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Biogas production through combined thermochemical and biochemical processing of grape pomace

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ABSTRACT

Grape pomace, the solid residue from winemaking, is produced in large seasonal quantities and represents a challenge for sustainable waste management due to its elevated lignin concentration (≈50 wt%, markedly higher than in other agricultural residues such as corn stover or wheat straw, ≈20 wt%), which severely limits its biodegradability in anaerobic digestion. Its potential as a feedstock for bioenergy production remains underexploited, largely because of this recalcitrant fraction.

This study investigates the use of mild hydrothermal pretreatment under pressurized conditions as a strategy to restructure the lignin matrix of grape pomace and thereby enhance its subsequent anaerobic digestion and biogas production. A combined thermochemical and biochemical process was conducted at laboratory scale with grape pomace as biomass. The effects of temperature and solid yield on lignin content and bioconversion efficiency were analyzed. Results show that thermochemical pretreatment increases the overall lignin content while inducing morphological changes that improve its fermentability. As a result, the pretreated samples produced higher biomethane volumes up to 29 % with respect to the as-received biomass and referred to the lignin fraction.

By comparison with literature on different biomasses, a correlation of biomethane yield with treatment temperature was obtained, showing a maximum increment of 20 % in the biomethane yield compared to the untreated biomass at around 130 °C.

The findings confirm the viability of combining mild thermochemical treatment with anaerobic digestion as a strategy to valorize grape pomace, aligning with circular economy principles.

1. Introduction

Solid biomass residues derived from forest maintenance or agriculture represent a sustainable and widespread feedstock [1], contributing significantly to the implementation of circular economy strategies in civil and industrial applications [2]. Among these, grape residue or pomace constitutes a primary solid by-product of the winemaking process, comprising skins, seeds, and stems [3]. Annually, global production of grape pomace surpasses 77 million tons, accounting for 20–30 % of the processed grape weight year [4,5]. Its availability is significantly affected by the seasonal nature of grape harvests, with production peaks occurring in autumn, thereby posing challenges for storage and management. Traditionally, grape pomace has been utilized in various applications, including animal feed, distillation, composting, soil amendment, and the extraction of bioactive compounds [6]. Nonetheless, grape pomace also presents environmental challenges, such as its high moisture content, which restricts storage and transport, necessitating prompt treatment like drying, and its high organic load: elevated BOD and COD levels can lead to pollution if not properly managed [5,7,8].

Apart from direct combustion, this kind of biomass can be converted into valuable byproducts through a range of thermochemical or biochemical processes [9] which in some cases are combined to increase conversion efficiency into platform chemicals such as butanol [10]. A suitable option for seasonal biomass with peak and discontinuous availability is thermochemical pyrolytic treatment—namely pyrolysis or

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torrefaction [11,12]. These processes allow the conversion of biomass into stable intermediate products in compact plants, effectively damping the production peak of biomass residues. The primary product of mild thermochemical treatments is biochar, which finds application in combustion or gasification, energy storage, gas adsorption, water purification, and soil amendment [13]. Alongside biochar, liquid and gas fractions (bio-oil and syngas) are produced from the thermal degradation of biomass constituents.

The main components of lignocellulosic biomass, extractives, cellulose, hemicellulose, and lignin [14], are differently converted depending on treatment temperature, residence time, and the biomass pre-treatment conditions. Extractives and inherent moisture are typically volatilized first, whereas the thermal degradation of cellulose and hemicellulose requires higher temperatures than that of lignin, due to their higher activation energy [15].

In the biochemical conversion of lignocellulosic biomass, lignin is the principal component responsible for recalcitrance to anaerobic digestion [16], leading to reduced biodigester efficiency and increased volumes of residual digestate sludge. The lignocellulosic complex, composed of cellulose, hemicellulose, and lignin, creates a rigid protective structure that hinders microorganisms and enzymes from accessing fermentable carbohydrates [17]. Since the hydrolysis of cellulose and hemicellulose into fermentable sugars is a crucial step in the anaerobic digestion process, the presence of lignin strongly limits conversion efficiency. Several pretreatments have therefore been reported to enhance the biodegradability of lignocellulosic wastes. Their role is to disrupt the lignocellulosic matrix, increase the surface area accessible to microbes, and improve hydrolysis yields, while at the same time minimizing the formation of inhibitory compounds and proving economically sustainable [17]. More specifically, physical methods such as comminution or irradiation can facilitate enzymatic hydrolysis. Thermo-chemical processes like pyrolysis and steam explosion (160–260 °C) promote structural disruption and increase surface accessibility [18,19]. Biodelignification by microbial consortia of fungi and bacteria can selectively degrade lignin, and when combined with steam explosion, lignin removal of 35–44 % within 7 days was achieved [20]. Chemical methods include organosolv pretreatment [21,22] and oxidative processes using ozone [23,24] or active chlorine [25]. Although effective, these strategies often require harsh reagents or complex setups, unlike the mild hydrothermal pretreatment investigated in this study.

With reference to grape pomace, its lignin content typically ranges between 40 and 60 wt%, depending on cultivar and processing conditions [26]. This is markedly higher than in many other agricultural residues such as corn stover or wheat straw (≈20 wt%) and is therefore considered a major limiting factor for anaerobic digestion. The anaerobic digestion of grape pomace has been investigated, with studies confirming its technical feasibility as a substrate for biogas production, though yields remain relatively modest (typically below 200 NL/kg [27]). Failla and Restuccia [28] demonstrated that untreated grape pomace can produce methane through anaerobic digestion and noted that crushing grape seeds can slightly improve methane content; however, they observed no statistically significant differences in final yields among untreated, seedless, and crushed pomace samples, suggesting limited benefit from mechanical pretreatment alone. Silva et al. [29] evaluated the influence of the inoculum-to-substrate ratio, emphasizing its critical role in stabilizing the digestion process and achieving better methane production, and highlighted that optimizing this parameter is key to effective grape pomace digestion. Hungría et al. [30] confirmed that grape pomace can be digested alone or in co-digestion with other winery residues, and found that adjusting process conditions, particularly the inoculum-to-substrate ratio, significantly affects methane generation performance.

Previous studies have also highlighted that the high lignin content of grape pomace is a major factor limiting its biodegradability during anaerobic digestion [31], as lignin remains largely undegraded and forms a structural barrier to microbial attack. El Achkar et al. [32] showed that while cellulose and hemicellulose are partially broken down, lignin content remains effectively unchanged, significantly constraining methane yields. Colussi et al. [33] and Lempereur & Penavayre [34] further noted that strategies to address the recalcitrance of grape pomace often focus on overall pretreatment but do not specifically target the lignin component as a source of biogas. These findings indicate that while grape pomace shows potential for anaerobic digestion, its high lignocellulosic and lignin content inherently limits biodegradability, making it essential to optimize operational parameters, such as the inoculum-to-substrate ratio, and to consider co-digestion strategies or targeted pretreatments to improve methane yields and overcome the recalcitrance typical of this biomass.

