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A Mass Balance-Based Method for the Anaerobic Digestion of Rice Straw

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Abstract: Current rice straw disposal practices have serious repercussions on the environment and, in addition, do not consider its energy potential. On the contrary, the anaerobic digestion of rice straw makes it possible to produce renewable energy and to reintroduce into the soil the nutrients present in the digestate, at the same time, reducing greenhouse gas emissions from paddies. For rice straw of different geographical origin, by applying a mass balance method to the digester, the minimum requirements in terms of conditioners (nitrogen, phosphorus and potassium) and water, which allow obtaining the maximum production of methane, were calculated. The results obtained show that after the first 30 days (hydraulic retention time) for each ton of rice straw digested, the daily water consumption varies considerably from one country to another, from a minimum value of 1.5 m^3/d to a maximum of 4.3 m^3/d. After the same time, the addition of nitrogen and phosphorus is only required for the optimal anaerobic digestion of Indian rice straw. The low presence of these elements in Indian straw requires an addition of 3 kg/d of urea and 1.5 kg/d of superphosphate to compensate for the lack of nitrogen and phosphorus, respectively. In all the examined cases, the concentration of potassium, even if higher than the optimal value, does not reach levels that can significantly affect the methane production.

Keywords: rice straw; anaerobic digestion; chemical conditioners; water consumption; calculation method

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1. Introduction

The availability of fossil fuels closely linked to geopolitical aspects, together with their progressive depletion and their harmful impact on the environment, requires growing attention to renewable energy sources. Among all the options available, biomasses, especially those of agricultural origin, represent a source of great interest. The advantage linked to the use of agricultural waste is particularly evident considering that the two most important objectives to be achieved in the current century are the increase in the availability of food and energy.

In the case of rice, which, albeit to varying degrees, is grown all over the world [1], production in 2017 was estimated at over 750 million tons [2] with a mass of residual straw which, depending on the variety of rice, is from 0.41 to 3.96 times the rice produced [2,3]. The management of this agricultural residue currently takes place through open field burning (OFB) or soil incorporation (SI) [4–7] practices which, although advantageous, have a strong environmental impact. The first method sterilizes the soil but causes the production of particulate matter and greenhouse gases. The second method prevents the organic de-pauperization of the soil [8–10] but causes CH_4 emissions [11–13] whose extent depends, among other factors, on the flooding methods [14–19], on the Fe content in the water used for irrigation [20–23] and on the conditioners used [24–27]. The IPCC

[28] estimates CH_4 emissions from paddies on average at 1.82 kg/d/ha and forecasts an increase in the coming years due to global warming [29].

Following previous research [30] which suggested the collection and baling (CB) of rice straw (RS), this study proposes the energy enhancement of RS through anaerobic digestion (AD), a practice already followed in several countries including India [31,32] and China [33]. The choice of AD is linked to the fact that this method applied to RS has fewer limitations than pyrolysis and gasification which are, currently, applications still under study, to overcome problems such as the low production of syngas and the high presence of tar in the latter [34]. Anaerobic digestion compared to combustion [35,36], which is currently considered the best methodology from an economic point of view for the energy enhancement of RS [34], has the important advantage of also producing compost, which is a useful conditioner since it is rich in nutrients (N, P, K, Si, etc.) and is also able to counteract soil depletion due to its high carbon content.

Figure 1 shows a typical scheme of a digester for biogas production. In the plant, the RS is first reduced in size in the milling unit and then introduced into the blender together with water and organic and inorganic substances. The resulting mixture is then fed into the digester where the biogas (mainly CH_4 and CO_2) is produced. The extracted digestate is sent to the dewatering unit, which separates it into two fractions: the compost, mainly solid, and the sludge which is mainly liquid and which can be totally or partially (in case of drainage) recirculated.

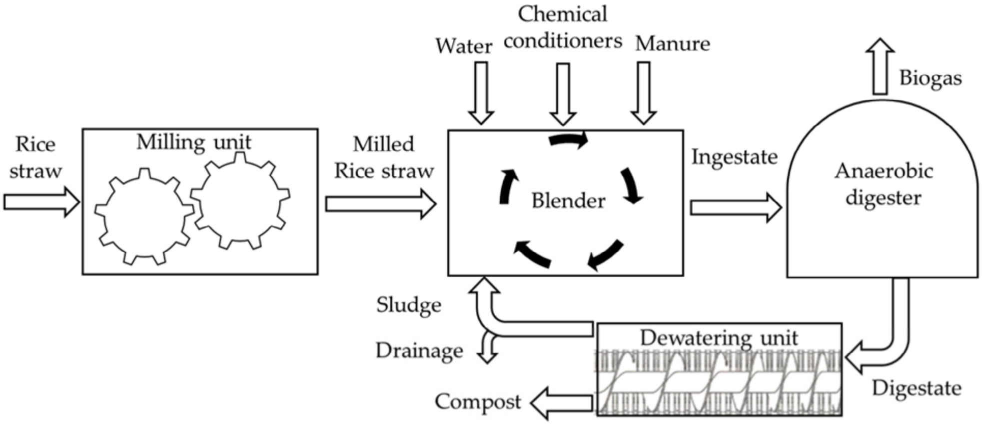


Figure 1. Schematic of a biogas plant.

