

Comparison of pyrolysis and anaerobic digestion processes for wheat straw biomass

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ABSTRACT

Due to the growing interest in using biomass as a renewable energy source, this study presents a comparative analysis between two prominent biomass conversion technologies—anaerobic digestion and biomass pyrolysis—focused on wheat straw biomass. The objective of this study is to evaluate and compare the efficiency, energy output, and environmental impact. Anaerobic digestion was performed under mesophilic conditions ($35 \pm 0.5^\circ\text{C}$) using the biochemical methanogenic potential (BMP) methodology. Pyrolysis was conducted through thermogravimetric analysis (TGA) to determine the thermal behaviour and kinetic parameters of the biomass. Biogas production led to better energetic results as high methane yields of over $11 \text{ mL CH}_4 \text{ g}^{-1} \text{ VS}$ were obtained. Additionally, the integration of both processes was considered by subjecting digestate from anaerobic digestion to pyrolysis process. Key findings demonstrate that the activation energy (E_a) for wheat straw ranged from 166.49 to $176.42 \text{ kJ}\cdot\text{mol}^{-1}$ across different kinetic methods, indicating its suitability for pyrolysis. In contrast, digestates exhibited significantly lower activation energies, with 1-week, 2-weeks, and 3-weeks digestates showing ranges of 53.27 – $60.79 \text{ kJ}\cdot\text{mol}^{-1}$, 38.69 – $46.86 \text{ kJ}\cdot\text{mol}^{-1}$, and 46.29 – $72.34 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. These results suggest that anaerobic digestion not only produces biogas but also yields a byproduct with potential for efficient pyrolytic conversion suggesting opportunities for integrated waste management and renewable energy production systems.

1. Introduction

The utilization of biomass as a renewable energy source has gained significant attention in recent years due to its potential to mitigate greenhouse gas emissions and reduce dependence on fossil fuels (Vakulchuk et al., 2020; Al-Mansour and Zuwala, 2010; Bilgili et al., 2017; Scarlat et al., 2015). Besides that, biomass offers numerous advantages, including its diversification of energy sources, and utilization of organic waste materials for energy production and waste management (McKendry, 2002; Field et al., 2008). Wheat straw is one of the most commonly used biomasses, due to its abundant availability, low cost and the conversion processes that transform the raw wheat straw into more efficient fuels (Taghizadeh-Alisaraei et al., 2023; Schreiber et al., 2022). As it is a large byproduct of wheat cultivation, it holds

significant potential as a feedstock for bioenergy production due to its availability and renewable nature. This study focuses on two promising technologies for valorising wheat straw biomass: anaerobic digestion and biomass pyrolysis.

Among the various biomass conversion technologies, anaerobic digestion and biomass pyrolysis have emerged as prominent methods for transforming agricultural residues into energy-rich products (Achinas et al., 2017). Anaerobic digestion involves the biological decomposition of organic matter in the absence of oxygen, resulting in the production of biogas rich in methane, carbon dioxide, and trace amounts of other gases (Deublein and Steinhauser, 2011). The CH_4 content can vary between 50 % and 65 % (Ferreira et al., 2019; Herwintono et al., 2020), although this proportion can increase up to 80 % CH_4 if easily degradable substrates are used and under optimal conditions (Llamas et al., 2020). In the same way, a liquid amendment, the digestate, is produced during the

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Nomenclatures

BMP	Biochemical methanogenic potencial
TS	Total solids, g·kg ⁻¹
VS	Volatile solids, g·kg ⁻¹
COD	Chemical oxygen demand, mg·L ⁻¹
VFA	Volatile fatty acids, g·L ⁻¹
<i>P</i>	Potential methane production, mL CH ₄ · g VS ⁻¹
<i>R</i>	Maximum methane production rate, mL CH ₄ · g VS ⁻¹ · day ⁻¹
<i>λ</i>	Lag phase, day
STA	Simultaneous thermal analysis
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
<i>β</i>	Heating rate, K·min ⁻¹

KAS	Kissinger-Akahira-Sunose
FWO	Flynn-Wall-Ozawa
<i>E_a</i>	Activation Energy, kJ·mol ⁻¹
<i>α</i>	Dimensionless conversion factor
<i>A</i>	Preexponential factor, min ⁻¹
<i>f(α)</i>	Reaction model
<i>R</i>	Universal gas constant, 8.314 J·mol ⁻¹ ·K ⁻¹
<i>g(α)</i>	Integral form of the reaction model
DTG	Thermogravimetric curve derivative
<i>T_p</i>	Temperature of maximum DTG, K
<i>ΔH</i>	Enthalpy, kJ·mol ⁻¹
<i>ΔG</i>	Gibbs free energy, kJ·mol ⁻¹
<i>ΔS</i>	Entropy, kJ·mol ⁻¹
<i>K_B</i>	Boltzmann constant, 1.38·10 ⁻²³ J·mol ⁻¹
<i>h</i>	Plank constant, 6.262·10 ⁻³⁴ J·s

process with a potential interest as organic fertilizer (Tambone et al., 2010; Chozhavendhan et al., 2023). Several carbon-based wastes have been explored as feedstock for management through anaerobic digestion, however, due to their high polysaccharide content and high availability lignocellulosic substrates are becoming more frequent despite their low degradability (Sawatdeenarunat et al., 2015; Hashemi et al., 2021; Wyman et al., 2018).

Studies on the digestion of wheat straw highlight that digester temperature and C/N ratio are key factors in biomethane production (Shi et al., 2018; Pohl et al., 2012). Mechanical pretreatment, which reduces particle size and increases the contact surface for microorganisms, can boost biogas production by 25–71 % (Gallegos et al., 2017; Álvaro et al., 2023). Other pretreatment methods, including thermal, chemical, ultrasonic, and biological techniques, also enhance methane production (Rajput, Zeshan and Visvanathan, 2018; Theuretzbacher et al., 2015; Naik et al., 2021; Kainthola et al., 2019).

Nevertheless, there are other conversion processes that produce efficient biofuels such as biomass pyrolysis. Biomass pyrolysis is a thermochemical process that breaks down biomass through heating in the absence of oxygen, yielding biochar, bio-oil, and syngas (Demirbas and Arin, 2002). Due to the versatility of the products obtained from biomass this process, it has gained relevance in the last decades (Lu et al., 2009; Hu and Gholizadeh, 2019). Moreover, biomass pyrolysis processes can be optimized to maximize energy efficiency, making it an attractive option for decentralized energy generation and cogeneration systems (Abbas et al., 2020; Fedyukhin et al., 2013). Several authors have studied pyrolysis through kinetic analysis using lignocellulosic biomasses finding out that the average activation energy ranges for hemicellulose, cellulose, and lignin were approximately 150–165 kJ/mol, 170–180 kJ/mol, and 175–200 kJ/mol, respectively (Várhegyi et al., 1997; Chen et al., 2015; Tsamba et al., 2006; Wang et al., 2017; Dhyani and Bhaskar, 2018).