In a previous study [35] the pressurized thermochemical conversion at mild temperature of grape pomace was systematically investigated, elucidating the dependence of the yield in liquid and solid fractions on temperature and residence time. Building on those findings, the present study aims to integrate thermochemical and biological processes for this biomass, with the goal of enhancing biogas production by specifically targeting the lignin component, an approach that, to the best of our knowledge, has not been previously reported for grape pomace. In this context, employing grape pomace as a feedstock for combined thermochemical processing and biomethane production emerges as an innovative strategy. This approach facilitates the valorization of grape pomace through the generation of renewable energy, thereby enhancing the sustainability of the wine industry and promoting the principles of a circular economy. The mild thermochemical pretreatment investigated here is expected to partially restructure the lignin matrix of grape pomace, thereby facilitating microbial access to polysaccharides and enhancing biomethane production. The experimental results, including the elemental composition of samples and lignin content, were analyzed through mass balances to calculate biomethane yields from both untreated and thermally treated samples and to assess possible synergistic (or antagonistic) effects of the integrated process.

2. Materials and methods

2.1. Materials

A grape pomace from red wine production, labeled GP, from a local factory (Caviro SpA, Faenza IT) was used as biomass feedstock. The sample was dried in an oven at 105 °C upon constant weight, subsequently ground by a cutting mill and sieved in the desired size 1.0–2.0 mm, as shown in Fig. 1. It was labelled GP00. Commercial high purity cellulose (MKCW7956 Sigma-Aldrich) and lignin (MKCT2707 Sigma-Aldrich) were used as reference materials in the form of powders. Bacterial slurry was purchased from a local industrial biodigester and used as the inoculum (Mattioli Energia S.r.l., Finale Emilia, Modena, Italy).

Fig. 1. Photograph of grape pomace after drying and grinding (GP00).

The inoculum, consisting of a bacterial slurry, was sourced from Mattioli S.r.l. biogas production facility located in Finale Emilia (Modena, Italy). This industrial digester operates under thermophilic conditions at approximately 55 °C and processes a mixture of corn silage and sewage sludge as a feedstock for anaerobic digestion. The inoculum was sampled directly from the active biodigestion tank and immediately transported to the laboratory in an insulated container designed to minimize temperature fluctuations and maintain conditions similar to those of the digester. Upon arrival, the bacterial slurry was maintained in a thermostatic bath at a constant temperature of 55 ± 1 °C during the sample preparation process until the start of the laboratory-scale biodigestion tests.

2.2. Physico-chemical characterization of biomass

Thermogravimetric tests were performed on a STA 449 C Jupiter thermogravimetric balance (NETZSCH, Selb, Germany). Thermogravimetric profiles were elaborated for deriving proximate analysis of biomass as well as its hemicellulose and cellulose content according to the Pseudo-component kinetic (PSK) method [15]. The extractives were gravimetrically determined by extraction in ethanol and hexane at room temperature in an ultrasound bath.

The elemental analysis of the pre-dried GP00 and thermo-chemically pre-treated biomass, lignin and cellulose samples was carried out in triplicate by a CHN analyzer (LECO 828 Series).

Scanning Electron Microscopy (SEM) observation was used to analyze morphological modifications in grape pomace, lignin, and cellulose before and after the thermochemical treatment. The analysis was carried out by a Sigma FEG instrument (Carl Zeiss Microscopy GmbH, Germany) on powders and granules (Au <20 nm plasma sputter coated), with parameters appropriately trimmed for such materials, by acting on apertures to decrease the spot current and checking the suitable accelerating voltage of the electron beam.

The lignin content, X_l, in both GP00 and thermo-chemically pre-treated samples was determined by INNVENTIA—Biorefinery Test Methods L 2:2016 [36]. In a 50-mL Erlenmeyer flask, 1 mL of 72 % H_2SO_4 was added to 100 mg of the sample. The mixture was stirred at 30 °C for 1 h until the sample dissolved completely. Subsequently, 28 mL of distilled water was added, and the solution was autoclaved at 120 °C for 1 h. After cooling to 80 °C, the solution was filtered using a pre-weighed glass fiber filter. The filtrate was transferred to another flask to determine the soluble lignin fraction by measuring the absorbance at λ = 205 nm. The precipitate was rinsed with warm water until a neutral pH was attained. The filter was dried at 105 °C overnight, and the lignin fraction was calculated based on the weight difference. The weight of acid-insoluble lignin (AIL, acid-insoluble residue) in mg was calculated as follows:

$$AIL = \frac{m}{M} \cdot 1000 \quad \text{Eq. 1}$$

where m is the weight of the lignin residue after drying (g), and M is the weight of the sample before acid hydrolysis (g). The weight of acid-soluble lignin (ASL) in mg was calculated as follows:

$$ASL = \frac{A \cdot D \cdot V}{a \cdot b \cdot M} \cdot 1000 \quad \text{Eq. 2}$$

where A is the absorbance at 205 nm, D is the dilution factor, V is the volume of the filtrate in L (0.029 L), a is the molar extinction coefficient of lignin in g/L cm (110 g/L cm, according to TAPPI UM 250), b is the optical path (1 cm), and M is the weight of the sample before acid hydrolysis in grams. The total lignin content (expressed in mg) was calculated as follows:

$$TLC = AIL + ASL \quad \text{Eq. 3}$$

2.3. Thermochemical treatment of grape pomace, lignin and cellulose

The thermal and chemical conversion of the biomass was carried out in a pressurized reactor made of AISI 316 stainless steel with tubular geometry, having 21 mm inner diameter, 200 mm height, 48 mL volume (Fig. 2a). An electronic pressure transducer and a K-type thermocouple are connected to the reactor, allowing the measurement and the acquisition of internal temperature (T) and pressure (P). In a single test, a biomass sample (M_f = 20 g) and deionized water (M_w) are loaded in the reactor, using a water-to-fuel mass ratio in the range 0.67–1.0, according to a previous study [35]. Finally, the reactor is introduced into a 2.0 kW electric furnace (WATLOW, USA) already heated-up at the preset furnace temperature T_f to obtain internal reactor temperature in the range of 150–210 °C, suitable for carrying out the thermochemical process.

The residence time was also set at a fixed value of 20 min, and for its entire duration, temperature T and pressure P inside the reactor were continuously monitored and recorded. After each test the converted biomass was placed in a desiccator until constant weight was reached. The yield in solid phase, Ψ, was computed as the ratio between the weight of the residual sample after drying and the weight of the dry pristine sample.

For comparison, similar tests were also carried out on reference materials, namely cellulose and lignin.

2.4. Biological treatment of grape pomace

The experiments were carried out using a laboratory-scale anaerobic digester system equipped with glass reactors, each with a working volume of 500 mL and sealed using GL45 twin hose plastic screw caps (Fig. 2b). A batch of 150 g of bacterial slurry (inoculum) having 7.48 % of total solids was added to 12.5 g of each dry sample, corresponding to a feed-to-inoculum (F/I) ratio of 1.1 (in terms of inoculum and sample total solids) and was maintained across all reactors under biological treatment, as described by Liu et al. [37]. Four sample types were tested: a blank control (containing only the inoculum), untreated grape pomace, and two treated grape pomace samples, GP01 and GP04. All tests were performed in triplicates.

