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Simultaneous production of biogas and volatile fatty acids through anaerobic digestion using cereal straw as substrate

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ABSTRACT

Cereal straw is one of the most abundant wastes worldwide, with 30.000 million tons produced per year. Bioconversion of this residual material into carboxylates by anaerobic digestion could potentially replace conventional production based on fossil feedstocks (oil). In this work, fundamental issues of this bioconversion have been explored, including: different kinds of straw (wheat, barley and rye), biomass size reduction, mass balances and modeling of the different steps of the digestion. Under optimum conditions, 44% of the raw material was effectively converted into VFAs (mainly acetate) when barley was used as substrate. Wheat and rye straw presented lower conversion rates due to the higher lignin content compared to barley straw. According to the modeling proposed, methanogenesis and hydrolysis presented very similar reaction rates, which resulted in a simultaneous production of VFAs and biogas. In view of these results, a process integration is proposed where biogas covers the thermal needs of the biotransformation of barley biomass into VFAs.

1. Introduction

Volatile fatty acids (VFAs) have multiple applications in the chemical, food and pharmacy industry (Lee et al., 2014; Zhou et al., 2018). Conventionally, these compounds are synthesized using oil derivatives as a feedstock. The industry market shows prices between €500 and €2500 per ton depending on the compound, but further rises are expected due to oil production decline. Short chain VFAs, such as acetic, propionic, butyric or valeric and medium chain fatty acids as caproic, are produced as intermediates during the anaerobic digestion process (Magdalena and González-Fernández, 2020). This bioprocess is normally addressed to the production of bioenergy such as biogas, rich in methane, generated after a sequence of different biological stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis). Accumulation of volatile fatty acids (VFAs) typically takes place since methanogenesis is often a limiting step with very slow reactions rates.

Several organic waste have been explored as a feedstock for VFAs production: sewage sludge, household wastes and microalgae among others (Komemoto et al., 2009; Li et al., 2018; Strazzera et al., 2021). A wide range of VFAs

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Table 1
Characteristics of substrates and inoculum.

Parameter	Wheat straw	Barley straw	Rye straw	Inoculum
Total solids (g/kg)	935.4 ± 1.5	920.0 ± 2.5	946.8 ± 4.1	17.9 ± 0.1
Volatile solids (g/kg)	896.0 ± 0.9	869.5 ± 2.6	904.6 ± 19.1	12.8 ± 0.1
COD (mg/g)	1422 ± 15	1351 ± 30	1523 ± 5	4941 ± 855

concentrations (from 2400 to 11,000 mg VFA/L substrate) and kinetics have been reported as consequence of the complex and variable chemical composition of these substrates. This disparity hinders the widespread implementation of this sustainable VFA production platform. Besides this, waste materials might contain pathogens and pollutants (such heavy metals or xenobiotics), which also endanger the viability of the production process and the later commercialization of the VFAs in certain industry sectors (such food or chemistry) (Angelidaki and Sanders, 2004). Moreover, VFAs production could be non compatible with biogas production in urban waste or wastewater treatment plants, where priority should be given to energy production in form of biogas or biomethane. In this context, highly available organic substrates must be considered as potential feedstock for VFAs production.

An ideal substrate should present homogeneous composition and lack of pollutants in order to guarantee a reliable product. In this framework, leftovers from widespread crops can play a key role on the quest for VFA production. Large quantities of lignocellulosic by-products, such as straw, remain unused. The world production of cereal is growing according to the latest FAO report with 3.3 billion tons of straw generated each year (FAO, 2021; Ruiz et al., 2015). Introducing this amount of organic matter into the chemical industry can replace the oil-based production (Wan Mahari et al., 2022). However, the implementation of the biotransformation these wastes into VFAs requires an in-depth understanding of yields, rates of the biochemical steps and the effect of biomass pretreatments.

In this work the optimal operational conditions of the acidogenic fermentation for the production of VFAs using straw obtained from wheat, barley and rye were studied.

Batch experiments were performed with these biomasses with and without physical pretreatment. The biochemical transformations were modeled through the validated equations and formulations applied for biogas production, and mass balances were calculated in order to assess bioconversion of different substrates. In addition, a novel biorefinery approach, including simultaneous biogas and VFAs generation, was herein validated. This proposed configuration maximizes bioconversion of biomass into bioproducts and guarantees the energy needs of the process.

2. Materials and methods

2.1. Feedstocks and anaerobic inoculum

Agricultural residues (straw) from wheat, barley and rye crops were collected from cereal crops placed in Soria province (Spain). Physical pretreatment was carried out to obtain particles of 1 and 4 mm (Eraky et al., 2021; Sharma et al., 1988) by means of a grinder (Moulinex, France). The anaerobic inoculum used was collected from the anaerobic digester of Soria sewage treatment plant (Spain). Chemical composition of the substrates in terms of dry matter, organic matter and Chemical Oxygen Demand (COD) content are shown in Table 1.

2.2. Biochemical methane potential tests for VFA

2.2.1. Anaerobic digestion tests

The anaerobic biodegradation of the agricultural residues was evaluated in batch mode for 40 days. Tests were started up according to the BPM methodology (biochemical methanogenic potential) with serological glass bottles of 120 ml and a working volume of 70 ml and a headspace volume of 50 ml. Temperature conditions were maintained at 35 ± 0.5 °C in an incubator (Hotcold-GL Selecta, Spain) provided with an orbital stirring plate (Rotabit Selecta, Spain). The inoculum to substrate ratio was set at ratio 1.5:1 in terms of volatile solids (Sawatdeenarunat et al., 2015). 1.5 g of $CaCO_3$/L were added as a buffer to avoid changes in pH (Magdalena and González-Fernández, 2020). The bottles were flushed with nitrogen to remove air from the system and achieve anaerobic conditions at the beginning of the experiment.