Biomass pyrolysis typically exhibits fast reaction rates resulting in a relatively quick conversion into biochar, bio-oil, and syngas (Lédé and Authier, 2011; SriBala et al., 2019; Van de Velden et al., 2010). Depending on the pyrolysis conditions and biomass feedstock pyrolysis byproducts differ, however, when applying fast pyrolysis the yields for biochar, bio-oil and non-condensable gases are around 13 %, 75 % and 13 % respectively (SriBala et al., 2019). Moreover, the pyrolysis process enables high heating rates, which contribute to faster thermal decomposition of biomass and enhances the overall reaction kinetics and allows for efficient conversion within shorter residence times (Zanzi et al., 1996; Johansen et al., 2016). Biomass pyrolysis can be conducted over different temperature regimes can target specific product yields and qualities (Hu and Gholizadeh, 2019; Akhtar and Saidina Amin, 2012; Xiao and Yang, 2013). In wheat straw pyrolysis, stages include drying, primary devolatilization, and secondary devolatilization, with

activation energy values ranging from 45 to 170 kJ/mol, and primary devolatilization occurring between 200°C and 400°C (Lanzetta and Di Blasi, 1998; Mani et al., 2010; Cai and Bi, 2009; Pešenjanski et al., 2016).

Overall, this study aims to address two questions: how do the efficiency, energy output, and environmental impact of anaerobic digestion and biomass pyrolysis of wheat straw biomass compare; and can the digestate from anaerobic digestion be effectively used as a feedstock for pyrolysis? To answer these questions there are a few hypotheses taken into account:

- Anaerobic digestion of wheat straw will produce high methane yields, effectively manage waste, and result in a reduced carbon footprint
- Biomass pyrolysis will offer the advantage of producing valuable biochar and bio-oil along with a versatile syngas stream, potentially providing a higher overall energy yield compared to anaerobic digestion
- The digestate from anaerobic digestion, when used as a feedstock for pyrolysis, will enhance the overall energy recovery from wheat straw, offering a viable integrated waste management solution

Because of that the objective of this study is to conduct a comparative analysis of anaerobic digestion and biomass pyrolysis processes for wheat straw biomass, a common agricultural waste. Also, this study intends to determine the potential for using digestate as a raw material for pyrolysis, thereby integrating anaerobic digestion and pyrolysis processes for enhanced energy recovery. The evaluation will encompass various aspects, including process efficiency, energy output, and environmental impact, to provide insights into the strengths and weaknesses of each technology and guide decision-making in biomass utilization. By comprehensively examining the efficiency, energy output, and environmental impact of anaerobic digestion and biomass pyrolysis for wheat straw biomass, this research intends to provide valuable insights into selecting the most suitable valorisation technology.

2. Material and methods

2.1. Samples

Wheat straw waste taken from an agricultural land (Soria, Spain, 41° 38' 52.20" N, 2° 38' 32.7" W), was used as sample in the present study. The sample was characterized using proximate analysis: 4.4 % moisture, 74.3 % volatile content and 6.7 % ash matter. Therefore, the fixed carbon content is 14.6 %. The sample was milled and sieved using a 1 mm sieve in order to reduce the particle size to increase biodegradability and fit the crucibles inside the STA apparatus.

Moreover, the digestate produced from wheat straw biodigestion was also used as a sample for thermogravimetric analysis in order to characterize the residue produced after biogas production. The digestate was dried at 105 °C during 24 hours to carry out simultaneous thermal analysis. The digestate was collected at three different times of the biogas production: after one week of digestion, after two weeks of digestion and after three weeks of digestion. The complete methodology scheme can be seen in Fig. 1.

2.2. Biogas production

For the anaerobic digestion process, the substrate of choice was raw wheat straw residues. To enhance the biogas production rate, The mechanical pretreatment applied was carried out using a grinder (Moulinex, France), involving a grinding step to reduce the particle size to less than 1 mm. This approach has been previously reported by Sharma (2020) and Dell’Omo and spena (2020a) to be effective (Sharma et al., 1988; Dell’Omo and Spena, 2020a). After pretreatment, serological bottles were prepared with substrate and inoculum in a 2:1 ratio in terms of volatile solids and supplemented with calcium carbonate (CaCO₃) as a pH buffer (Mohammad Rahmani et al., 2022). The working volume in each test was 70 mL with other 50 mL of headspace for biogas accumulation corresponding to 68 mL of inoculum and 1.94 g of wheat straw, with a substrate concentration of 28.6 g·L⁻¹. Anaerobic digestion was carried out in an incubator (Foc-200 Connect, VELP Scientifica, Italy) at 35 °C equipped with an orbital shaker (AG-200, Optik IVYMEN System, Germany), following the biochemical methanogenic potential methodology (BMP) for 41 days. The inoculum, obtained from the Anaerobic Treatment Plant of the Wastewater Treatment Plant in Soria (Spain), was adapted to the wheat straw substrate for a period of 4 weeks in a continuous reactor of 2 L volume. Biogas production was measured daily using a water displacement method by subtracting the endogenous production from the inoculum with a blank test. Biogas composition was analysed with a gas analyser (GeoTech Biogas 5000, United Kingdom). All tests were performed in triplicate.

The substrate and initial inoculum were characterized in accordance with the Standard Methods protocol to the determination of the following parameters: TS (total solids), VS (volatile solids), COD (chemical oxygen demand), and VFA (volatile fatty acids) concentration (Rice et al., 2012). Additionally, digestate samples were collected at regular intervals of 7 days during the experiment: a) one week after the start, b) two weeks after the start, c) three weeks after the start, and d) four weeks after the start.

The Table 1 provides the physico-chemical characteristics of the initial substrate and inoculum.

In addition, the Gompertz mathematical model was used to evaluate the kinetics of methane production following the next equation (Lay et al., 1996):

Table 1
Characteristics of substrate and anaerobic sludge used in the bioreactors.

Parameter	Wheat straw	Anaerobic sludge
TS. Total solids (g·kg ⁻¹)	935.4 ± 1.5	17.9 ± 0.1
VS. Volatile solids (g·kg ⁻¹)	896.0 ± 0.9	12.8 ± 0.1
COD (mg·L ⁻¹)	1422.4 ± 15.5*	4941.1 ± 854.8

* mg·g⁻¹

$$P(t) = P \bullet e^{\left\{ -e^{\left[\frac{R_{\bullet e}}{P} \bullet (\lambda - t) + 1 \right]} \right\}} \quad (1)$$

In this equation, $P(t)$ represents the accumulated methane production under standard temperature and pressure conditions (mL CH₄/g VS), where P denotes the potential methane production (mL CH₄/g VS), R represents the maximum methane production rate (mL CH₄/g VS·day), λ signifies the lag phase (days), and t indicates the elapsed time (days).

