates.

^d N/A: not available.

is particularly rich in lignin (40%) but lacks in polysaccharides (14%), similarly to what was reported by Mancini et al. [25]. The AS composition is balanced in glucose (23%), xylose (20%), and lignin (31%) as elsewhere observed [59]. The chemical composition of SCG reported in the literature is more variable, with a lignin content ranging from 20 to 30% and a cellulose and hemicellulose content of 10 and 30–40%, respectively [60]. However, some studies reported a lower lignin content for SCG [56,61]. This study showed SCG as a hemicellulose-rich material (34%), with cellulose and lignin being 9 and 20% of the dry matter, respectively. The variation in chemical composition might be attributed to the different origin of the coffee beans, and different processing during the production of coffee grounds [60].

The main aim of organosolv pretreatment is lignin removal [13].

Given this, a positive effect was expected for AS and HS, both particularly rich in lignin. Despite this, only the HS composition significantly changed due to the pretreatment, showing a lignin decrease and increase in total sugar content (Table 4, Fig. 3S). Lignin is considered the most relevant factor for LMs recalcitrance [13], and lignin removal showed a positive effect on the biomethane yield in several studies on different LMs [25,43,44].

The ineffectiveness of organosolv pretreatment on SCG is most likely attributed to the loss of non-structural compounds during the pretreatment and subsequent washing steps (Table 4). These compounds include free sugars, such as sucrose, glucose, and fructose, which are excellent substrates for biofuel production through fermentation pathways [44]. However, the catalyst addition and a higher pretreatment temperature allowed to

compensate for this loss by increasing the structural sugar bioavailability. This is supported by the fact that methane production from pretreated SCG increased with the severity of pretreatment, from 175.8 up to 322.9 mL CH₄/g VS. Nevertheless, the pretreatment was not effective enough to significantly balance this loss.

None of the pretreatment conditions had a positive effect on the cumulative methane production from AS, likely due to the hard structure of the substrate, which should be tackled by a different pretreatment. In particular, the authors hint to explore a pretreatment that can be performed for longer, without the risk of losing the biodegradable sugars. In this perspective, the ionic liquid is suggested as an alternative to the organosolv pretreatment tested in the present study. The ionic liquid pretreatment duration ranges from 1 to 24 h [62], which is expected to be sufficient for a complete soaking of the AS. This pretreatment acts directly on the cellulosic part of the LMs, by decreasing the crystallinity index and swelling up the cellulose, reducing the risk of losing biodegradable substances as a result of the longer duration of the pretreatment [62].

Besides, the compositional analysis highlights the potential of HS and SCG for a deeper biorefinery approach, using a preliminary extraction step to remove the non-structural compounds. HS and SCG are extremely extractives-rich materials, with organosolv pretreatment able to remove only a maximum of 24 and 19% of them, respectively (Table 4, Fig. 3S). The extractives are defined as non-bound substances, soluble in water or ethanol, mainly composed of non-structural sugars, proteins, fats, chlorophyll, and waxes [31,63]. The early separation of these substances provides the dual advantage of recovered valuable compounds and removal of inhibitors for the AD process. Non-structural compounds such as cell wall proteins, pectin, and lipids are also involved in the recalcitrance of LMs. Their degradation results in the accumulation of ammonia and long-chain fatty acids, which are inhibitors of the microorganisms involved in the AD [64,65].

5.3. Impact of the pretreatment on LMs structure and water swelling capacity

WSC is defined as the amount of water retained by the biomass with no external force application. Water contributes to increasing the accessible surface area, but also affects cellulose crystallinity and lignin bonds, solubilizes part of the hemicellulose, and promotes the hydrolysis step [66]. The ineffectiveness of pretreatment on AS and SCG might be attributed to the low porosity of these materials.

The WSC was 1.45 and 2.76 g/g, respectively, for raw AS and SCG, while it was 5.53 g/g for raw HS (Table 5). A low WSC shows a low capacity of the substrates to retain water molecules in the cell wall pores, thus indicating that also solvents have difficulty in penetrating the material. The WSC is used as an indicator of the interior accessible surface area for enzymatic hydrolysis, based on the principle that no enzymes can enter the pores of LMs if water cannot [25]. Thus, the lower accessible surface area might explain the ineffectiveness of a solvent-based pretreatment on AS and SCG, due to a low substrate-solvent contact. The lack of contact might be overcome by combining a pre-milling step to the organosolv pretreatment to increase the accessible surface area of the AS. Alternatively, a more intrusive pretreatment, such as steam explosion, might be considered on AS to penetrate its hard external surface. Despite steam explosion often leads to sugar loss into the liquor, it is capable of disrupting the cell wall structure of agricultural residues [11]. On the other hand, the already small particle size of SCG suggests to use an alternative pretreatment, such as e.g., ionic liquid that is reported to be effective on cellulose swelling up [29].

To the best of the authors' knowledge, the WSC prior to and after

pretreatment has never been reported for HS, SCG, and AS. Sanchez et al. [66] studied the hydration of different straws and bagasses, reporting WSC values ranging between 4 and 10 (g/g). The experimental procedure for WSC determination is often missing details, which makes comparison between different works difficult. Despite this, a study on high-crystalline cellulose revealed the relation between porosity and methane production, showing that the BMP was proportional to the WSC of the cellulose [29]. However, in this study, no correlation was observed between WSC and methane production, most likely due to the low cellulose content of the three LMs.