Three parallel tests were set up per substrate. Control tests with the inoculum were included to measure the endogenous production of biogas and VFA from the added with the inoculum. Endogenous production was subtracted from the measurements of the test with the residual substrates. Biogas generated was daily measured by water displacement. Volume of biogas was corrected to normal conditions considering the ambient pressure and operation temperature. Biogas composition was analyzed with a ‘‘GeoTech Biogas 5000’’ gas analyzer.

2.2.2. Production of VFAs

5 ml of digestate were withdrawn from each flask after 3, 9, 16 and 21 days of incubation. Samples were filtered through 0.45 micrometers prior to centrifugation at 5000 rpm (Centromix, Selecta). Subsequently, a second centrifugation at 13,000 rpm (Micro Star 17, VWR) was performed before filtration through 0.22 micrometers. VFAs concentration was determined through a gas chromatographer (Agilent 7820). In order to stablish a mass balance, VFAs and CH_4 were transformed into COD according to the stoichiometry equations for oxidation of each VFA presented in Eq. (1)–(4). In terms of mass ratios, the following values were calculated: acetic acid (1.07 g DQO/g VFA), propionic acid (1.51), isobutyric acid (1.82), butyric acid (1.82), isovaleric acid (2.04), valeric acid (2.04) (Yu et al., 2012). Methane conversion (4 g DQO/g methane) is also shown in Eq. (5).

$$\text{Acetic acid: } C_2H_5O_2 + 2O_2 \rightarrow 2\,CO_2 + 2\,H_2O \tag{1}$$

$$\text{Propionic acid: } C_3H_6O_2 + \frac{7}{2}O_2 \rightarrow 3\,CO_2 + 3\,H_2O \tag{2}$$

$$\text{Butyric acid: } C_4H_8O_2 + 5O_2 \rightarrow 4\,CO_2 + 4\,H_2O \tag{3}$$

$$\text{Valeric acid: } C_5H_{10}O_2 + \frac{13}{2}O_2 \rightarrow 5\,CO_2 + 5\,H_2O \tag{4}$$

$$\text{Methane: } \frac{1}{2}CH_4 + O_2 \rightarrow \frac{1}{2}\,CO_2 + H_2O \tag{5}$$

2.2.3. Analytical procedure

Total Solids (TS) and Volatile Solids (VS) were analyzed according to methods of the American Public Health Association Standard Methods (Apha, 2012). TS and VS were calculated drying the substrates for 24 h in an oven at 105 °C and subsequent incineration in a muffle furnace for 30 min at 550 °C.

Chemical Oxygen Demand (COD) of each substrate was analyzed with the standard methodology. Therefore, 15 g of straw sample were digested with 15 ml of potassium dichromate and 35 ml of silver sulfate with sulfuric acid. After 2 h of digestion at 148 °C the absorbance at 600 nm was measured in a spectrophotometer (Genesys 10uv, Thermo Spectronic).

2.3. Mass balances

Mass balances in terms of COD were calculated for each BMP test according to the following Eq. (6): (Metcalf & Eddy, 2014):

$$COD_0 = COD_t CH_4 + COD_t VFAs + COD_t \text{ anaerobic biomass} + COD_t \text{ biomass} \tag{6}$$

Where COD_0 corresponds to the initial *COD* concentration of organic matter at beginning of the experiment, $COD_t\ CH_4$ corresponds to the organic matter transformed into methane and $COD_t\ VFAs$ is the COD concentration transformed into volatile fatty acids. COD_t *biomass* is the substrate not transformed from the original form. COD_t *anaerobic biomass* corresponds to the anaerobic microorganisms generated during anaerobic digestion, which was in turn calculated according to the following Eq. (7):

$$\text{Anaerobic Biomass} = \frac{Y(COD_{in} - COD_{out})}{1 + K_d * (ET)} \tag{7}$$

Where Y is the cell production coefficient (estimated as 0.08 g VS/g COD), K_d is the endogenous decay coefficient (0.03 g/gd) and ET is the elapsed time (40 days).

2.4. Modeling

2.4.1. Biogas production

Biogas evolution along the BMP tests was adjusted to the Gompertz model developed in Eq. (8). This approach allows to assess the effect of biomass pretreatment by particle reduction in terms of rate of biogas generation and duration of the lag phase due limitations in the hydrolysis phase. (Jyi Lay et al., 1996; Nopharatana et al., 2007):

$$P(t) = P \cdot e^{\left\{-e^{\left[\frac{R \cdot e}{P} \cdot (\lambda - t) + 1\right]}\right\}} \tag{8}$$

Where $P(t)$ is the cumulative methane production at standard temperature and pressure (mL CH_4/g VS), P is the potential methane production (mL CH_4/g VS), R is the maximum methane production rate (mL CH_4/g VS· day), λ the lag phase (days) and t the elapsed time (days). The model fit to the experimental data was achieved by least squares methodology (Cano et al., 2014).

Table 2
State variables for the hydrolysis, acidogenesis and methanogenesis phases.