To start anaerobic digestion, the headspace of each reactor was immediately flushed with nitrogen gas following the addition of biomass. The reactors were then incubated in a thermostatic water bath maintained at temperature of 55 °C, based on the operating conditions of the anaerobic digester from which the inoculum was collected, with manual agitation by shaking the reactors approximately 60 times within 1 min, and this operation was repeated until gas release was measured. Biogas production was monitored daily for 30-day period.

The methane content in the biogas was determined by passing the gas stream through a CO_2-absorbing trap containing a 3M NaOH solution with 0.4 % thymolphthalein as a pH indicator. The biogas volume was measured using the water displacement method, in which the gas displaced a corresponding volume of water in an inverted graduated cylinder connected to the digester system. One end of the tubing was connected to the digester and the other to a submerged measuring cylinder.

Daily biogas production was recorded in milliliters and converted to normalized cubic meters (Nm^3), representing the volume of gas under standard conditions (20 °C and 1 atm), corrected by subtracting the biogas volume produced in the blank assays [38].

The normalized biogas volume was calculated using the following equation:

$$V_0 = V^* \frac{(p_l - p_w)^* T_0}{P_0{}^* T} \quad \text{Eq. 4}$$

where.

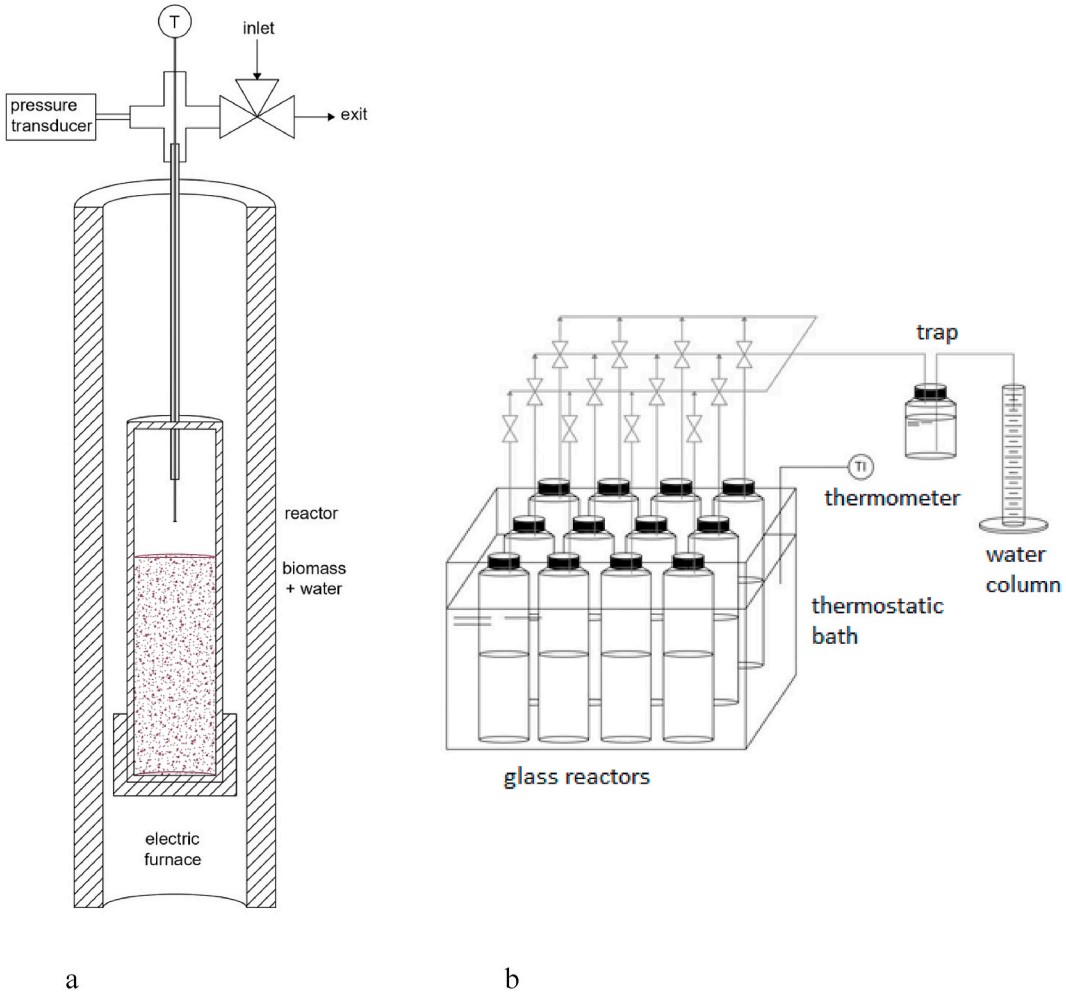

Fig. 2. Schematic diagram of thermochemical reactor (a) and bio-digestion laboratory plant (b).

. V_0: normalized biogas volume (Nm^3)
. V: measured biogas volume (m^3), based on displaced water
. p_l: ambient atmospheric pressure (atm)
. p_w: water vapor pressure at room temperature (atm)
. T_0: standard temperature (293 K = 20 °C)
. P_0: standard pressure (1 atm)
. T: room temperature (K)

In parallel tests dedicated to collecting the biogas without CO_2 absorption, the volumetric fraction of CH_4 and CO_2 was measured by means of a Pollutek 3160 gas analyzer.

3. Results

3.1. Biomass characterization

"The results of proximate, ultimate, and macro-component analyses for grape pomace (GP00) are reported in Table 1, together with the values reported in the literature for comparison purposes.

Compared to values found in studies of Tunisian grape pomace, the sample GP00 exhibits relatively low moisture (~6.5 wt%), high volatiles (~63.5 wt%), moderate fixed carbon (26.4 wt%) and low ash (~3.6 wt %) on an "as received" basis [39].

On a dry basis, the ultimate analysis reveals 47.8 wt% C, 6.3 wt% H, 1.6 wt% N, 40.4 wt% O and ~3.9 wt% ash—values that align closely with ranges reported for grape pomace in Europe and Australia (e.g., C: ~47–55 wt%, H: ~5.8–6.3 wt%, O: ~30–39 wt%, N: ~1.9–2.4 wt%, ash: 4.2–9.5 wt%) [40]. The carbon content of 47.8 wt% in Table 1 was already noted to be similar to the values reported by Casazza et al. [26] for Croatina cultivar pomace in untreated (50.1-wt%) and extracted (54.9 wt%) samples. This value also aligns well with published values: 42.2 wt% C for Tunisian pomace and ~50 wt% for European/Australian pomace [39].

Elemental analysis provided C, H, and N values of 43.4, 6.8 and 0.1 wt% for cellulose and 63.9, 5.7 and 0.3 wt% for lignin.

Moving to macro-component composition, our pomace contains extractives (12.7 wt%), hemicellulose (11.2 wt%), cellulose (14.0 wt%), and lignin (52.0 wt%). These numbers are consistent with the literature: grape seeds often have ~36.8 wt% sugar polymers (hemicellulose + cellulose), ~43.8 wt% lignin, ~17 wt% extractives, and ~2–3 wt% ash [41].