SEM analysis showed the strong and dense external surface of raw AS (Fig. 2c), in contrast with raw SCG (Fig. 2b) and raw HS (Fig. 2a). The methanol-organosolv pretreatment drastically affected the surface of HS (Fig. 2a–d) by exposing the cellulose fibers, as similarly observed by Papirio [67] who treated the same material with a 1.6% (w/w) NaOH solution. The external surface of pretreated SCG (Fig. 2e) appeared weaker and softer than the raw material after the pretreatment (Fig. 2b). In the case for AS, the pretreatment seemingly destroyed the original external pores (Fig. 2c), with the treated samples exhibiting more fragile bundles and a higher accessible surface (Fig. 2f). However, the changes in AS structure after pretreatment were still not enough to improve the methane production. The organosolv pretreatment has been reported to be effective on several LMs by causing lignin disruption and an increase of the available surface area [44,47,68]. The increased accessible surface, together with the higher porosity and lignin content reduction, leads to an easier digestibility and subsequent enhanced biomethane production [65]. In this study, the methanol-organosolv pretreatment disrupted the linkages between cellulose, hemicellulose, and lignin of HS (Fig. 2d), exposing the cellulose fibers to the enzymatic attack. The increased cellulose bioavailability, coupled to the partial removal of lignin and extractives, led to a significant ($p < 0.05$) increment of the BMP from HS.

Apart from the lack of major changes in the AS chemical composition and porosity after the pretreatment here used, the recalcitrance of AS also largely depends on the material processing in the production process of almonds before being discarded. While both SCG and HS are roasted during the production chain, AS remains a raw material. Oliveros et al. [69] studied the effects of the roasting process on coffee beans, showing an increase of the void fraction from 9.88 to 34.24%, compared to the unroasted beans. Those authors noticed that the volume of the coffee beans increased up to 1.8 times, with the SEM images showing a more fragile material after roasting. The increase in pore volume during the roasting process was also confirmed by Perren and Escher [70] in their study on nuts quality, including almonds and hazelnuts. Overall, the low porosity (Table 5) and compact external surface area (Fig. 2c–f), coupled with the particle size of AS (1–2.5 mm), justify the low BMP of AS as substrate, both raw and pretreated (Table 3).

5.4. Energy assessment and waste stream management

The energy balance assessment showed that only the HS pretreatment led to a positive energy balance (Table S3), due to the low improvement in methane production obtained by treating SCG and AS. The optimal net heat energy gain was achieved by treating HS at 130 °C with catalyst addition, resulting in an energy production of 1.46 kWh/kg VS. Despite the pretreatment temperature did not show a particular effectiveness on the methane production itself, it is an important factor in keeping the energy consumption low. The pretreatment energy demand was reduced from 1.19 to 0.71 kWh/kg VS of HS by reducing the pretreatment temperature from 200 to

130 °C. However, several authors include heat recovery by heat exchangers in the energy assessment. The recoverable energy is widely assumed to be 85% of the energy consumption [71]. Considering the heat recovery, the effective energy recovery ($E_{R, eff}$) of the process achieves a positive value of 1.35 kWh/kg VS under the pretreatment condition at 130 °C, which maximized the methane production from HS. Finally, to take into account the difference between laboratory and real scale, a scale-up factor of 0.85 can be applied to adjust the final cumulative biomethane production value [72].

The recycling and utilization of the spent liquid waste stream after pretreatment are required to further improve the assessment of cost effectiveness of the entire process chain and to close the energy loop of organosolv pretreatment. In this perspective, the optimization of the S/L ratio during the pretreatment might offset the processing costs by reducing the amount of waste and producing a liquid stream richer in valuable compounds [13]. Unlike other solvents (i.e. ionic liquids, sodium hydroxide, and sodium carbonate), organic solvents do not generally create inhibition during the AD process if present in moderate concentrations, since they are intermediates of the process, or useable by methanogens for methane production [46,73]. This results in a low water volume to use in the washing step of the pretreated materials, which, together with the easy solvent recovery by evaporation, makes the organosolv pretreatment more cost-effective compared to other chemical pretreatments [46]. Besides, methanol has been successfully tested as an electron donor for several environmental technological applications, such as denitrification [74] and selenate bioreduction [75], offering an alternative use to the organosolv pretreated waste stream.

6. Conclusion

Methanol-organosolv pretreatment is an effective technique for enhancing the AD of HS, attaining an 18-fold increase in methane production compared to the untreated material. The lignocellulosic compositional analysis on HS showed a reduction of the lignin content from 35.0 to 29.4%. In particular, the lowest pretreatment temperature and the addition of catalyst resulted in the highest methane production from HS (310.6 mL CH₄/g VS). An energy-saving of about 62% can be achieved by lowering the pretreatment temperature from 200 to 130 °C. For SCG and AS, no significant improvement in methane production was observed under all pretreatment conditions investigated, most likely due to the lower porosity of the raw substrate and loss of non-structural compounds during the washing steps.

CRediT authorship contribution statement

A. Oliva: Conceptualization, Data curation, Investigation, Resources, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **L.C. Tan:** Supervision, Writing - review & editing, Project administration. **S. Papirio:** Supervision, Writing - review & editing. **G. Esposito:** Supervision, Writing - review & editing. **P.N.L. Lens:** Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This publication has emanated from the research supported by Science Foundation Ireland (SFI) through the SFI Research Professorship Programme *Innovative Energy Technologies for Biofuels, Bioenergy and a Sustainable Irish Bioeconomy* (IETS BIO³; grant number 15/RP/2763) and the Research Infrastructure research grant *Platform for Biofuel Analysis* (Grant Number 16/RI/3401). The authors would like to thank the Centre for Microscopy and Imaging (CMI, www.imaging.nuigalway.ie) at NUIG for their assistance in SEM analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2020.12.095>.

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