Process	S_0	S_1	S_2	X_1	X_2	Reaction rate	
Hydrolysis	−1	1	0	0	0	$r_{hydrolysis} = \left(\mu_0 \cdot \frac{S_0}{k_x \cdot X_1 \cdot S_0}\right) \cdot X_1$	(12)
Acidogenesis/Acetogenesis	0	−1	1-Y_a	Y_a	0	$r_{acidogenesis} = \left(\mu_a \cdot \frac{S_1}{k_a + S_1}\right) \cdot X_1$	(13)
Methanogenesis	0	0	−1	0	Y_m	$r_{methanogenesis} = \left(\mu_m \cdot \frac{S_2}{k_m + S_2 + S_2^2/K_i}\right) \cdot X_2$	(14)

Table 3
Parameters of the Gompertz model for the production of biogas from wheat straw, barley straw and rye straw. (M) Mesophilic conditions with particle size of 1 (1) or 4 (4) mm.

Substrate	Experimental biomethane production (ml)	**R**. Biomethane production rate (mL CH_4/gVS·d)	**λ**. Lag phase (days)	**P**. Biomethane potential production (mL CH_4/gVS)	Regression coefficient
Wheat Straw M1	288	12.51	0	288	98.63%
Barley Straw M1	317	14.89	0	317	98.17%
Rye Straw M1	304	12.30	0.43	304	99.26%
Wheat Straw M4	167	7.82	3.01	167	98.57%
Barley Straw M4	241	10.66	2.68	241	98.49%
Rye Straw M4	168	6.67	3.29	168	98.73%

2.4.2. Anaerobic digestion phases

A three-reaction based process was used to evaluate the duration of each of the phases of the anaerobic digestion (hydrolysis, acidogenesis and methanogenesis). In this sense, the values found in the fitting of the equations of ADM1 (Anaerobic Digestion Model 1) were compared in the different assays corresponding to different substrates. This approach allows to evaluate rates of VFAs generation and consumption, providing the fundamental knowledge required for a process implementation. Simplified equations obtained from ADM1 were used according to (Donoso-Bravo et al., 2015). Table 2 shows the Eqs. (9)–(11).

$$Hydrolysis : S_0 \xrightarrow{r_{hydrolysis}} S_1 \tag{9}$$

Where S_0 is the particulate organic matter and S_1 is the soluble organic matter.

$$Acidogenesis : S_1 \xrightarrow{r_{acidogenesis}} Y_{X_1} \cdot X_1 + (1 - Y_{X_1}) \cdot S_2 \tag{10}$$

Where S_2 is the VFAs equivalent; X_1 is the acidogens concentration, and Y_{X1} is the acidogens yield.

$$Methanogenesis : S_2 \xrightarrow{r_{methanogenesis}} Y_{X_2} \cdot X_2 + (1 - Y_{X_2}) \cdot CH_4 \tag{11}$$

Where X_2 is the methanogens concentration and Y_{X2} is the methanogens yield.

For the hydrolysis phase, the Contois model was chosen in spite of the classic first-order equation (Ramirez et al., 2009). Thus, a reduction of the hydrolysis rate due to mass transfer limitations was considered. Monod kinetics were used in acidogenesis/acetogenesis and methanogenesis phases. No inhibitions were considered since under BMP conditions concentrations of substrates were considerable reduced. Eqs. (12)–(14) are shown in Table 2 and parameters description in Table 4. The model's validation was developed in Excel Office software.

2.5. Process integration

In order to study the energy self-sufficiency of a hypothetical digester devoted to VFAs production, an energy balance was calculated considering standard dimensions and configurations of anaerobic digesters. This part of the study was motivated by the simultaneous occurrence of methane and VFAs detected in all assays. Average outdoor conditions and standard size digester were considered. Performance of barley BMP tests was used as reference for this calculation due to its higher methane and VFAs production rate as can be seen in Section 3.2. A 3000 m^3 cylindrical digester placed in a temperate area with 15 °C of average temperature, and fed with barley straw at a concentration of 100 g/L was used. Energy demand of the hypothetical digester can be calculated with Eq. (15):

$$Q_T = Q_D + Q_S \tag{15}$$

Where Q_T is the total thermal energy demand, Q_D is the energy demand to maintain the mesophilic temperature inside the reactor and Q_S is the energy demand to increase the temperature of the inlet substrate from ambient temperature to 35 °C. Q_D can be calculated considering the total heat losses through the surfaces of the digester (wall, cover and ground) as described in Eq. (16)

$$Q_D = Q_w + Q_c + Q_G \tag{16}$$

Table 4
Stoichiometric and kinetic parameters for the hydrolysis, acidogenesis and methanogenesis phases of wheat, barley and rye straw anaerobic degradation.