2.3. Simultaneous thermal analysis and kinetic analysis

Simultaneous thermal analysis was carried out using a TG-DSC T50 Mettler Toledo apparatus which allowed to determine thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). For TGA test conditions were selected according to previously published literature (Xiao et al., 2020; Escalante et al., 2022) and are predefined as follows:

- Heating rates (β): 10, 15 and 20 K·min⁻¹
- Initial temperature: 30 °C
- Final temperature: 800 °C
- Gas flow: nitrogen 50 mL·min⁻¹
- Sample mass: 10 ± 1 mg

Heating rates should always be lower than 50 K/min (Zhang et al., 2004; Mehrabian et al., 2012). As the isoconversional kinetic models require at least 3 different heating rates, several authors have used heating rates between 5 and 20 K/min (Burra and Gupta, 2019). In this study, Friedman, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods were used to define activation energy (E_a). The mathematical model for Friedman is shown in Eq. (2), KAS model is shown in Eq. (3) and FWO model in Eq. (4).

$$\ln\left(\beta \frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (2)$$

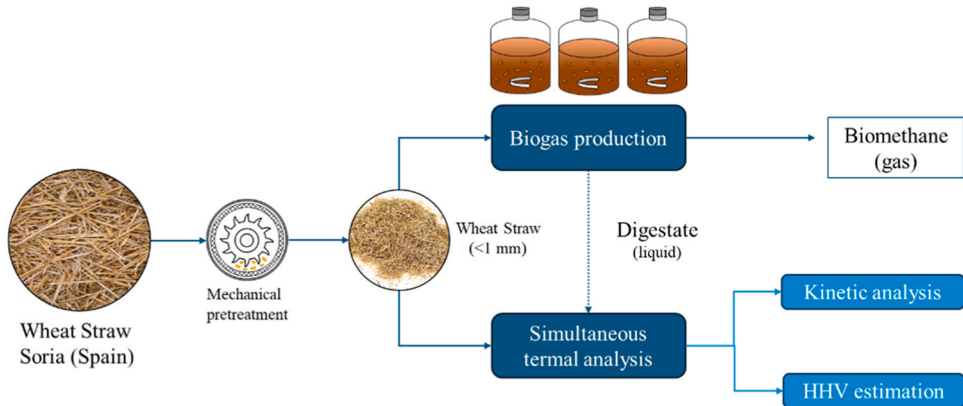


Fig. 1. Methodology scheme.

$$\ln(\beta) = \ln \frac{AEa}{Rg(\alpha)} - \frac{Ea}{RT} \quad (3)$$

$$\ln(\beta) = \ln \frac{AEa}{Rg(\alpha)} - 5.331 - 1.052 \frac{Ea}{RT} \quad (4)$$

Where β represents the heating rate ($\text{K}\cdot\text{min}^{-1}$), α the dimensionless conversion factor, A the preexponential factor (min^{-1}), $f(\alpha)$ the reaction model, Ea the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R the universal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T the temperature (K), and $g(\alpha)$ the integral form of the reaction model.

When applying these methods, it is necessary to assume a model in order to obtain the pre-exponential factor (A). A model-free non isothermal method to calculate the pre-exponential factor developed by Kissinger was applied to define this parameter (He et al., 2019). Eq. (5) shows the pre-exponential factor determination:

$$A = \left[Ea \cdot \beta \cdot \exp\left(\frac{Ea}{R \cdot T_p}\right) \right] / (R \cdot T_p^2) \quad (5)$$

Where T_p represents the temperature at which the first TG curve derivative (DTG) reaches its maximum value, which is the DTG peak. It can be noticed that, as the pre-exponential factor is defined using β and T_p , three different values can be obtained depending on the selected heating rate. In the present study only the average value is reported.

The kinetic parameters allow to define thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) (He et al., 2019). Those parameters can be obtained using activation energy, preexponential factor and temperature. Eq. (6) defining enthalpy, Eq. (7) Gibbs free energy, and Eq. (8) entropy as follows:

$$\Delta H = Ea - R \cdot T \quad (6)$$

$$\Delta G = Ea + R \cdot T_p \cdot \ln \left(\frac{K_B \cdot T_p}{h \cdot A} \right) \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \quad (8)$$

Where K_B represents the Boltzmann constant ($1.381 \cdot 10^{-23} \text{ J}\cdot\text{mol}^{-1}$) and h the Plank constant ($6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$).

Regarding differential scanning calorimetry the applied test conditions were as follows:

- Heating rates (β): $20 \text{ K}\cdot\text{min}^{-1}$
- Initial temperature: 30°C
- Final temperature: 700°C
- Gas flow: oxygen $50 \text{ mL}\cdot\text{min}^{-1}$
- Sample mass: $10 \pm 1 \text{ mg}$

As the DSC is used to estimate the high heating value, it is necessary to simulate a fast oxidation in which all the volatile matter suddenly releases producing an exothermic reaction. The conditions previously mentioned allow a fast combustion of the sample which leads to a peak in the heat transfer curve from the DSC. When calculating the integral of this peak, the area beneath the curve is obtained, and represents an estimate value of the high heating value, which means that it is possible to address the potential as combustion fuel of the sample.

3. Results and discussion

3.1. Biogas production

Fig. 2 illustrates the daily and cumulative biomethane generation of various implemented trials spanning a 41-day period. During this timeframe, there were noticeable fluctuations in both daily and cumulative biomethane production.

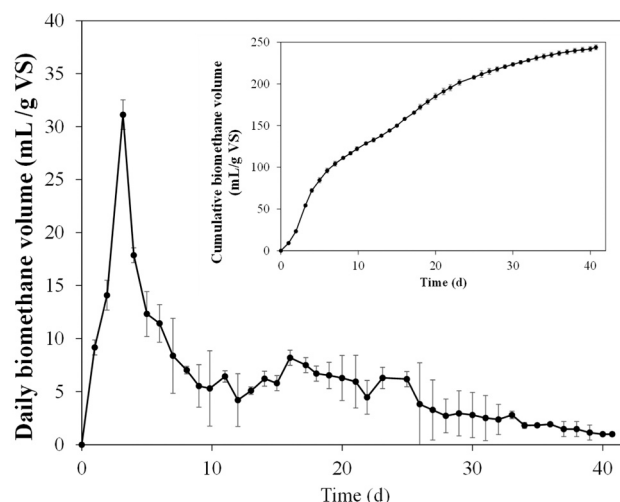


Fig. 2. Daily and cumulative biomethane production from the anaerobic digestion of wheat straw.

The production of biomethane was maximal in the first days of the trials, surpassing the generation of $30 \text{ mL}\cdot\text{biomethane}\cdot\text{g}^{-1}$ of VS on third day, which indicates the high efficiency of the mechanical pretreatment applied and the adaptation of the anaerobic inoculum. From day fifth onwards, the daily production showed oscillations, with some days decreasing and others increasing, maintaining an average level of biogas production between days 10 and 25, marking the stationary phase of the process. At this point, biomethane production has already surpassed 85 % of the final production, indicating a rapid biodegradation process. This is particularly noteworthy given that the substrate used is ligno-cellulosic, which is typically more resistant to anaerobic digestion. From day 26th the production gradually decreased due to the depletion of transformable organic matter. At the end of the experiment, the final cumulative production registered was $244 \text{ mL}\cdot\text{biomethane}\cdot\text{g}^{-1}$ VS.

The achieved biomethane production closely aligns with values reported in other studies within the literature Yadav and Vivekanand (2021) documented a biogas production of $263 \text{ mL}\cdot\text{g}^{-1}$ VS, while Dell'Omo et al. (2020a) reported $250.3 \text{ mL}\cdot\text{g}^{-1}$ VS in their control BMP experiments (Dell'Omo and Spena, 2020b; Yadav and Vivekanand, 2021).