3.2. Thermochemical treatment of grape pomace, lignin and cellulose

The operating conditions (fuel/water ratio and internal temperature) and the results of thermochemical conversion tests, in terms of solid yield (Ψ) and C content (X_C), are reported in Table 2. The measured internal pressure ranges between 10 and 20 bar for all tests.

In all cases, the carbon mass fraction of the solid increased relative to the untreated biomass (Table 1), consistent with the release of more volatile matter. While a complete carbon balance would require the carbon content of the condensed/gaseous phases (not measured here), a relevant trend can be quantified via the solid-phase carbon retention, $R_C = \Psi X_C / X_{C,0}$, being $X_{C,0}$ the C content in GP00 (Table 1). The values

Table 1
Physical and chemical properties of grape pomace (GP00, this study) compared to literature data.

Proximate analysis (a.r.)	GP00 (this study) wt %	Tunisian [39] wt%	European/ Australian [40] wt%	Croatina cultivar [26] wt%
moisture	6.5 ± 0.1	7.5	–	5.3
volatiles	63.5 ± 0.3	51.4	–	–
fixed carbon	26.4 ± 0.2	28.8	–	–
ash	3.6 ± 0.1	12.3	–	4.2
Ultimate analysis (d. b.)	**wt%**			
C	47.8 ± 0.2	42.2	47–55	50.1
H	6.3 ± 0.1	3.5	5.8–6.3	14.2
N	1.6 ± 0.1	3.0	1.9–2.4	8.4
O	40.4 ± 0.2	37.7	30–39	27.3
ash	3.9 ± 0.1	13.3	4.2–9.5	–
Macro-components (a.r.),	**wt%**			
extractive	12.7 ± 0.2[a]	–	–	–
hemicellulose	11.2 ± 0.3[b]	–	–	–
cellulose	14.02 ± 0.3[b]	–	–	–
lignin	52.02 ± 0.5[c]	–	–	41.2

a.r. = as received, d.b. = dry basis.
[a] extraction.
[b] PSK.
[c] INNVENTIA.

Table 2
Tests of thermochemical conversion of grape pomace (GP), cellulose (C) and lignin (L).

Sample	fuel/water	temperature, °C	Solid yield (Ψ), -	C content (X_C), %
GP01	1.0	150	0.88	51.3 ± 0.1
GP02	1.0	151	0.80	56.7 ± 0.3
GP03	1.0	163	0.84	52.0 ± 0.2
GP04	0.67	187	0.69	54.9 ± 0.1
GP05	0.67	210	0.42	61.1 ± 0.1
C01	1.0	156	0.70	46.2 ± 0.2
C02	1.0	176	0.87	42.8 ± 0.3
C03	1.0	180	0.97	43.3 ± 0.2
C04	1.0	212	0.98	47.3 ± 0.1
L01	1.0	156	0.98	65.8 ± 0.3
L02	1.0	163	0.88	63.3 ± 0.2
L03	1.0	181	0.73	65.7 ± 0.1
L04	1.0	199	0.59	73.7 ± 0.2

are 0.94 (GP01), 0.95 (GP02), 0.91 (GP03), 0.79 (GP04), and 0.54 (GP05), indicating progressively higher transfer of carbon to non-solid phases at higher severity, alongside the observed enrichment of carbon in the residual solid (e.g., the largest value, 61.1 wt%, for the sample GP05 obtained at the highest temperature, i.e.210 °C). As for the reference materials, the carbon content is practically identical to that of the starting material, as could be expected.

Fig. 3 displays the values of Ψ obtained for the three materials as function of temperature at constant residence time (20 min). Despite a certain dispersion of the data, a clear tendency can be observed for the yield to decrease for grapes and lignin and to increase for cellulose. The latter is attributable to the cellulose hydrolysis with formation of smaller molecules, e.g. glucose, that include the hydroxyl group [42]. The trend of GP is more similar to that of lignin, i.e. decreasing yield with increasing temperature indicating that both the loss of volatiles and the partial decomposition of lignin counterbalance the weight increase of the cellulose fraction.

Table 3 reports the total lignin content (TLC) for selected samples

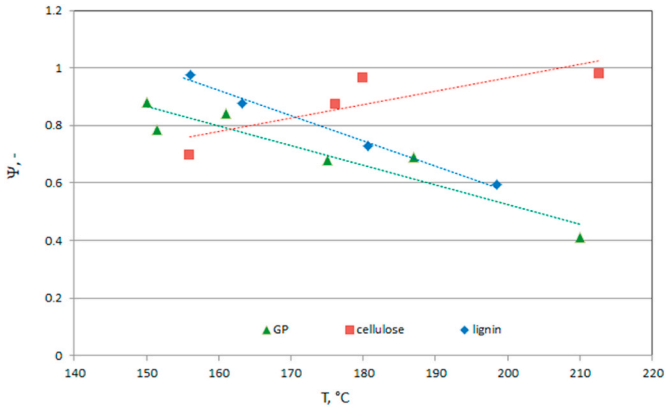

Fig. 3. Yield of solid fraction (Ψ) as function of temperature.

Table 3
Content of AIL, ASL and TLC in selected samples GP00, GP01, GP03, GP04 and GP05.

	T, °C	AIL mg/g	ASL, mg/g	ASL/AIL	TLC, mg/g
GP00	25	466.3	53.8	0.146	520.1 (52.01 %)
GP01	150	570.0	28.9	0.051	598.9 (59.89 %)
GP03	163	642.9	32.9	0.051	675.8 (67.58 %)
GP04	187	694.4	32.6	0.047	726.9 (72.69 %)
GP05	210	747.8	32.5	0.044	780.3 (72.69 %)

obtained from the thermochemical treatment, ordered by increasing process temperature. Both acid insoluble (AIL or Klason) and soluble (ASL) fractions [43] have been reported, with the former being prevalent. The as received biomass exhibits the highest ratio AIL/ASL that decreases at increasing T, since the soluble fraction is likely dissolved under the thermal treatment in presence of water. In general, an enrichment in lignin is noted in comparison to the as received biomass, owing to the release of extractives and of more reactive hemicellulose [44]. Congruently, the increase is greater under more severe temperature conditions. Some PSK tests were carried out for determination of cellulose and hemicellulose content in treated GP samples, revealing their congruent decrease.

3.3. Biological conversion of grape pomace

Biological conversion was performed on two samples obtained from thermochemical treatment, namely GP01 and GP04, which were selected due to their significantly different processing temperatures and resulting solid yields (Table 2), as well as marked differences in total lignin content (TLC) (Table 3). For comparison the biological conversion was also conducted on a.r. grape pomace GP00.