	Parameter	Description	Units	Value Wheat	Value Barley	Value Rye
Hydrolysis parameters	μ_0	Hydrolysis coefficient	d^{-1}	0.5	0.42	0.6
	K_X	Contois affinity constant	$gCODs \cdot gCODx^{-1}$	1	2.2	3
	S_0	particulate organic matter	gCODs	Variable values		
Acidogenesis parameters	μ_a	Maximum growth rate of the acidogenesis	d^{-1}	4	4	4
	K_a	Affinity constant acidogenesis	$gCOD \cdot L^{-1}$	0.05	0.05	0.05
	X_a	Acido/aceto concentration	gCODx	125	125	125
	Y_a	Acidogens yield	$gCODx \cdot gCODs^{-1}$	0.05	0.05	0.05
	S_1	soluble organic matter	gCODs	Variable values		
Methanogenesis	μ_m	Maximum growth rate of the methanogenesis	d^{-1}	0.56	0.52	0.52
	K_m	Affinity constant of metanogenesis	$gCOD \cdot L^{-1}$	10	10	10
	K_i	Inhibition constant of metanogenesis	$gCOD \cdot L^{-1}$	200	200	200
	X_m	Methanogens concentration	gCODx	225	225	225
	Y_m	Methanogens yield	$gCODx \cdot gCODs^{-1}$	0.05	0.05	0.05
	S_2	VFAs equivalent	gCODs	Variable values		

Where Q_W stands for the heat losses through the vertical walls of the cylinder, which is the thermal energy transferred from liquid content of the digester to the air. Qc is the heat losses emitted through the cover of the digester (heat transfer between biogas and air). Q_G correspond to the heat losses due to the heat transfer through the ground and the reactor. The values of Q_W, Q_C and Q_G can be calculated according to the Eq. (17).

$$Q = U \cdot A \cdot (T_o - T_i) \tag{17}$$

Where U stands for is the heat transfer coefficient of each surface (W/m$^2\cdot$ C), A (m^2) is the area of each surface considered (walls, cover or ground), T_i is the temperature inside the digester (35 °C) and T_o is average ambient temperature of the chosen location. Heat transfer coefficient (U) was calculated following the PN-EN ISO 6946 (International Organization for the Standarization, 2021) in Eq. (18):

$$U = \frac{1}{R_i + \sum_{i=1}^{n} \frac{d_i}{k_i} + R_o} \tag{18}$$

Where R_i and R_o are the resistance to the heat transfer through the internal and external surfaces of the digester, respectively. K is the thermal conductivity coefficient of the digester thickness layer of a polystyrene material with a value of 0.05 W/m· °C. The heat transfer coefficients inside and outside the reactor were 4000 and 400 W/m^2 °C, respectively (Deublein and Steinhauser, 2008).

The energy flow required to heat the substrate was calculated according to Eq. (19).

$$Qs = F_s \cdot C_{H_20} \cdot (T_{ext} - T_i) \tag{19}$$

Where F_S is the substrate yield per day, C_{H_20} is the specific heat capacity of water (4.18 kJ/kg °C), and T_{ext} and T_i are the temperatures outside and inside the reactor.

Energy demand of the hypothetical VFAs production was considered taking into account the average yields of CHP (Combined Heat and Power) system (39 and 50% for electrical and thermal energy) (Malet et al., 2023). Since the VFAs concentration reached in the test presented moderate values (less than 5 g COD/l), a concentration step was considered in order to produce a final solution useful for industrial application. One of the most mature technologies for carboxylate concentration, an electrodialysis system with an average consumption of 2 kWh per kg of COD as VFA, was considered in this preliminary analysis (Andersen et al., 2015).

3. Results and discussion

3.1. Particle size reduction

Particle size clearly impacted the biogas yields and the rates of anaerobic digestion. An increase of 71.8 ± 3.5% was obtained in tests with 1 mm substrate size compared to 4 mm (523.0 ml biogas g/VS *vs.* 304.4 ml biogas g/VS) for wheat straw. This trend was observed in the three substrates (Fig. 1). Gompertz model was applied for the biomethane production in the six cases, obtaining the fitting depicted in Fig. 2 and the parameter values of Table 3. Higher rates of biogas production, expressed as R in the model, indicate a reduction of the limiting step of the hydrolysis phase. In this sense, the reduction of the lag phase was evidenced by the lower λ values. In view of these results, 1 mm particle size biomass was chosen for the experiments addressed to mass balances studies and biochemical steps modeling.

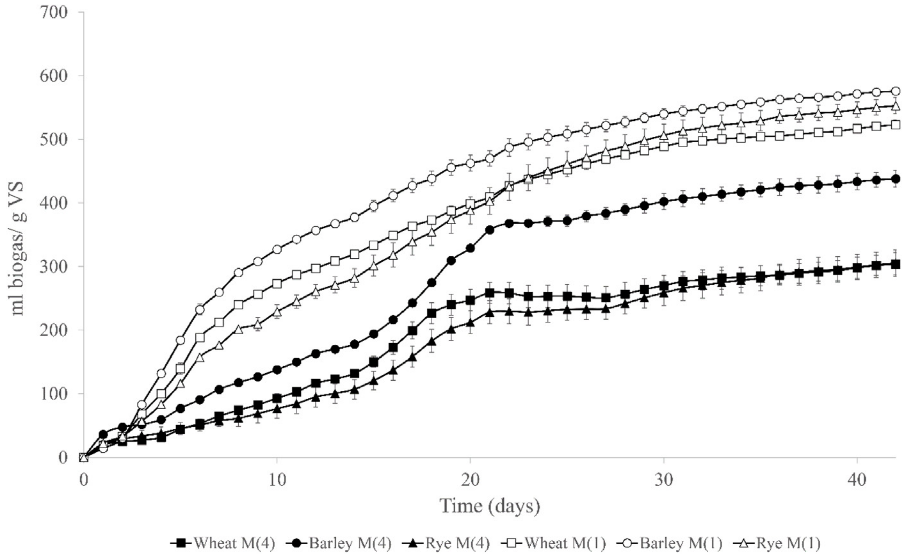

Fig. 1. Biogas production (ml) per amount of volatile solid (g) for wheat, barley and rye straw under mesophilic conditions (M) of 35 °C with particle size of 1 (1) or 4 (4) mm.