Fig. 3 provides data regarding the concentration of volatile fatty acids (VFAs) throughout the experiments as an intermediate indicator of the metabolic pathway of complete anaerobic digestion of the wheat straw compounds (C5 and C6 molecules) to methane (C1 molecule). The

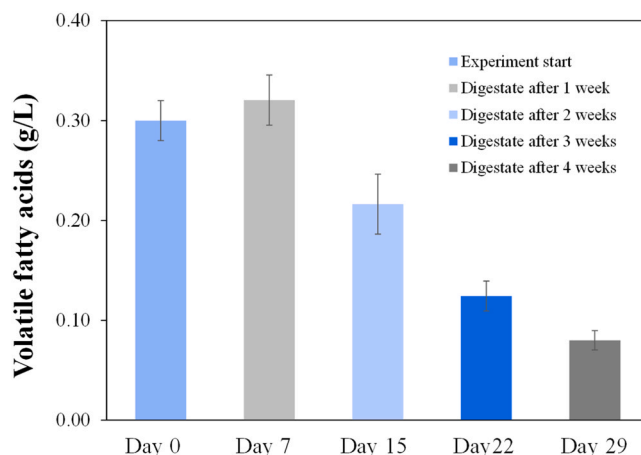


Fig. 3. Changes of total volatile fatty acids concentrations throughout the test with wheat straw.

initial concentration was $0.30 \text{ g}\cdot\text{L}^{-1}$, corresponding to the anaerobic inoculum medium. Over the course of 7 days, there was an increase to $0.32 \text{ g}\cdot\text{L}^{-1}$, attributed to the first hydrolysis and the subsequent acidogenesis stage where VFAs are generated (mainly acetic C2 molecule, propionic C3 molecule, butyric C4 molecule or valeric C5 molecule), which coincides with the peak of biomethane production (Liu et al., 2021). This swift transformation is also a result of the inoculum adaptation process, which ensures robust bacterial and archaeal adaptation to the wheat straw substrate and its transformation into the methane.

Subsequently, after day 15th, a noticeable decline in the concentration was observed, indicating a shift in microbial dynamics due to organic matter consumption. Finally, by day 29th, the concentration

reached its lowest point at $0.08 \text{ g}\cdot\text{L}^{-1}$, coinciding with the lowest bio-methane production as well. This VFAs trend during the anaerobic digestion process has been also developed in different studies with other lignocellulosic wastes (Alvaro et al., 2023; Ghofrani-Isfahani et al., 2020), exhibiting a rapid and effective conversion of the lignocellulosic content of the wheat straw into short-chain carboxylic acids or VFAs (Fig. 3), followed by its subsequent bioconversion into biogas (Fig. 2).

Additionally, the results of the Gompertz model reveals a bio-methane production rate of $11.05 \text{ mL CH}_4\cdot\text{g}^{-1}\text{VS}\cdot\text{d}^{-1}$. Notably, the experiment exhibited a lag phase (λ) of 0 days, indicating no retention period. Additionally, the regression coefficient computed for the data stands at 97.4 %.

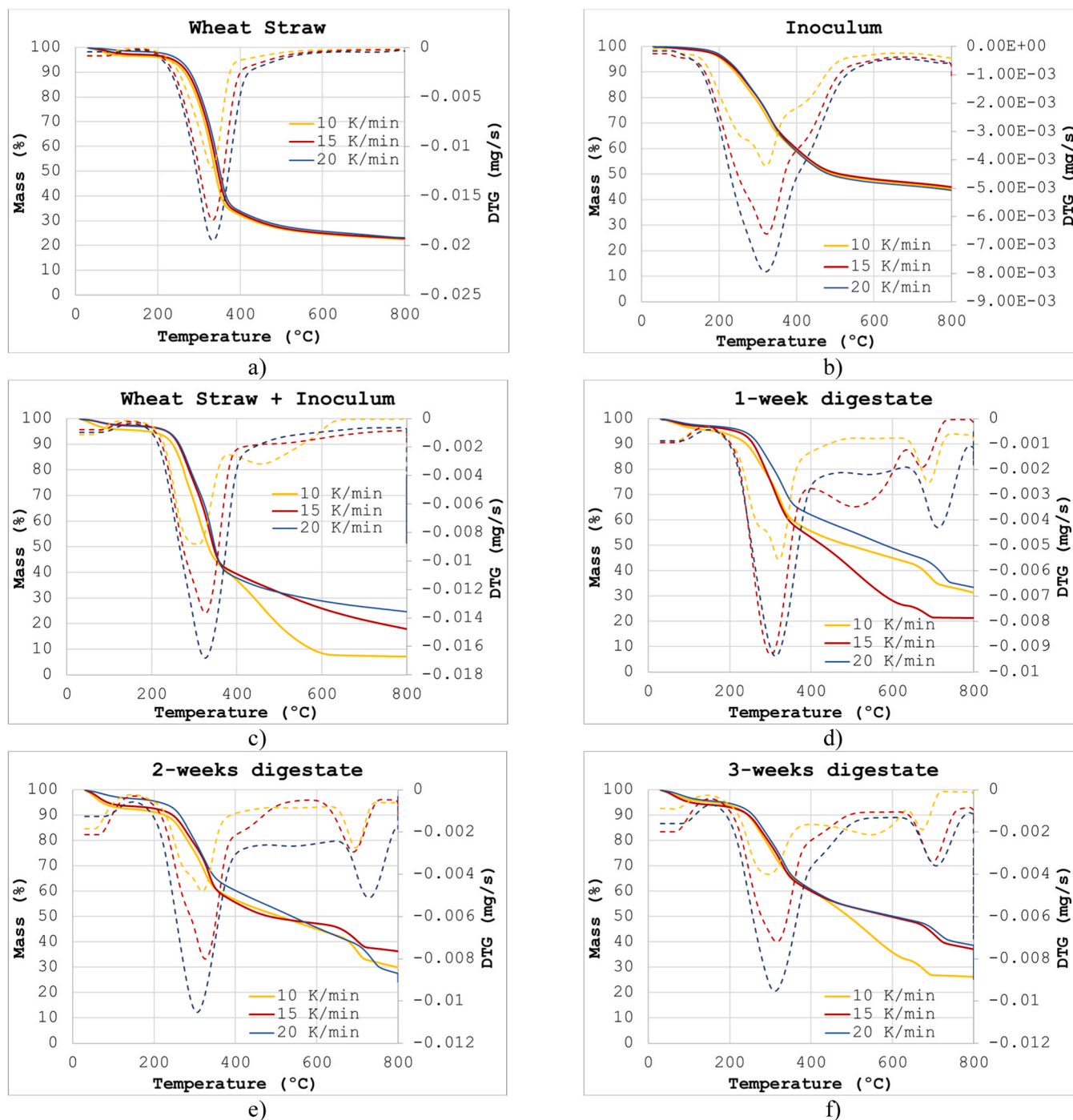


Fig. 4. TGA - line and DTG - dash curves for a) wheat straw b) inoculum c) mixture of wheat straw and inoculum before digestion d) digestate waste after 1 week biogas production e) digestate waste after 2 weeks biogas production f) digestate waste after 3 weeks biogas production.

These discoveries offer valuable insights into the dynamics of the biomethane production process and enable meaningful comparisons with another research. Mohammad Rahmani et al. (2022) recorded a biomethane production rate of 10.14 mL/g VS, while García et al. (2022) reported 12.51 mL·g⁻¹ VS (Mohammad Rahmani et al., 2022; Alvaro et al., 2023), using wheat straw as substrate.

3.2. Simultaneous thermal analysis results

As mentioned before, six different samples can be tested using STA: raw wheat straw, inoculum, mixture of raw wheat straw and inoculum, and digestate after one, two and three weeks. TGA curves obtained from this analysis, together with the first derivative (DTG) curve are plotted in Fig. 4.