Many studies on the AD of RS are reported in the literature. Some of these address aspects related to both physical and chemical pre-treatments [32,37–40] which, together with the amount of volatile solids (VS) contained in the biomass [41], influence methane production. The temperature (20–45 °C for mesophilic AD and 46–60 °C for thermophilic AD), pH (5.5–6.5) and mixture homogeneity are basic variables for the process as reported in [42–45]. The dependence of the biogas yield on the bacterial population and the growth rate of the latter, both strongly correlated to the amount of nutrients (N, P and K), are examined in [42,46–48]. The effect of the carbon to nitrogen ratio (C/N) in the digester affecting bacterial growth is reported in [49–59] and an optimal range of 20 to 30 is suggested. For RS showing C/N values higher than optimal, several studies reported examples of co-digestion with animal manure [60–62] which is useful for correcting the nutrient ratios and for supplying the initial bacterial load [32].

Conversely, in the current literature there is no evidence of analytical studies based on mass balances, which aim to optimize the anaerobic digestion process of RS. Although mass balances are proposed in [63], the methods and objectives are different. Firstly, the authors in [63] carried out an experimental activity while the study proposed here is numerical. In addition, in study [63], the mass balances aim to evaluate the quantities of

C and nutrients in the digestate as well as in the compost and sludge while in the present work, the main aim is to minimize the consumption of both chemical additives and water.

In this work, the proposed method has been applied to rice straw of different geographical origins and a method has been suggested for the daily control of the digester, which is valid for both the start-up phase and for the steady-state management.

2. Materials and Methods

2.1. Rice Straw Characteristics and Biogas Production

The chemical composition of RS changes according to the rice variety [64], soil characteristics [65] and fertilization methods [66]. Conversely, moisture content simply depends on how long the straw is left on the field. The results of a literature review on the characteristics of RS in different countries are shown in Table 1. The values used for the following calculations are written in bold and refer to a specific analysis among those considered. Table 1 reports the mass fraction percentages for C and for nutrients (N, P and K) and the C/y ratios ($y = N, P, K$). The mass fraction of C in the table is not split in two parts (cellulosic and lignin) because only the cellulosic fraction produces methane but both fractions are used to evaluate C/y. In the table, all the other elements contained in the rice straw are lumped in the term Others (Oth). The water (W) content was assumed equal to 20% (W) because for the CB, a higher humidity could cause spontaneous fermentations. In Table 1, as in the following tables and figures, the names of the countries examined are reported using the country code abbreviations based on ISO 3166-1 alpha3.

Table 1. Ultimate analysis of rice straw (mass fraction percentages) and C/y.

State	C	N	P	K	Oth	C/N	C/P	C/K
			[% db [a]]				[−]	
USA [67,68]	38.24–41.00	0.70–0.87	0.61	1.70–2.09				
	38.24	**0.87**	**0.61**	**2.09**	**58.19**	**43.95**	**62.69**	**18.30**
THA [69–71]	35.95–38.7	0.34–1.19	0.14	1.94			**[–]**	
	38.30	**0.62**	**0.14**	**1.94**	**59.00**	**61.77**	**273.57**	**19.74**
MYS [72,73]	35.51–39.98	0.53–4.43	0.27	1.70				
	35.51	**0.53**	**0.27**	**1.70**	**61.99**	**67.0**	**131.52**	**20.89**
CHN [74–76]	38.14–52	0.20–1.23	0.12–0.29	0.01–1.04				
	38.14	**0.51**	**0.29**	**1.04**	**60.02**	**74.78**	**131.52**	**36.67**
IND [77,78]	**38.80**	**0.20**	**0.05**	**1.02**	**59.93**	**194.0**	**776.0**	**38.04**
ITA [79,80]	**41.20**	**1.00**	**0.11**	**0.96**	**56.73**	**41.2**	**374.55**	**42.92**

[a] db: dry basis.

The attitude of an organic waste to produce biogas (biogas potential—BP) depends on its content in volatile solids (VS) which are a fraction of the total solids (TS). The amount of VS and the BP are variable as is the chemical composition of the RS [32,60]. Table 2 reports the values used in this study. Starting from the reported data (Table 2), for each ton of RS, a biogas yield of 270 m^3 at room condition (25 °C, 1 atm) can be expected [60,81].