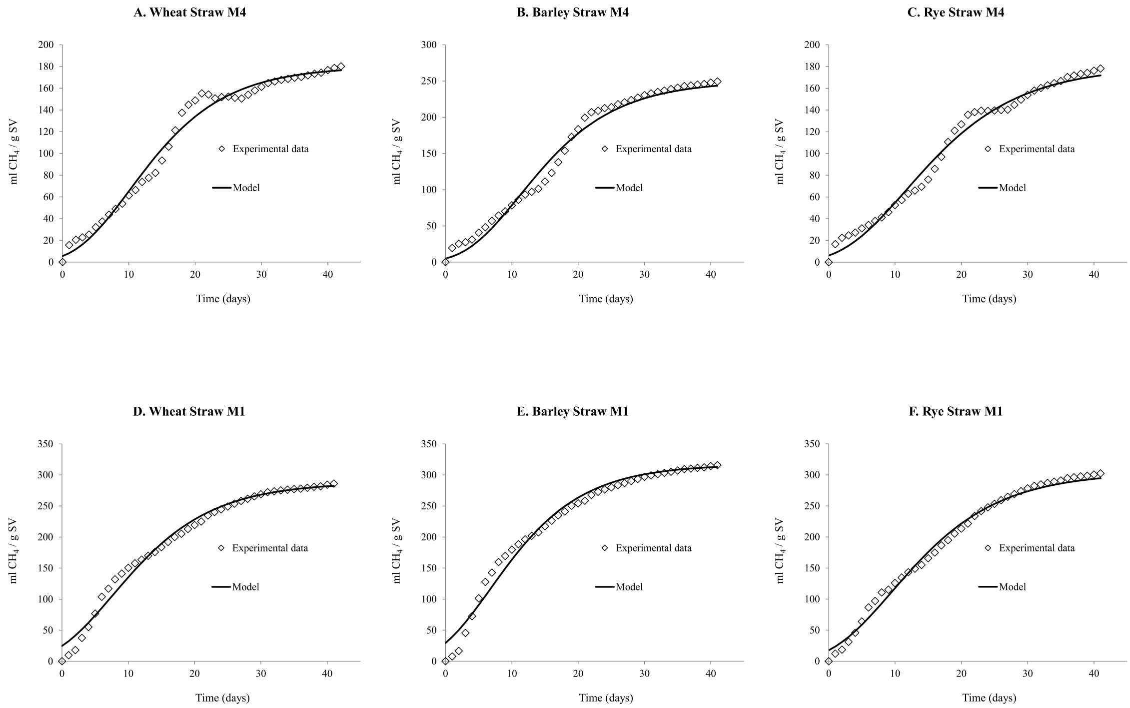

Fig. 2. Biomethane production (ml) per amount of volatile solid (g) for wheat, barley and rye straw under mesophilic conditions (M) of 35 °C with particle size of 4 (a,b,c) or 1 mm (d, e, f). Gompertz modeling..

Similar increases as a consequence of substrate pretreatment were reported in previous works. For instance, Rajput et al. (2018) reported a R value of 4.97 ml biogas/gVS· d for wheat straw without pretreatment and 9.98 ml biogas/gVS· d with a chemical pretreatment (which corresponded to a 101% increase), Petersson et al. (2007) found an increase of 34% applying an enzymatic hydrolysis to rye straw and Theuretzbacher et al. (2015) reported a 116% increase with a steam explosion pretreatment of wheat straw. In this work, significantly higher rates of biogas production were detected during the exponential phase, averaging 12.30 and 14.89 ml CH_4/gVS· d for rye and barley straw, respectively, using a simple mechanical pretreatment. Reduction of particle size resulted in a decrease of the lag phase of the anaerobic digestion, from

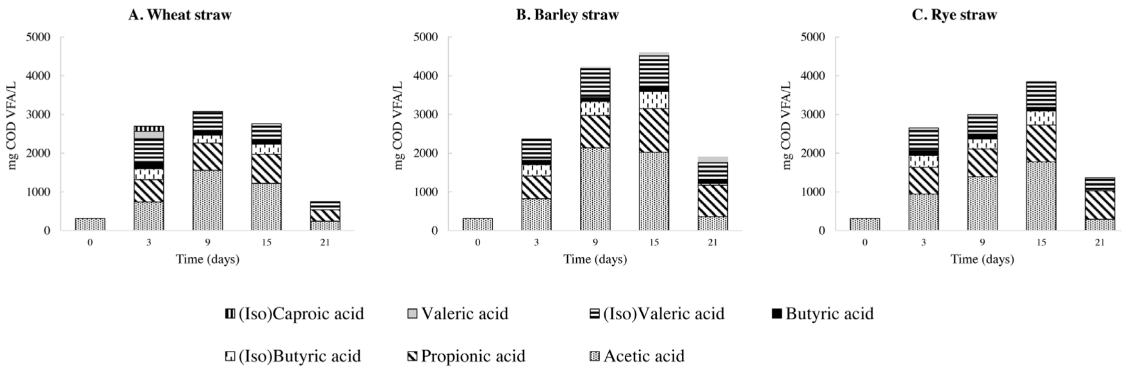

Fig. 3. Changes of total volatile fatty acids concentrations and throughout the test with wheat, barley and rye straw.