From the obtained results it can be noticed that heating rate does not produce a significant change when addressing raw wheat straw leading to a residue after pyrolysis a slightly greater than 20 %. The DTG curve of this sample shows one devolatilization stage in which cellulose, hemicellulose and part of the lignin content degrade simultaneously between 250 °C and 400 °C. After that, the mass loss produced up to 800 °C is due slow lignin degradation (Burhenne et al., 2013). It has to be noted that the overall production of volatiles in the pyrolysis process is the sum of the contributions of each polymer (Manyà et al., 2003). Previously published literature has characterized the composition of wheat straw, reporting values between 32 % and 45 % for cellulose, 20 % and 45 % for hemicellulose and 11 % and 26 % for lignin (Zhang et al., 2022). Those results are consistent with the curves plotted in Fig. 4 – a in which the main devolatilization process corresponds to hemicellulose and cellulose. Indeed if these curves are compared to previous studies of wheat straw hemicellulose (Peng and Wu, 2010) significant similarities arise, which means that the main polymer of the wheat straw sample of this research is hemicellulose. Due to the devolatilization sensitivity, great amounts of hemicellulose lead to a better pyrolysis of the product (Zong et al., 2020), which can be noticed also when addressing the activation energy.

When addressing the inoculum (Fig. 4 – b), the final residue is set around 45 % of the mass, and the DTG curves show different devolatilization stages. These stages are more clearly seen in 10 K/min curve, as the thermal lag is lower at this heating rate. Between 200 °C and 500 °C, the mass significantly decreases due to the availability of microorganisms (Gómez et al., 2005). When addressing these DTG curves it is noted that the heating rate presents a clear impact on inoculum samples but not so much wheat straw. Inoculum exhibits multiple devolatilization stages due to the presence of microorganisms and other complex organic matter. These stages are more pronounced at lower heating rates because of reduced thermal lag, allowing more detailed observation of the various devolatilization phases. The complexity and variability in the composition of the inoculum lead to a noticeable impact of heating rate on the TG/DTG curves, while the simpler composition of wheat straw results in consistent thermal decomposition patterns across different heating rates.

The mixture of biomass and inoculum seems to be the more affected due to the thermal lag (Fig. 4 – c), as the behaviour for 10 K/min curve significantly differs from the 15 K/min and 20 K/min curves. It can be noted that there are two decomposition stages. The first one from around 250 °C up to 350 °C, where again the hemicellulose, cellulose and part of the lignin content are devolatilized. The second one seems to continue up to 600 °C leading to a lower residue than in the previous curves. Therefore, it seems that bacteria are reacting with the biomass leading to a different behaviour.

This fact is indeed noticed in Fig. 4 – d where the digestate residue after one week of biogas production is analysed. When a heating rate of 10 K/min is applied, a small shoulder in the DTG curve can be noticed, similar to the one found in when addressing inoculum but narrower due to the digestion that has modified the composition. A second peak is also noticed, similar to the one found when analysing the mixture of

inoculum and wheat straw. Nevertheless, after one week of digestion this peak is significantly greater, and the two devolatilization stages are more clearly seen. Indeed, if Fig. 4 – e is considered, it can be noticed that after two weeks of digestion the same shoulder appears at the left of the first peak. Both curves show similarities, and the same tendency of stages are followed. However, when considering the digestate after three weeks of digestion (Fig. 4 – f) the curve slightly changes as the first stage does not longer present a shoulder and the slope produced due to the pyrolysis of the sample is less sharp. These two-stage process is often attributed to the pyrolysis of the hemicellulose and cellulose in the first phase and lignin pyrolysis in the second phase (Karaeva et al., 2022a). As previously mentioned, the amount of lignin present in the wheat straw is significantly lower than hemicellulose and cellulose, therefore, the second stage is less intense than the first pyrolysis stage.

Again, it is shown that the heating rate has different effects on the TG/DTG curves for samples with different digestion times. This can be explained due to the composition and thermal stability of the digestate over the digestion period. When applying high heating rates the sample does not reach the temperature homogeneously, hampering the degradation of more stable compounds (Gašparovič et al., 2010). After one week of digestion, there are still significant amounts of readily degradable organic matter, resulting in noticeable peaks in the DTG curve due to the rapid decomposition of these components. On the other hand, after two and three weeks of digestion, the DTG curves show peaks associated with the decomposition of more stable compounds, indicating a shift in the thermal stability of the digestate.

If the TGA curves are considered after 400 °C, slight differences can be noticed for the mixture of biomass and inoculum and the following digestates (Fig. 4 – c, d, e and f). It is shown that the effect of the heating rate is more noticeable in this stage that at the beginning of the reaction. Indeed, for Fig. 4 – c and f, the lower heating rate produces the lower residue after the reaction, which means that the sample presents lower thermal lag, and more mass undergoes the reaction. However, Fig. 4 – d presents a different behaviour as the lowest residue is obtained at 15 K/min. However, some previous research has already shown that the high heating rates can produce lower residues (Akor et al., 2021). It is well known that the higher the heating rate the larger the temperature range of decomposition, but also the height of the DTG peak, nevertheless further analysis in the ash composition and the pyrolysis products of each heating rate should be carried out to properly understand the effect of the heating rate in the pyrolysis process.

Moreover, as mentioned before, digestate presents a second peak in the DTG curves at the end of the reaction, attributed to the mass loss produced between 600 °C and 800 °C. There is a second devolatilization process at the end of the pyrolysis which is not shown in the raw biomass nor the inoculum. Therefore, it seems that the digestate production leads to a new composition in which volatiles are clearly differentiated in two temperature ranges. This fact was already reported by other authors which explained that at higher temperatures there is a decomposition of the carbonaceous residue but also pyrolysis gas formation (Atienza-Martínez et al., 2020; Karaeva et al., 2022b). At the end of the curves there is a final residue around 30 % for most of the heating rates, which is consistent with correspond to the pyrolysis ashes (Akor et al., 2021).

Regarding DSC results, the curves can be seen in Fig. 5. As mentioned before, the area beneath the peak in the DSC can be interpreted as an estimation of the calorific value of the sample. These areas, which can be considered an estimation of the high heating value, expressed in J·g⁻¹ are reported in Table 2.