Fig. 4 shows the evolution of biogas volume V_{bg} (mL) over a 30-day period for the three selected samples GP00, GP01 and GP04. The experiments were performed in triplicate and each data point represents the mean value, with the associated error bar. The biogas production profiles exhibited a similar overall trend, characterized by a pronounced initial increase in gas generation during the initial days, followed by a gradual decline and stabilization towards the conclusion of the 30-day digestion period. The untreated pomace (GP00) demonstrated the highest initial gas production rate, achieving a maximum peak within the first 2–3 days, with values surpassing 700 mL. Following this rapid increase, gas generation declined sharply, approaching near-zero levels after approximately 10 days, and remained low and stable for the remainder of the experiment. The thermally pretreated samples (GP01 and GP04), corresponding to grape pomace pyrolyzed at 150 °C and 187 °C, respectively, displayed similar kinetic patterns but with slightly lower peak values and a more gradual decline compared to the untreated

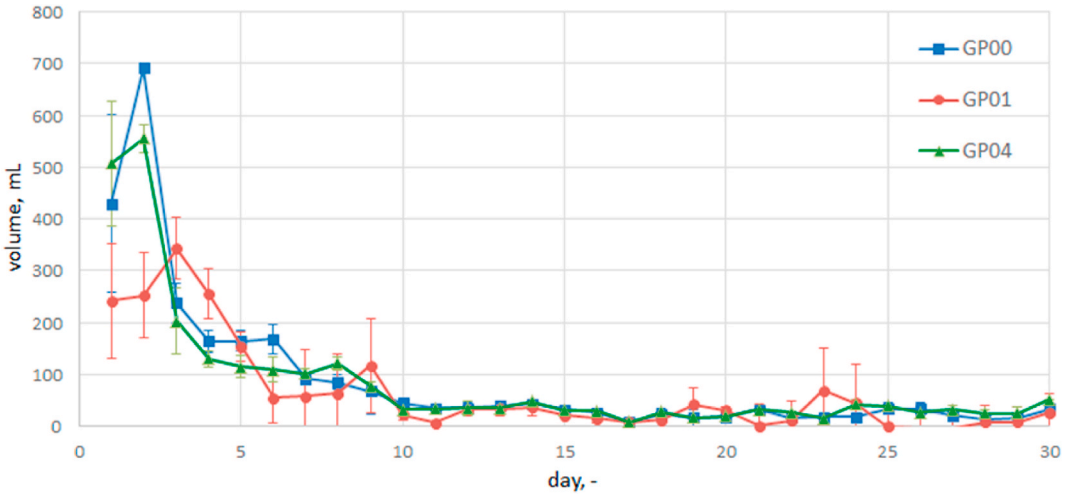

Fig. 4. Biogas volume as function of time for GP00 and treated samples GP01 and GP04. Average value and standard deviation bar of triplicate tests.

sample. Notably, GP01 exhibited earlier stabilization of gas production, whereas GP04 showed greater variability during the first week of digestion. After the 10th day, all samples reached a quasi-steady state with minimal daily gas production, suggesting that the readily biodegradable fraction had been largely consumed. The convergence of the three curves in the later stages indicated comparable ultimate biodegradation extents, despite the initial kinetic differences.

With reference to the biogas composition, the CH_4/CO_2 ratio on N_2 and H_2O free basis slightly increased along the time. The average value of CH_4/CO_2 ratio was equal to 1.12, 1.30, 1.10 for GP00, GP01 and GP04, respectively, in agreement with results reported in the literature for agricultural mix [45].

Table 4 reports the gross biogas volume after 30 days for the inoculum and samples in column 1. The biogas gross volume (column 1) is very similar for GP00 and GP01 samples, the latter being obtained at moderate temperature. The net biogas yield (Y_{bg}, NL/kg) after 7 and 30 days is reported in columns 2 and 3, respectively. It was calculated by subtracting the contribution of the inoculum $V_{bg.i}$, per unit mass of substrate m_s on ash and moisture free basis (Eq. (4)), where X_a and X_m are ash and moisture content in the sample, respectively.

$$Y_{bg} = \frac{V_{bg.s} - V_{bg.i}}{m_s(1 - X_a - X_m)} \quad \text{Eq. 5}$$

In all cases the 7 days net yield accounted for around 2/3 of the 30 days value, as a consequence of the rapid decay of biogas evolution (Fig. 4). The reported values align with literature data on biogas production from GP, as this is a lignocellulosic biomass that also contains readily fermentable sugars [46].

The pH of the digestate at the end of the process ranged from 8.2 to 8.7, showing a modest increase in alkalinity relative to the initial value of 8.1 and being just above the optimal range 5.5–8.5 [47]. This shift occurred under uncontrolled conditions and reflects the typical behavior of batch-operated digesters during the late conversion stage. The lignin content of the digestate, expressed on an inoculum-free basis, was 42.5 %, 64.6 %, and 38.0 % (w/w) for samples GP00, GP01 and GP04, respectively.

The net yield was maximum for the as-received sample (237 NL/kg), while decreases of 8 % (GP01) and 28 % (GP04) were observed in the treated samples. These reductions can be attributed to the higher TLC of the pretreated samples, which likely increased their recalcitrance to microbial degradation. In particular, the sample with the highest TLC (GP04) exhibited the most pronounced yield reduction, consistent with the well-known inhibitory effect of lignin on enzymatic and microbial access to fermentable polysaccharides during anaerobic digestion [48–50].

Table 4
Total biogas yields after 7 and 30 days bioconversion.

Sample	30-day gross volume, NL	7 days Y_{bg}, NL/kg	30-day Y_{bg}, NL/kg	pH
	1	2	3	4
Inoculum	1.768 ± 0.062	–	–	9.3
GP00	4.681 ± 0.143	173	237	9.0
GP01	4.551 ± 0.179	147	218	9.5
GP04	3.915 ± 0.372	119	171	9.2

a.r. = as received.

3.4. Microstructural analysis of grape pomace, lignin and cellulose

Figs. 5–7 display the SEM images of selected samples of grape pomace, lignin and cellulose, at different magnification, i.e. 1000x and 30000x, before and after the thermochemical treatment.

The grape pomace in coarse granules (Fig. 5a) comes from residues from grape processing consisting of pomace, seeds, stalks, etc. At high magnification for the a.r. GP00 sample the plant structures are evident with traces of woody parts, cell walls, etc. (Fig. 5b). In the treated grape pomace sample (Fig. 5c and d), the SEM analysis reveals distinct morphological alterations attributable to the applied thermal process. The cellular structure exhibits shrinkage, wall thinning, and partial tearing, features consistent with thermally induced degradation of hemicellulose and cellulose components. These morphological changes are comparable to those observed in hydrothermally treated poplar, where cell walls became thinner and shrank, and intercellular detachments emerged as treatment severity increased [51,52]. A further particularly relevant analogy comes from Lizasoain et al. [17], who applied steam explosion pretreatment to reed biomass and observed similar SEM changes—namely, collapse of plant cell structures, increased porosity, and surface fragmentation. These microstructural shifts were directly linked to enhanced enzymatic access and methane yield. The study highlights how pretreatment severity controls the balance between structural loosening and inhibitor formation, offering a meaningful comparison to the behavior of grape pomace under thermochemical processing. Some labile traces, as thin cracks few nanometers wide, may be observed just somewhere on the in the treated sample surfaces and some exogenous material and particles (as granules/spherules sized below 1 μm and larger crystals of different habitus) were detected (Fig. 5d). EDS investigations on the crystalline particles revealed presence of Ca^{2+} and K^+, which likely may imply the presence of carbonates (rhombohedral elongated shape) and tartrates (monoclinic prismatic shaped). The presence of these common substances may