2.7–3.3, to 0–0.4 days, in barley and rye straw, respectively. This reduction of the lag phase is similar to the values achieved in literature with chemical pretreatments in the same kind of biomass (Rani et al., 2022). This modeling analysis revealed two important issues regarding particle size reduction: hydrolysis phase is the limiting step of the target bioprocess and higher conversions of biomass into VFAs will be achieved by mechanical size reduction. Particle size reduction improves methane yield since cellular compounds of substrate are released increasing the available surface for microorganisms and therefore raises biodegradability (Dai et al., 2019). Sharma et al. (1988) reported the effects of particle size of agricultural and forestry residues on biogas generation through batch experiments increasing 84% the biomethane production from rice straw.

3.2. VFAs production along substrate biodegradation

The time course of VFAs concentrations is shown in Fig. 3. A progressive increase in VFAs concentration was detected in the three substrates with maximum values in barley assays of 4590.9 mg COD/L after 15 days of incubation. Significantly lower values were detected in case of rye and wheat straw by day 15: 3844.1 mg COD/L and 2760.3 mg COD/L, respectively. These considerable higher concentrations (20 and 65% in VFAs produced respectively) could be explained with the lower lignin content of the barley straw compared to wheat and rye straw as studied in previous studies. Satpathy et al. (2014) reported a lignin content of 8.9% for barley straw, Sun et al. (2002) found a 16.8% for wheat straw and Salehi et al. (2014) reported a 17.8% for rye straw. VFAs concentration decreased from day 15 onwards as a result of the higher methane production rate compared with the acid production rate at this stage.

Similar conversion yields have been reported with different substrates: microalgae, sludge or green wastes. Feng et al. (2022) found a maximum VFAs production of 4001 mg COD/L with food wastes as substrate and Magdalena and González-Fernández (2020) found a maximum production of 4887 mg COD/L using microalgae biomass. Waste activated sludge is the most reported substrate in literature, where VFAs production varies between 3580 and 6070 mg COD/L after intense chemical or thermal pretreatments (Jiang et al., 2021; Liu et al., 2018). VFAs production with lignocellulosic substrate has not been extensively studied. Park et al. (2015) studied the VFAs production with rice straw, which present a similar lignin content than wheat and rye (Shoaib et al., 2018), obtaining a VFAs concentration of 3350 mg COD/L without pretreatment and 4800 and 5100 mg COD/L with chemical pretreatment consisting of 2% NaOH and HNO_3, respectively, and thermal hydrolysis at 150 °C (Liu et al., 2021) reported a maximum yield of 5815 mg COD/L after 10 days using CeO_2 nanoparticles with wheat straw.

Acetic acid accounted for most of the carboxylate concentration in all the tested conditions, followed by propionic and isovaleric (Fele Žilnik and Likozar, 2019; Wei et al., 2021). On the same way, Fig. 3 shows the VFAs distribution for each substrate. The acetic acid concentration varies according to the days of transformation, reaching an average of 47 ± 4% of total carboxylate concentration between days 9 and 15. The short length chain carboxylates propionic and isovaleric acid reached their maximum production by day 21 of incubation, representing up to 45 ± 9% of total VFAs prevailing in the anaerobic broth.

3.3. COD balances for each substrate

Mass balances in terms of COD allow for an estimation of the total biomass conversion into bioproducts. Fig. 4 depicts the mass balances in terms of % of initial COD transformed after 3, 9, 15 and 21 days of operation. Barley biomass exhibits the highest transformation with more than 70% of the initial COD transformed into methane and VFAs. As mentioned in Section 3.2, this value could be explained by the specific barley lignocellulosic structure, which contains less percentage of lignin than wheat and rye straw, thus resulting in an easier biological degradation. Wheat and rye straw resulted in conversion efficiencies of 50 and 53%, respectively. Barley tests resulted in a 44.3% biomass conversion to VFAs,