Besides inoculum, all the samples showed an exothermic peak between 250 °C and 300 °C, which corresponds to the fast oxidation of the organic matter. Indeed, if the estimated heating values are considered it can be noticed that the maximum is obtained for the mixture of wheat straw and inoculum, although the value for wheat straw sample is quite similar. On the other hand, if the inoculum alone is considered, it can be noticed that the smallest peak is obtained, but also at higher

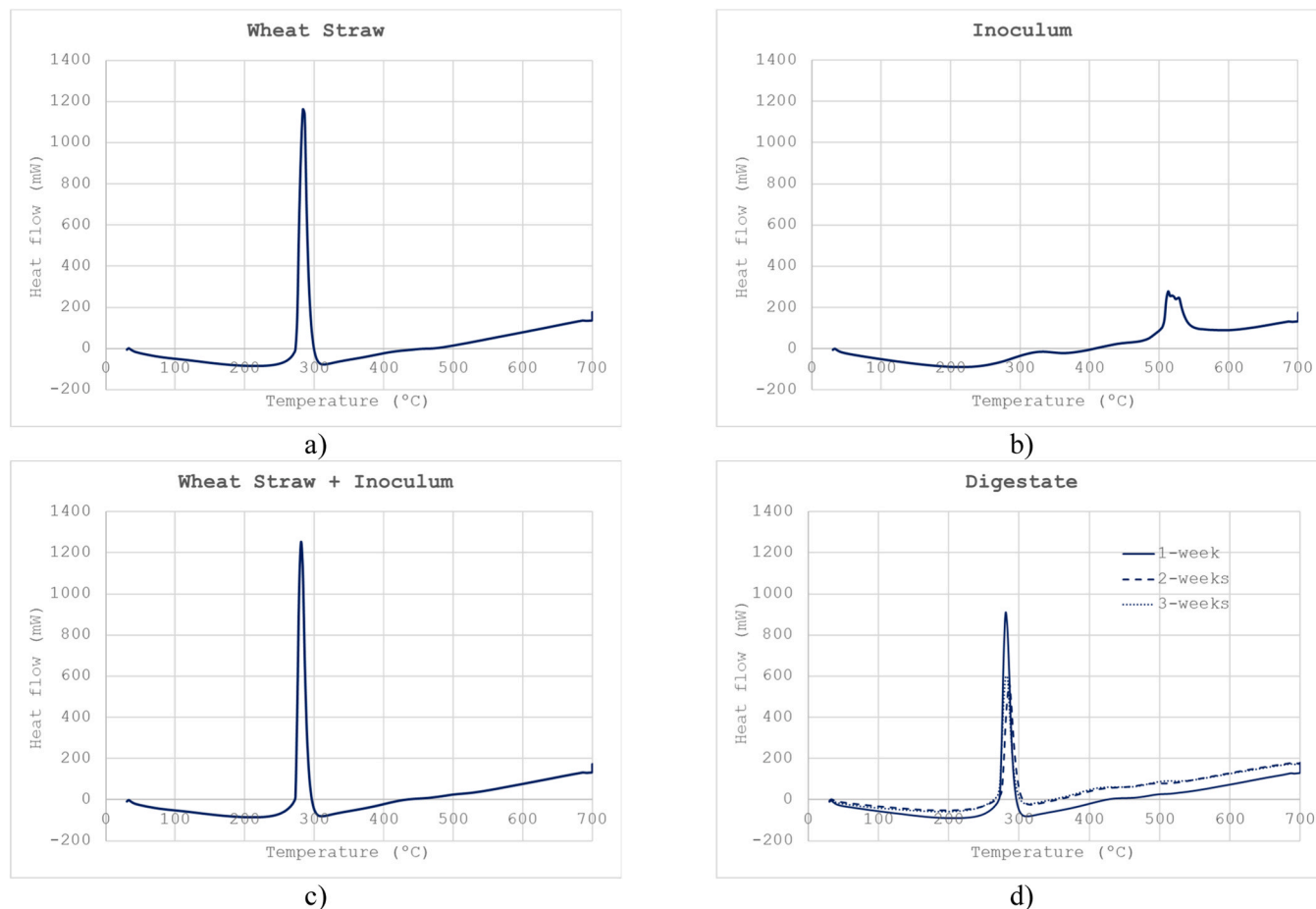


Fig. 5. DSC curves for a) wheat straw b) inoculum c) mixture of wheat straw and inoculum before digestion d) digestate.

Table 2

Estimated high heating value as the area beneath the DSC peak and temperature at which the peak is obtained.

	Estimated high heating value (J·g ⁻¹)
Wheat Straw	4868.30
Inoculum	2069.04
Wheat straw + inoculum	4911.24
1-week digestate	4040.73
2-weeks digestate	3054.90
3-weeks digestate	2852.76

temperatures (between 500 °C and 600 °C), as it cannot be considered as a biofuel and no significant exothermic reaction is produced due to its combustion. When addressing the digestate results, it is clear that the longer the biogas production process the lower the amount of combustible matter. Because of that 1-week digestate peak is significantly smaller than wheat sample. Moreover, when the biomethane production was reported in Fig. 1, it was noticed that the first 10 days of digestion led to the most of the biomethane production, which is consistent with the fact that the 2-weeks digestate DSC shows a significant difference if compared to 1-week digestate, but not if compared to 3-weeks digestate. Therefore, it seems that after a certain period of time, the biomethane production is reduced and the heating value of the digestate stabilizes.

If the DSC wheat straw results are compared to biomethane production, it seems that in terms of energetic potential, biogas production is a better option than combustion. Nevertheless, it has to be taken into account that the digestate could be used for combustion, as the temperature in which the peak is produced is the same at which the wheat straw peak is produced, and there is still matter susceptible to

combustion which leads to an exothermic reaction. Therefore, both processes combined (biogas production and digestate combustion) lead to a more efficient energetic approach. Nevertheless, the use of digestate as a fuel requires the drying of the sludge, which is already a common practice to treat the digestate (Czekała et al., 2022; Salamat et al., 2022; Baştabak and Koçar, 2020). However, in order to consider the digestate as a fuel, it is important to use an efficient and low cost drying process such as air drying or drying beds, so it can be economically viable.

3.3. Kinetic results

As previously pointed out, three different kinetic methods were applied to define the activation energy (E_a). Fig. 6 shows the activation energy values obtained for each dimensionless conversion factor, for the three kinetic methods and the four different samples. For almost each sample and method, the figures show a strong dependency between the activation energy and the conversion factor which indicates complex compositions with different thermal stability (Fernandez et al., 2020).

In all the samples, the differences between KAS and FWO methods are negligible as both methods approach the data in a similar way. When addressing Friedman method differences are found although the same tendency can be observed for every method, which means that the results are consistent. When considering wheat straw samples, E_a increases up to $\alpha = 0.4$, and then, it stabilizes around 170 kJ·mol⁻¹ which is consistent with previously published literature (Singh et al., 2022).

On the other hand, inoculum activation energy presents an increasing tendency that can be divided into two different stages due to the change of slope which can be found around $\alpha = 0.55$. On the other hand, when addressing the mixture of biomass and inoculum it can be