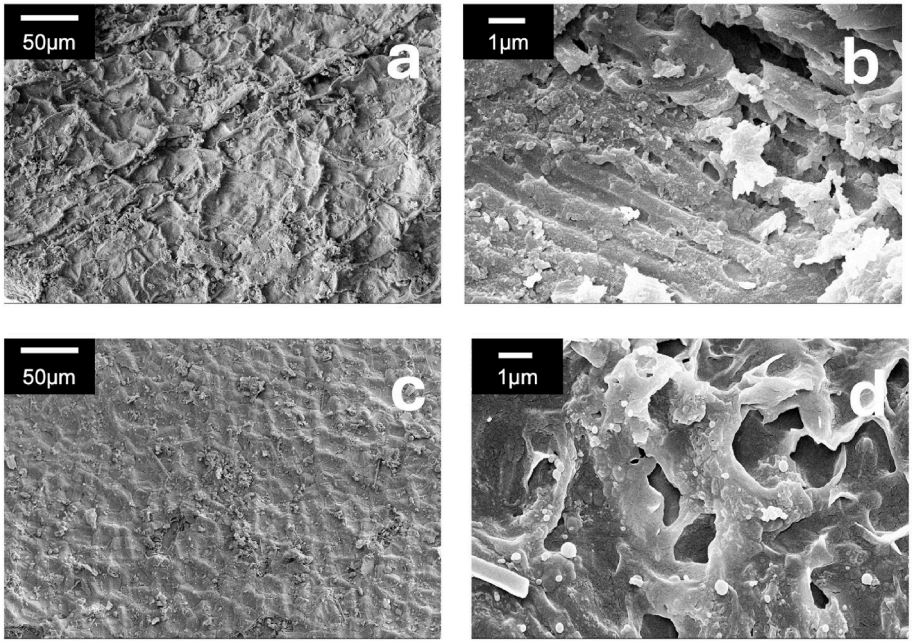

Fig. 5. SEM images of grape marc before (untreated, GP00) and after thermochemical treatment (treated, GP04). (a) GP00 at 1000 × magnification. (b) GP0 at 30 000 × magnification. (c) GP04 at 1000 × magnification. (d) GP04 at 30 000 × magnification.

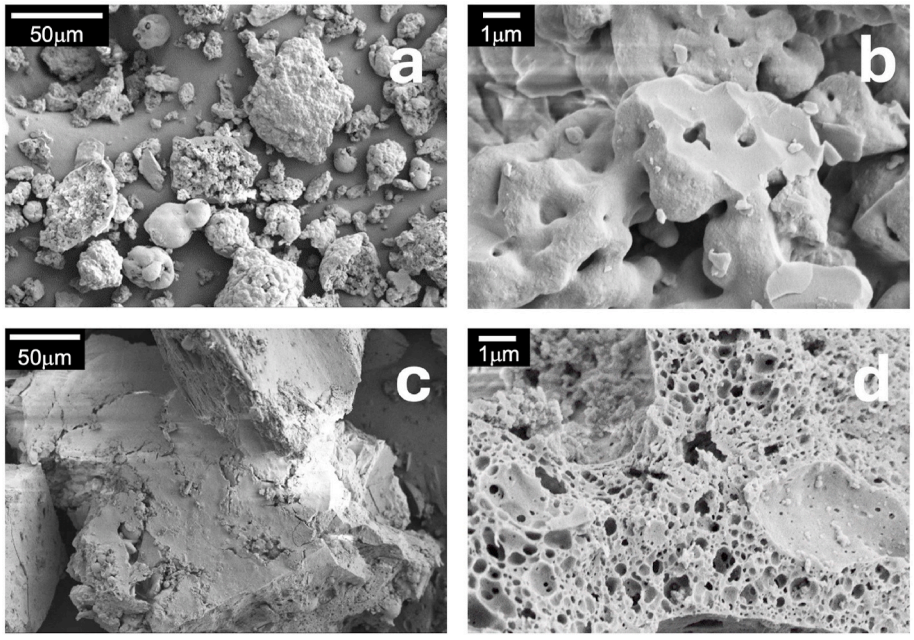

Fig. 6. SEM images of lignin before (untreated) and after thermochemical treatment (treated, L02).(a) untreated lignin at 1000 × magnification. (b) untreated lignin at 30 000 × magnification. (c) L02 at 1000 × magnification. (d) L02 at 30 000 × magnification.

be attributed to their presence in the original material as exogenous pollutants (carbonates and silicates). Such inclusions are also reported in hydrothermal carbonization studies on lignocellulosic biomass, where SEM revealed morphological collapse and transformation from fibrous matrices into carbonaceous spheres and irregular particles, particularly under subcritical conditions [53].

The lignin samples appear very different at low magnification, with presence of isolated small particles for the pristine lignin (Fig. 6a) and large coalesced particles after thermochemical treatment (Fig. 6c).

The microstructure analysis at larger magnification (30000×) of the a.r. lignin (Fig. 6b) may recall to a sintered body composed of consistent volumes and some intergranular-like pores, with smooth glass-like surface fractures. This densified arrangement of the material, as a volume of viscous-like particles, probably is due to the synthesis-extraction process of the lignin.

Fracture surfaces in the treated lignin (Fig. 6d), at the same magnification, exhibits large voids as well, with a diffuse finer porosity included in the material solid mass; somewhere the porosity shows even a fluidic oriented texture, likely attributable to an intense degassing effect exploited in a mass of a viscofluid consistence. These observations are consistent with literature. SEM analyses by Seehra et al. [54] demonstrate that hydrothermal treatment of commercial lignin yields