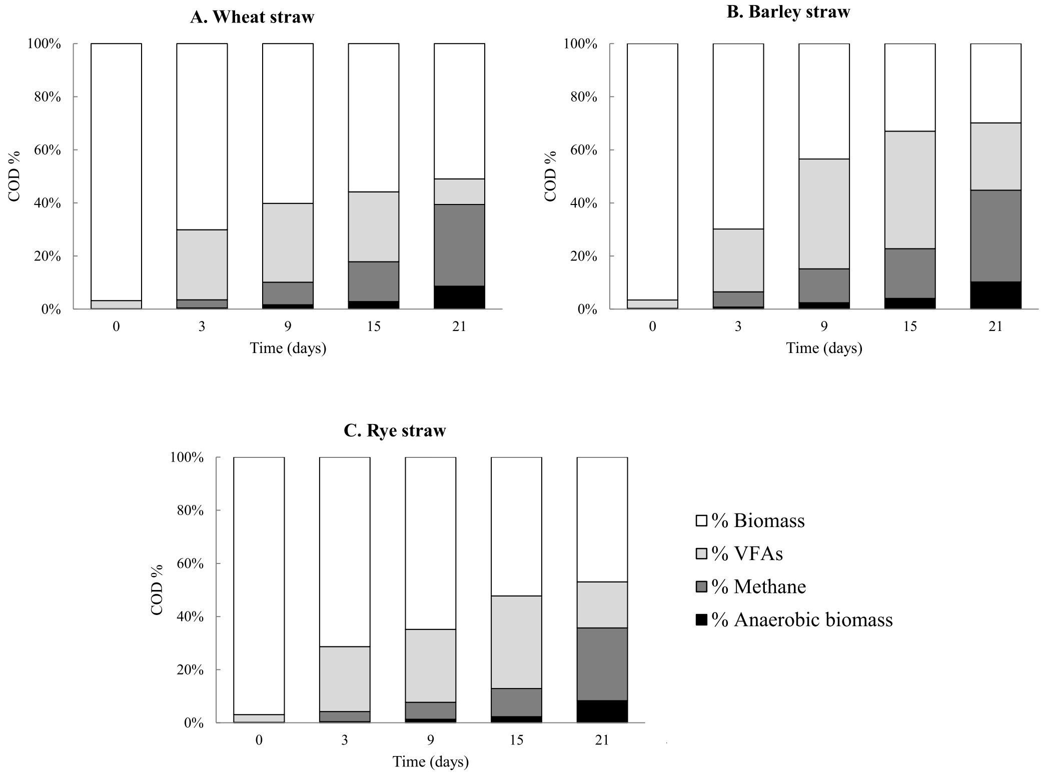

Fig. 4. Time course of COD distribution during the anaerobic digestion of wheat, barley and rye straw.

considerably higher than that of rye and wheat with a 34.8 and 29.7%, respectively. It is worth to note that production of carboxylates with barley biomass presented values similar to those documented in optimized processes with specific biomasses and pretreatments. For instance, Magdalena and González-Fernández (2020) observed a 41.5% bioconversion of microalgae biomass pretreated with enzymes (proteases and cellulases).

The tests herein conduct showed a high rate of organic matter conversion of cereal residues into VFAs. The maximum concentrations of VFAs were detected after 9–15 days of operation. According to previous studies, carboxylates peaks were identified between 8–12 days of anaerobic incubation (Kuruti et al., 2017). In this context, particle size reduction with a simple physical pretreatment (mechanical grinding) is a sufficient biomass conditioning to ensure an effective bioconversion in comparison with other more complex and expensive pretreatments (Thamizhakaran Stanley et al., 2022; Uthirakrishnan et al., 2022). Mechanical pretreatments are commonly used devices at full-scale to reduce the size of feedstock and to increase methane production, improving mixing, heat, and mass transfer into the anaerobic digesters of biogas plants (Garuti et al., 2022). On the other hand, other pretreatments (thermal, chemical or biological) require considerable higher installation and operation costs, reducing the viability of the bioenergy or bioproducts generation.

Beside this, barley biomass is a very cheap and widespread substrate with a non-wood fibres annual production over 50 million tons worldwide (Tye et al., 2016).

3.4. Modeling of biochemical stages

Modeling of each of the process steps is depicted in Fig. 5. Similar values were found for the key parameters of the model applied for each substrate as seen in Table 4. Some parameters ($\mu_{a,}$ $K_{a,}$ K_m and Y_m) were defined in the model and compared with previous works under mesophilic conditions (Donoso-Bravo et al., 2015; Siegrist et al., 2002).

The anaerobic process was characterized by a slow hydrolytic phase, which appears as the limiting step of the process with values of the hydrolysis coefficient of 0.42 and 0.6 d^{-1} for barley and rye straw, respectively. At this point, it must be stressed that the hydrolysis coefficients were comparable to the described for other substrates used for biogas and VFAs production (Girault et al., 2012). Similarly, the methanogenesis rate exhibited medium-low values. (Donoso-Bravo et al., 2015) reported 0.4 d^{-1} for μ_m for sewage sludge degradation under mesophilic conditions, while in this study the values found ranged between 0.52 and 0.56 d^{-1} (slightly higher than those recorded in the hydrolysis phase). However, this fact should not be regarded as a limitation for VFAs production. This factor reduces the potential inhibition due to excessive