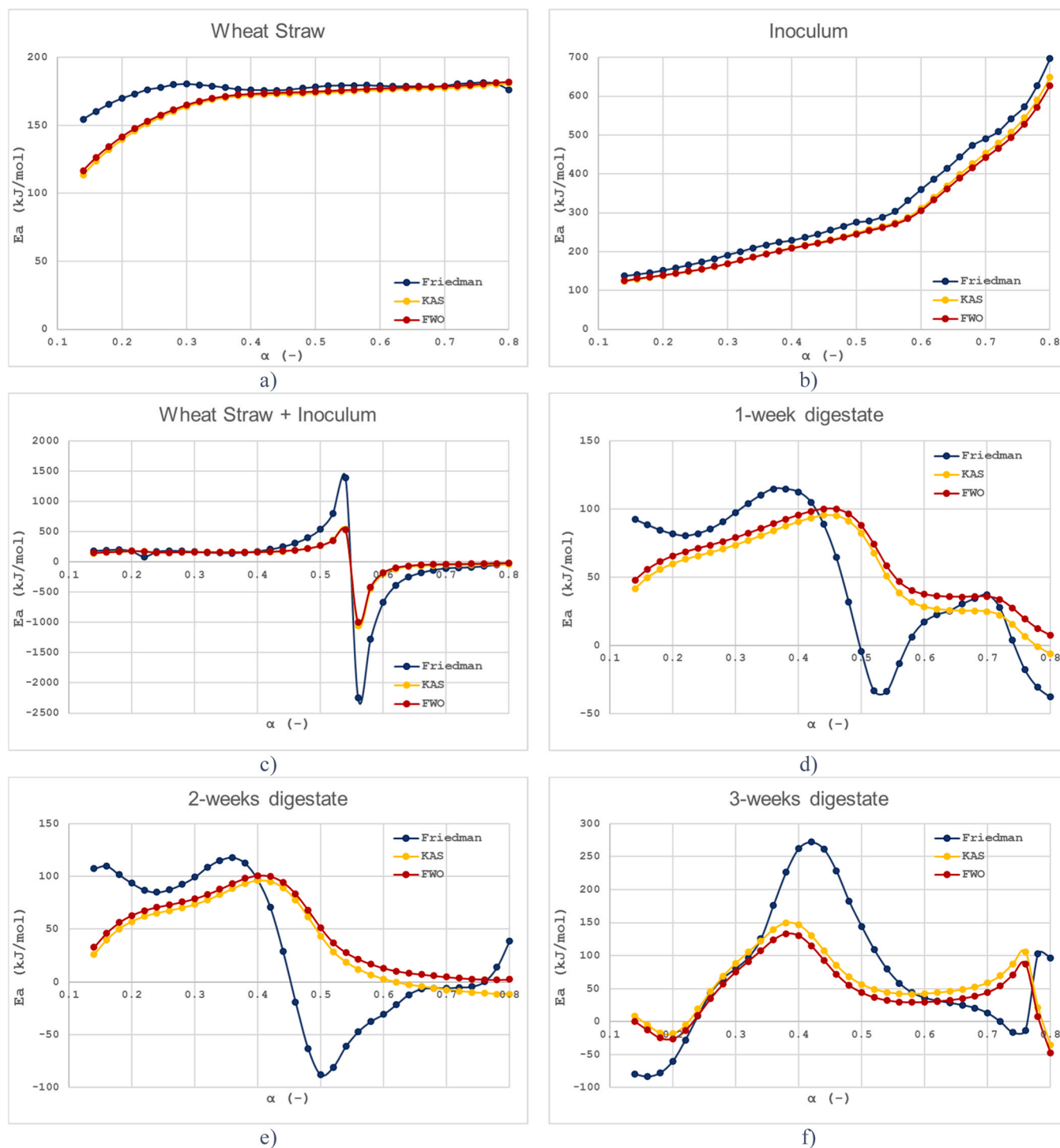


Fig. 6. Kinetic results for a) wheat straw b) inoculum c) mixture of wheat straw and inoculum before digestion d) digestate waste after 1 week biogas production e) digestate waste after 2 weeks biogas production f) digestate waste after 3 weeks biogas production.

noticed that E_a slightly varies up to $\alpha = 0.4$, resulting into an almost straight line. However, after reaching $\alpha = 0.4$, E_a increases and when reaching $\alpha = 0.5$ drops to negative values, which later stabilize around $0 \text{ kJ}\cdot\text{mol}^{-1}$. Finally, if activation energy values for digestate are considered it has to be noticed that the activation energy significantly decreases in comparison with the other samples. Besides that, the tendency remains similar and consistent with previous studies, although presenting lower values (Akor et al., 2021) which can be explained to the differences of the samples and the kinetic methods applied. When addressing digestate, significant differences are found when comparing

Friedman method to KAS or FWO. This fact can be explained due to the application of conversion rate data when applying Friedman, as it might relies more on the experimental conditions (Vyazovkin et al., 2011a; Jiang and Wei, 2018). Nevertheless, it has to be taken into account that while 1-week and 2-weeks digestate present similar curves and behaviours, 3-weeks digestate curves are remarkable different. Although every digestate sample finds its maximum E_a around $\alpha = 0.4$, in 3-weeks digestate the activation energy initially decreases until $\alpha = 0.2$, and then a positive slope is defined up to the maximum E_a , while in the other digestate samples E_a increases from the beginning until $\alpha = 0.4$. These

different stages are consistent with the phases that the digestate undergoes during the thermogravimetric analysis: devolatilization in two phases and carbonaceous char decomposition (dehydration has been removed), as the activation energy maximum values are obtained during the pyrolysis. In this stage E_a values locate around 100 kJ/mol (greater for 3-weeks digestate) which is slightly lower than the values reported by Karaeva et al. (Karaeva et al., 2022a). This can be explained due to the digestion residence time, as higher times lead to higher pyrolysis E_a values.

To comparatively assess the results of different methods and samples, average activation energy values are reported in Table 3, together with the preexponential factor (A) that will be used for the determination of thermodynamic parameters:

From the reported results, it can be noticed that slightly differences are found among methodologies, especially when considering the Friedman method. Indeed, for the mixture of wheat straw and inoculum, the average activation energy is significantly lower due to the negative peak produced between $\alpha = 0.5$ and $\alpha = 0.6$; however, when addressing digestate, that showed a different curve, and the average values are not so different among the three methods. Moreover, when addressing Friedman average value for 3-weeks digestate sample, a significantly high value is obtained. The discrepancies presented in the Friedman method can be explained due to the fact that it is an integral method and that both KAS and FWO lie in a very similar mathematical model. However, Friedman curves present more similarities to the TGA curves, which makes easier to visualize the stages as the peaks are more intense. The fact that Friedman method assumes a single step kinetics instead of a first-order decomposition (KAS and FWO assumption) contributes to the discrepancies noted (Vyazovkin et al., 2011b). Therefore, the error associated to the use of this model should be considered.

The average values reported in Table 3 for digestate are significantly lower the values reported in previous research (Liu et al., 2020; Karaeva et al., 2022c), which can be explained due to the fact that in this study the complete pyrolysis process is considered instead of the devolatilization stages, but also the biomass used for the anaerobic digestion. If only activation energy values of the main devolatilization process are considered (between 0.3 and 0.5 conversion factor), high values are obtained, due to the break of stronger chemical bonds in the molecules. Using the average values of activation energy and the equations mentioned in Section 2.3, the values for enthalpy, Gibbs free energy, and entropy are defined and reported in Table 4:

If enthalpy values are considered it can be noticed that every pyrolysis reaction is endothermic as all the values are positive. Inoculum absorbs the greatest amount of heat, followed by wheat straw. On the other hand, the mixture of wheat straw and inoculum, and digestate samples present significantly lower values. The fact that the digestate do not require high activation energies nor present high enthalpy values suggest that the sample could be used for pyrolysis production, therefore, providing a second stage of re-using waste after biogas digestion. Which means that not only combustion of the dried digestate is an option for waste valorisation but also, it can be submitted to a different process that might lead into a more efficient fuel. Nevertheless, when approaching DSC results it was noticed that 3-weeks digestate released the lowest amount of heat, however, when addressing the pyrolysis results it can be noticed that the enthalpy values are higher than for 1-

week and 2-weeks digestate. Therefore, it seems that after long digestion period the digestate might be more suitable for pyrolysis than for direct combustion.