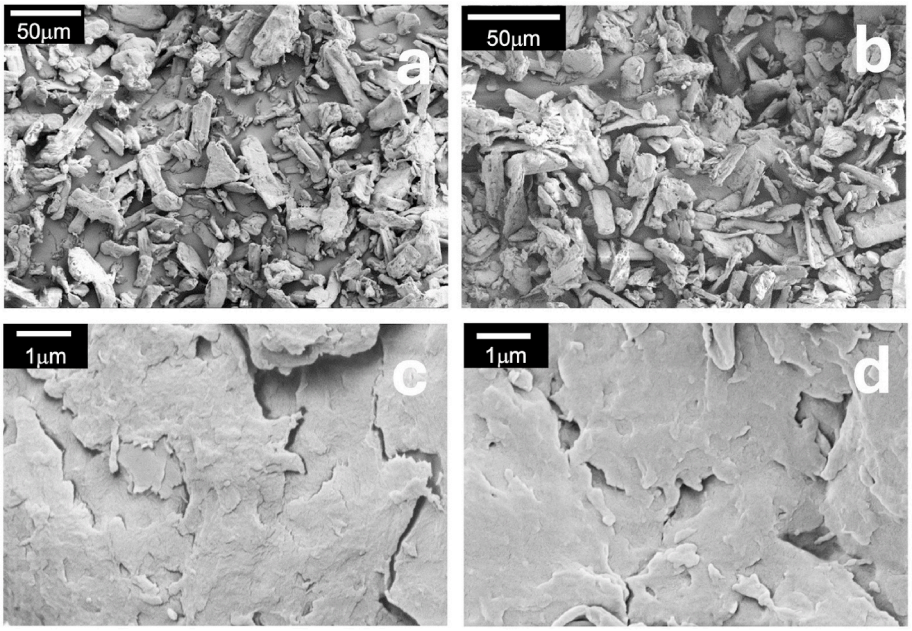

Fig. 7. SEM images of cellulose before (untreated) and after thermochemical treatment (treated, C02). (a) untreated cellulose at 1000 × magnification. (b) untreated cellulose at 30 000 × magnification. (c) C02 at 1000 × magnification. (d) C02 at 30 000 × magnification.

nanoscale spherical carbonaceous particles and disrupted surface morphologies, which aligned with the features observed in this study. Similarly, Yu et al. [55] report that higher hydrothermal temperatures (200–300 °C) lead to increased surface porosity and molecular restructuring in kraft lignin, with smooth-to-rough surface transitions and partial depolymerization.

The cellulose samples, either the pristine or the treated ones, do not show evident differences, at low (Fig. 7a and c) and high magnification (Fig. 7b and d). Irregular granules, shreds and agglomerates appear similar in the two samples, confirming the stability of cellulose during the mild thermochemical treatment. Such stability has been documented in hydrothermally treated cellulose systems by Zhang et al. [56], where cellulose-rich fractions showed negligible microstructural changes below 200 °C. These findings affirm the high degradation threshold of cellulose under moderate hydrothermal conditions.

4. Discussion

Furfural compounds are known to reduce biogas yield. These molecules typically originate from dehydration of pentoses and hexoses during harsh thermochemical treatments or from lignin depolymerization into phenolic derivatives. Under the mild hydrothermal conditions applied in this study, the formation of such inhibitors is expected to be minimal. Previous studies have shown that the conversion of hemicellulosic and cellulosic sugars to furfural and HMF becomes significant mainly above 200–220 °C or under acidic catalysis [57,58]. Conversely, at neutral pH and moderate temperatures the dehydration of sugars proceeds very slowly, yielding only trace amounts of furanic compounds [59]. Therefore, the observed decrease in biogas yield is attributed primarily to the loss of cellulose and hemicellulose rather than to the accumulation of inhibitory species.

Moreover, the solid and liquid phases were separated before anaerobic digestion, further minimizing any potential influence of soluble compounds on the microbial activity. Therefore, the observed decrease in biogas yield is attributed primarily to compositional and structural changes in the lignin fraction rather than to the accumulation of inhibitory species.

Assuming that lignin is recalcitrant during bio-digestion, not contributing to biogas generation. Thus, a comparison between two alternative routes, as depicted in Fig. 8, would be.

1) A mass m_{ar} (kg) of as received biomass is directly subjected to bioconversion yielding a biogas volume V_{bg} (NL) under normal conditions, the biogas yield being equal to $Y_{bg} = V_{bg}/m_{ar}$ (NL/kg).
2) A mass m_{ar} of as received biomass is mixed with water m_w (kg) and subjected to thermochemical process, losing volatile matter V_{vol} (NL) and obtaining a thermally treated solid $m_t = \Psi\, m_{ar}$ (kg), being Ψ the solid yield. The latter is subsequently subjected to bioconversion, resulting in biogas volume V'_{bg} (NL).

Likely V'_{bg} is smaller than V_{bg} due to the volatiles loss during the thermochemical treatment. However, a different behaviour of the thermochemically treated biomass, particularly the possible generation of biogas from the modified lignin, could mitigate this difference.

Equations (6)–(8) summarize the biogas yield estimation and comparison between untreated and thermochemically treated biomass. The following assumptions were made.

i) only the fraction different from lignin can generate biogas upon bioconversion;
ii) the biogas generation from the thermally treated biomass is proportional to that of the as received biomass;
iii) the ash is inert and is conserved during thermal treatment.

$$Y'_{bg} = \frac{(1 - X_a - X_m - X_l)}{(1 - X_{a0} - X_{m0} - X_{l0})} Y_{bg} \Psi \quad \text{Eq. 6}$$

$$X_a = X_{a0}/\Psi \quad \text{Eq. 7}$$

$$\Delta Y_{bg} = \frac{Y''_{bg} - Y'_{bg}}{Y'_{bg}} \quad \text{Eq. 8}$$

where:

Y_{bg} = biogas yield of untreated biomass (NL/kg);
Y'_{bg} = theoretical biogas yield after pretreatment (NL/kg);
Y''_{bg} = experimental biogas yield after pretreatment (NL/kg);
X_l, X_a, X_m = mass fractions of lignin, ash, and moisture (−);
Ψ = solid yield after thermochemical treatment (−);

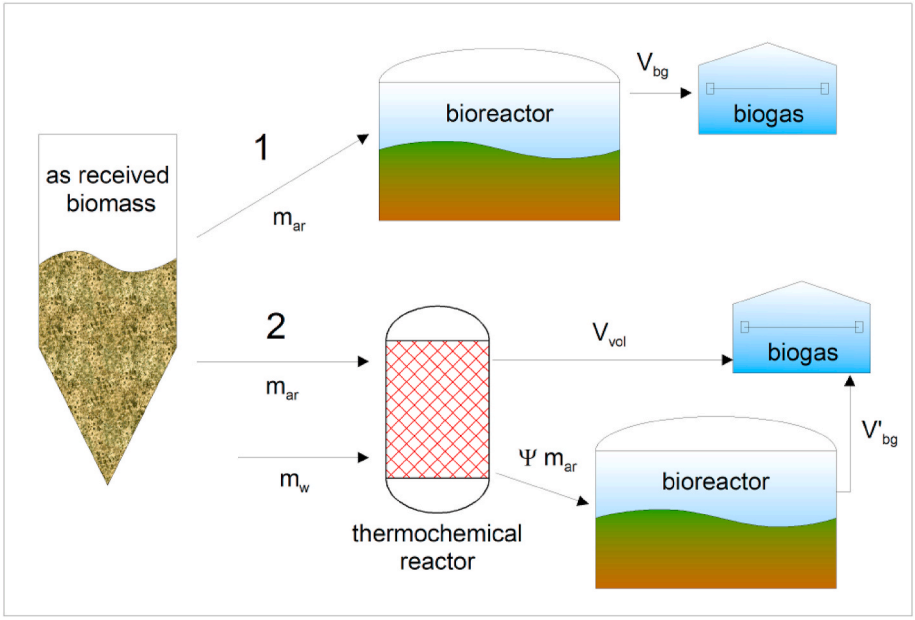

Fig. 8. Flow diagram of alternative routes for biomass bioconversion.