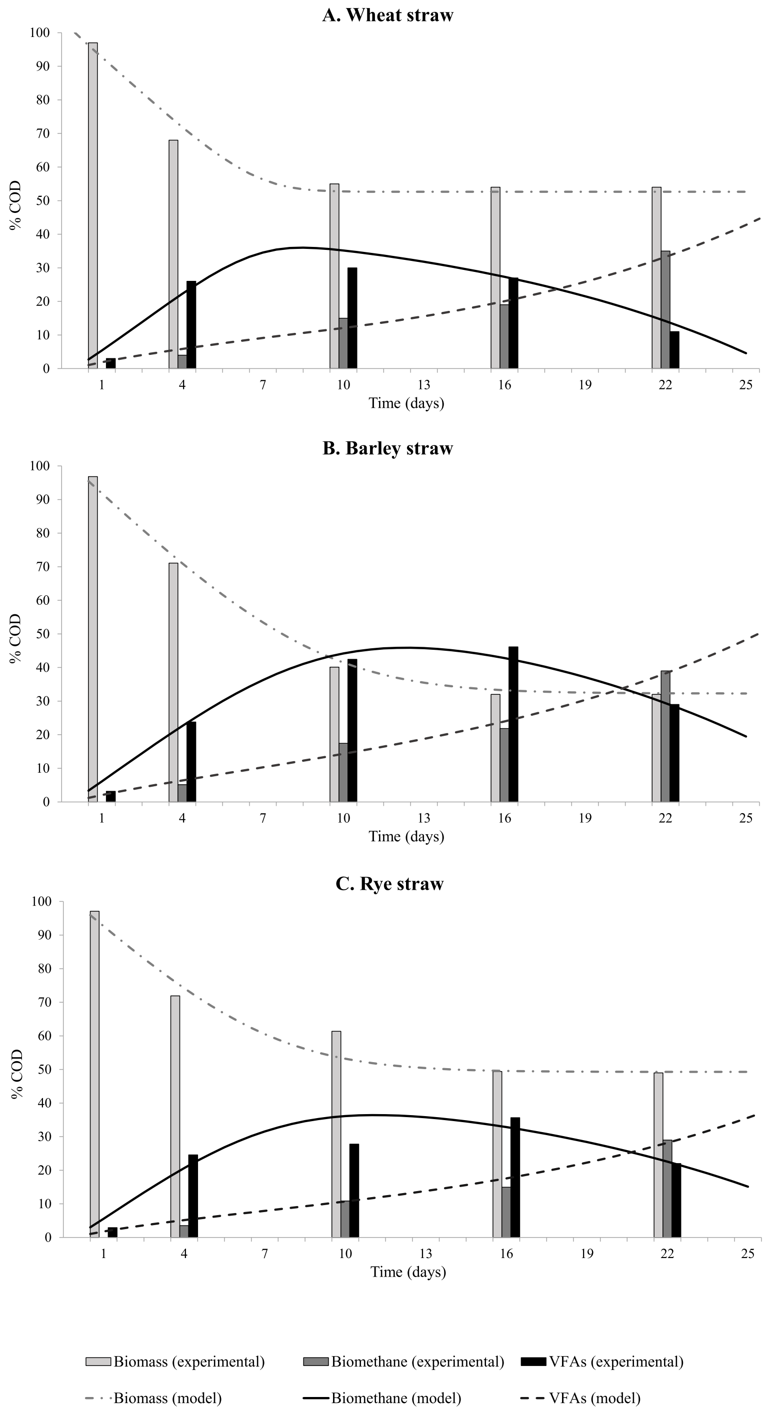

Fig. 5. Time course of the experimental and modeled COD balance throughout the trial for wheat, barley and rye straw.

acids accumulations since carboxylates are concomitantly produced and consumed resulting in moderate concentrations during the fermentation process. Experimental results confirmed the optimal retention times for optimization of organic acids production: 9 days for wheat and barley straw and 12 days for rye straw. It is estimated that this should be the appropriate hydraulic residence time for a system operated under continuous feeding conditions. Simple modeling through the validated formulations of the ADM1 confirmed very close rates of hydrolysis and methanogenesis (between

0.42–0.52 d^{-1}), resulting in a slow release and degradation of carboxylates, which in turns resulted in simultaneous production of biogas and VFAs. In view of these results, a carboxylate production process supported by the energy of the produced as biogas during the fermentation was proposed in Section 3.5.

3.5. Process integration

The simultaneous VFAs and biogas production observed during straw digestion must not be regarded as a disadvantage since anaerobic digesters require energy in form of heat, and the biogas inherently produced along with VFAs during anaerobic digestion can be used for this purpose. In the sense, the conventional design of biogas plants where a boiler burns the biogas to maintain digester temperature will be adequate for VFAs production.

According to the energy balance carried out in the theoretically designed facility devoted to the fermentation of 9000 kg per day of barley straw working with an HRT of 22 days, a total potential production of 3191 kg of VFAs per day could be reached with a simultaneous production of 1718 m^3 of methane, equivalent to 17,000 kWh of energy. Considering a cogeneration system with an average electric and thermal energy efficiency of 39 and 50% respectively, 6529 kWh of electrical energy and 7732 kWh of thermal energy per day would be available for biogas operation and VFAs recovery through the electrodialysis process (Malet et al., 2023). At this point it must be noticed the information about energy consumption in carboxylate concentration is scarce. According to Andersen et al. (2015) 2 kWh of electricity are required per kg of COD as VFA concentrated, using one of the most mature technologies for this purposes (electrodialysis). This concentration step will result in an electricity demand of 6382 kWh. On the other hand, thermal demand of the digester was estimated in 5390 kWh according to the energy balance. Therefore, a digester provided with a CHP system will provide sufficient energy for heat supply and carboxylate concentration. The energy surplus, which accounted for more of 20%, will guarantee the possible heat and electricity demand peaks due to seasonality variations.

4. Conclusions

VFA production from cereal straw offers multiple advantages over fermentation of other residual materials. Barley straw supports a 30 and 35% higher conversion rate than rye and wheat straw, respectively, likely due to the lower lignocellulose content favoring its biodegradability. Mechanical pretreatment mediated an increase in both the yields bioconversion of straw into biogas and carboxylates, and the kinetics of the anaerobic digestion process (up to 40%). The modeling of the anaerobic digestion phases helped to understand the process and to establish a strategy to maximize the production of VFAs, thus establishing HRT of between 9 and 12 days, resulting in a VFAs total concentration of 4600 mg/L. Finally, the simultaneous production of VFAs and biogas allows an adequate design of the process, where the energy demand will be totally covered by the biogas produced in the anaerobic digester.

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CRediT authorship contribution statement

Alfonso García Álvaro: Conceptualization, Methodology, Writing. **César Ruíz Palomar:** Methodology. **Daphne Hermosilla Redondo:** Supervision. **Raúl Muñoz Torre:** Supervision, Review and editing. **Ignacio de Godos Crespo:** Review and editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article

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