When considering Gibbs free energy and entropy values the same tendency can be found, besides 3-weeks digestate. Those high values together with enthalpy data and the fact that the entropy presents negative values, although low, suggest that no spontaneous reaction was produced in any test, which means that the efficiency of the reaction is reduced. Regarding the 3-weeks digestate sample, anomalies can be found when addressing both Gibbs free energy and entropy. As the kinetic results also showed deviations for this sample, so it does the thermodynamic parameters. The obtained are in range with previously reported data, although it has to be noticed that wide ranges of values for each thermodynamic parameter have been reported in literature (Petrović et al., 2021; Nishu et al., 2024).

Considering the results from the kinetic analysis the pyrolysis of anaerobic digestion sludge can be considered a viable and efficient process for the thermal conversion of these organic wastes into useful products. The thermogravimetric analysis focuses on the process and biochar production; however, pyrolysis byproducts include also syngas and bio-oil. These byproducts have been assessed through previously published literature, focusing on wheat straw samples with similar proximate analysis values as the sample used in the present study. As noted in TGA curves, the pyrolysis residue for wheat straw was ~23 % of the total mass. This biochar is slightly lower to the values reported by Biswas et al., 2017 (Biswas et al., 2017) (32.4 % at 450 °C), Mani et al., 2011 (Mani et al., 2011) (31 % at 500 °C) or Sedmihradská et al. (2020) (24.3 % at 800 °C). When syngas and bio-oil are considered, the differences between the data reported in bibliography increase, as the values vary between 15.6 % and 58 %. Similar trend is found when addressing bio-oil, which varies between 11 % and 52 %. As the pyrolysis process carried out in this study reached 800 °C, the results from Sedmihradská et al. (2020) can be used to approach syngas and bio-oil production, as not only provides data for this temperature, but also presents the most similar char yield. Therefore, it can be estimated that syngas and bio-oil yields are 22.4 % and 52 % respectively. According to these results, the liquid byproduct represents the highest energy yield (41.8 %) followed by char (39.7 %) and gas (14.4 %). Nevertheless, literature indicates that wheat straw pyrolysis should be carried out at lower temperatures (between 500 °C and 600 °C) in order to obtain optimal biochar. When digestate pyrolysis is addressed, it was noted that biochar increased up to ~30 %. According to Basinas et al., 2023 (Basinas et al., 2023) biochar produced at 700 °C showed the optimal characteristics for pollutant absorption, prevention of nutrient leaching, and enhancement of soil water retention. They also determined the non-condensable gases (12.3 %) and the bio-oil (46.6 %). Although this values significantly depend on the feedstock and the digestion conditions, it is clear that these byproducts can be used as fuels contributing to the minimization of environmental impacts associated with the management of anaerobic digestion sludge (Karaeva et al., 2023).

4. Conclusions

The present study provides a comparative analysis of anaerobic digestion and biomass pyrolysis, using wheat straw biomass. The results

Table 3
Average activation energy (E_a) and preexponential (A) values for each method and sample.

	KAS		FWO		Friedman	
	E_a (kJ·mol ⁻¹)	A (min ⁻¹)	E_a (kJ·mol ⁻¹)	A (min ⁻¹)	E_a (kJ·mol ⁻¹)	A (min ⁻¹)
Wheat Straw	166.49	6.17E+12	167.71	6.16E+12	176.42	7.38E+12
Inoculum	281.88	5.71E+12	277.39	5.72E+12	309.42	7.55E+12
Wheat straw +Inoculum	57.21	5.98E+12	63.90	5.97E+12	20.58	6.64E+12
1-week digestate	53.27	6.24E+12	60.79	6.22E+12	48.99	6.84E+12
2-weeks digestate	38.69	6.22E+12	46.86	6.20E+12	31.76	6.73E+12
3-weeks digestate	59.35	6.40E+12	46.29	6.43E+12	72.34	6.38E+12

Table 4
Thermodynamic parameters for each sample and method.

	Enthalpy (kJ·mol ^{−1})			Gibbs free energy (kJ·mol ^{−1})			Entropy (kJ·mol ^{−1} ·K ^{−1})		
	Friedman	KAS	FWO	Friedman	KAS	FWO	Friedman	KAS	FWO
Wheat Straw	171.45	161.52	162.73	505.44	485.25	487.72	−0.55	−0.53	−0.53
Inoculum	304.45	276.91	272.42	771.49	715.92	706.89	−0.78	−0.73	−0.72
Wheat straw + Inoculum	15.56	52.19	58.88	189.37	260.56	273.46	−0.29	−0.35	−0.36
1-week digestate	43.65	47.93	55.45	239.67	247.91	264.27	−0.33	−0.34	−0.35
2-weeks digestate	26.44	33.37	41.54	205.22	217.03	233.90	−0.30	−0.31	−0.32
3-weeks digestate	96.68	68.00	57.48	155.27	78.06	83.30	0.18	0.15	0.17

showed that both processes present unique advantages and different challenges.

Anaerobic digestion showed significant advantages due to high methane yields, effective waste management, and a reduced carbon footprint. However, the effectiveness of the process and of the involved microorganisms depend on the heat input, that is, 35 °C in the case of this essay. Biogas produced can be a viable renewable energy source, but also biomass pyrolysis generates valuable by-products such as biochar, bio-oil, and syngas, which can be used in various energy applications.

The kinetic analysis showed that the activation energy for pyrolysis, determined using the Friedman, KAS, and FWO methods, falls within the range of 166.49–176.42 kJ/mol, consistent with literature values for different biomasses. Thermodynamic parameters such as enthalpy, Gibbs free energy, and entropy indicate that the pyrolysis reactions are endothermic and non-spontaneous. It has to be pointed out that the 3-weeks digestate sample showed significant deviations in both kinetic and thermodynamic parameters, suggesting that further studies should consider a deeper approach to its kinetic behaviour. Nevertheless, from an energy perspective, pyrolysis requires higher temperatures and thus more energy input compared to anaerobic digestion, which is a simpler process. However, the byproducts of pyrolysis, particularly biochar, which due to the high carbon content, presents high potential to be used as a fuel for combustion or gasification.

Additionally, this study has approached the integration of both processes by performing the pyrolysis of digestate. The combination of both technologies provides a secondary valorisation route, and a potentially efficient waste management strategy. The results obtained from the thermal analysis suggest that the digestate retains enough volatile matter to be effectively used in pyrolysis, providing an alternative use for this waste product. Nevertheless, the generated digestate after full biogas production should be further assessed to properly understand the potential of this material as an energetic source. For future research, it is suggested to delve into the optimization of conversion processes and the evaluation of the energy and environmental performance of integrated systems. Future challenges include addressing issues related to logistics, waste management and economic viability on a commercial scale, as well as exploring innovative approaches to maximize the efficiency and sustainability of these technologies.

CRedit authorship contribution statement

Blanca Castells: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Alfonso García Álvaro:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Isabel Amezcua:** Writing – original draft, Methodology, Investigation. **David León:** Writing – review & editing, Methodology, Investigation, Data curation. **Antonio Gascó:** Writing – review & editing, Validation, Methodology, Investigation, Funding acquisition. **Marcelo F. Ortega:** Writing – review & editing, Visualization, Validation, Supervision. **Daphne Hermosilla:** Visualization, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Daphne Hermosilla reports financial support was provided by Spain Ministry of Science and Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Data availability

No data was used for the research described in the article.

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