ΔY_{bg} = relative variation in biogas yield (%).

In Equation (6) the terms in brackets (1- X_{a0} - X_{m0} - X_{l0}) and (1- X_a - X_m - X_l) represent the mass fraction of bio-convertible constituents, in pristine and thermally treated biomass respectively. The ratio between the brackets expresses the assumed proportionality of biogas generation. Equation (7) states the ash conservation.

Table 5 presents a comparison between the expected biogas yield, Y'_{bg}, calculated according to Equation (6), and the actual yield, $Y''_{bg} = \Psi Y_{bg}$, which is the biogas volume produced per unit mass of pristine biomass. The latter was determined from the above reported experimental results of bioconversion for the GP00, GP01, and GP04 samples (Table 4). Congruently, Y'_{bg} and Y''_{bg} are equal for the untreated sample GP00. In contrast for both GP01 and GP04, Y''_{bg} is larger than Y'_{bg}, indicating that the actual biogas volume produced was greater than the estimated value. This finding demonstrates that the assumption that the lignin fraction does not contribute to biogas generation (Eq. (6)) does not hold true for thermochemically treated biomass.

Therefore, the thermochemical treatment can be considered effective in reducing the biomass recalcitrance to bioconversion, as confirmed by the lower residual lignin content in the digestate. The most significant improvement in the biodegradability index ($\Delta Y_{bg} = 27\%$) was observed for sample GP04, treated at higher temperature than GP01 (Table 2). Nevertheless, the overall biogas yield was lower for both thermochemically treated samples (−19% for GP04 and -50% for GP01) because part of the easily degradable organic fraction was lost during the thermal pretreatment as volatile and soluble compounds. These compounds, although contributing to the total carbon balance, were removed before biodigestion and thus did not participate in the subsequent biogas formation. When considering the remaining solid phase alone, the increased bioconversion efficiency clearly indicates that the thermochemical treatment enhanced the digestibility of the recalcitrant fraction of the biomass. In literature, lower biogas yield after thermochemical treatment is reported in the case of Giant Reed [60], and Corn Stover [61], strongly depending on temperature and residence time. Ahmed et al. [62] report as optimal conditions for biomass treatment a temperature in the range 150–180 °C and a residence time between 10 and 30 min, not different from those of present study.

The optimization of the thermochemical treatment is required for maximizing ΔY_{bg} due to the interplay of two opposing effects: i) too mild treatment fails to significantly alter the biomass structure, resulting primarily in the loss of volatiles and soluble components such as extractives; ii) too severe treatment leads to excessive alteration of macrocomponents, shifting the biomass toward the low oxygen-to-carbon ratio region in the Van Krevelen diagram [63] characteristic of highly carbonized organic materials.

Fig. 9 shows the values of the yield ratio $\xi = Y_{bg}/Y_{bg,0}$, where $Y_{bg,0}$ is the biomethane yield of untreated biomass, calculated on the basis of results of present study (GP) and those taken from literature for giant reed (GR) [60] and corn stover (CS) [61]. Even with a rather high dispersion ($R^2 = 0.614$), the data-points fit rather well on a curve that presents a fairly evident maximum corresponding to 20 % higher yield

Table 5
Comparison of volumes of biogas between as received and treated samples.

	X_l, -	X_a, -	X_m, -	Ψ, -	Y'_{bg} [a] NL/kg	Y''_{bg} [b] NL/kg	ΔY_{bg} %
GP00	0.52	0.036	0.061	1.00	237	237	0
GP01	0.60	0.041	0.030	0.88	174	192	10
GP04	0.73	0.052	0.021	0.69	93	118	27

[a] Equation (2).
[b] Experimental results.

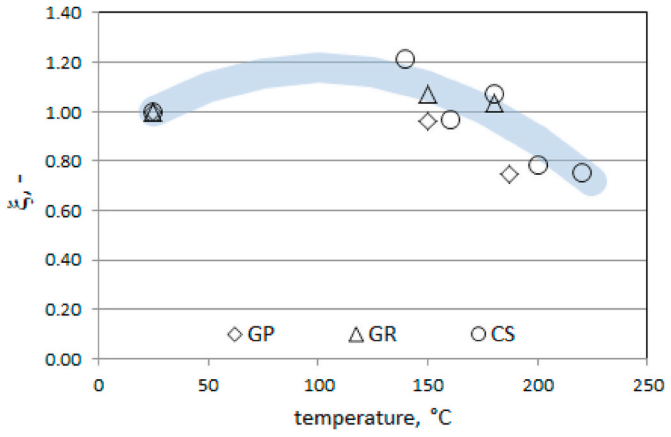

Fig. 9. Yield ratio ξ as function of T for different biomass; present study (GP); giant reed (GR) [60]; corn stover (CS) [61].

of biomethane at a temperature of around 130 °C. Afterwards, a sharp decay of the yield ratio occurs, because of the excessive loss of volatiles in the pretreated biomass.

Notably, the correlation applies to three lignocellulosic biomasses of different origin, all having variable lignin content depending on treatment temperature.

5. Conclusions

This study demonstrates that a mild thermochemical pretreatment of grape pomace stabilizes the biomass and modifies the lignin matrix, enhancing its susceptibility to anaerobic biodegradation. Although the pretreatment increases the relative lignin content due to the removal of labile components, the induced structural and morphological alterations promote partial lignin conversion and result in higher-than-expected methane yields. At 187 °C and 20 min residence time, the measured biogas yield exceeded theoretical predictions by about 29 %, confirming a synergistic effect of the integrated process, owing to the tangible contribution from the modified lignin that was less recalcitrant during anaerobic digestion.

Nevertheless, the overall biogas yield of pretreated samples was lower than that of untreated biomass, with reductions up to 27% at 187 °C, mainly attributed to volatile losses during the thermal step. This trade-off emphasizes the need to optimize pretreatment severity, particularly temperature and residence time, to balance structural modification and energy recovery. The combined thermochemical–biological approach thus represents a promising route for grape pomace valorization, supporting renewable energy generation and sustainable management of agro-industrial residues. Future research should refine process parameters and explore synergistic improvements via co-digestion or enzymatic enhancement.

CRediT authorship contribution statement

S. Costa: Writing – original draft, Supervision, Conceptualization. **I. Gugel:** Validation, Investigation. **L. Polchri:** Investigation. **M. Mazzocchi:** Visualization, Investigation. **P. Ammendola:** Writing – original draft, Conceptualization. **F. Raganati:** Writing – original draft, Data curation. **F. Miccio:** Writing – original draft, Conceptualization.

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Nomenclature

AIL	acid insoluble lignin
ASL	acid soluble lignin
m	mass, g
T	temperature, °C
TLC	total lignin content
V	volume, L
X	mass fraction, %
Y	biogas yield, mL g^{-1}

Greek symbols

ξ	yield ratio
Ψ	solid yield

Acronyms

C	cellulose
CS	corn stover
GP	grape pomace
GR	giant reed
L	lignin
PSK	Pseudo-component kinetic

Data availability

Data will be made available on request.

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