Table 2. Biogas production: parameters.

Parameters	**Value**
TS	89% wet basis [60]
VS	71% TS [60]
BP	0.43 $m^3 kg_{VS}^{-1}$ [81]
CH_4	55% [31,81,82,83]
CO_2	45% [31]

During *AD*, in addition to biogas, negligible quantities of other chemical substances (N_2O, H_2S, NH_3) and water can be produced which will not be considered in the calculations [84]. Moreover, it has been assumed that the biogas production rate, closely related to the growth of bacteria, is described by the Gompertz function [85] as better explained later.

2.2. Plant Features: Anaerobic Digester and Dewatering Unit

The system assumed as reference for this study is a single-stage low solids anaerobic digester ($LSAD$) with a dry matter (DM) content lower than 15% [86].

In the digester, the production of biogas requires a period of time, called Hydraulic Retention Time (*HRT*). The *HRT* depends on both chemical (i.e., *VS* content) and physical (i.e., dimensions of the incoming biomass) factors and it affects the size of the digester. In this study, a *HRT* of 30 days [31,87] was assumed as reference.

After the *HRT*, the biomass residues are extracted from the digester and a new fresh charge of ingestate is introduced. The characteristics of the digestate change according to the variety of rice while the composition of both the solid fraction (e.g., compost) and the liquid one (e.g., sludge) depends not only on the digestate but also on the characteristics of the dewatering unit [88] sketched in Figure 1.

The dewatering unit considered in this study is a typical screw press separator. Inside the separator, the digestate flows along a cylindrical screen and it is partially drained. At the end of the screw axle, digestate is pressed against a steel filter completing the dewatering process. The dimensions of the particles contained in the digestate and the size of the pores of the filter determine the separation factor of the device [89].

Equation (1) reports the separation factor (S_f) which is the ratio between the mass of compost (M_{com}) and the mass of digestate (M_{dig}):

$$S_f = \frac{M_{com}}{M_{dig}}. \tag{1}$$

In this study, the numerical value for S_f was determined referring to [90], using Equation (2), which is valid for a percentage content of dry matter (*DM*%) in the range of 4.5%–10%:

$$S_f = \frac{DM\% - 4.618}{13.428}. \tag{2}$$

Equation (2) reports that, for a specific dewatering unit, S_f depends on the quantity of *DM* in the digestate—the higher the *DM* content in the digestate, the higher the percentage of compost. The distribution between compost and sludge of the i_th constituent of the digestate (*DM*, *C*, *N*, *P*, *K*) is reported in Table 3 [90].

Table 3. Percentages of digestate constituents in compost (i_th, com) and sludge i_th, com valid when *DM*% = 7.3 [90].

Digestate i_th Constituent	$\boldsymbol{i\_th, com}$ [%]	$\boldsymbol{i\_th, slu}$ [%]
DM	61.8	38.2
C	64.2	35.8
N	31.4	68.6
P	51.5	48.5
K	28.2	71.8

To obtain a digestate with *DM*% = 7.3 [90], at each charge of RS, the amount of water to be added must be evaluated based on the *DM* already present in the digester. The *DM*% contained in the substrate of a stirred digester is the same found in the digestate (ideal condition).

2.3. Carbon to Nutrients Ratios

As written above, the growth of bacteria and the biogas yield depend on the amount of nutrients. In the literature [47,49–59], the optimal quantities of nutrients are related to the C content into the digester (Table 4).

Table 4. $LSAD$ suggested C/y ratios.

y	C/y [kg · kg^{-1}]
N	20–30 [49–53]
P	150–320 [50,57]
K	16–77 [59]

The comparison between the ratios reported in Table 4 and those of Table 1 highlights the need for an addition of N and P whose quantities must be determined taking into account that a fraction of the C contained in RS leaves the reaction environment as biogas (about 40% of the total amount). On the contrary, the comparison between the C/K ratios warns against an excessive accumulation of K into the digester that could reduce the production rate of biogas.

2.4. Chemical and Natural Conditioners: Characteristics

Usually, to regulate the C/y too high, an addition of chemical conditioners is recommended: urea (46% N), superphosphate (20% P) and potash (63% K). Furthermore, as written above, the use of manure (e.g., pig, cattle, chicken) is useful to increase the quantity of N and the initial bacteria population [32,60–62].

Table 5 highlights the ultimate analysis and the moisture content W for the chemical and natural conditioners selected for this study.

Table 5. Conditioners ultimate analysis and moisture content: mass fraction percentages.

Conditioner	C	N	P	K	Oth	W
			[% db [a]]			[% wb [b]]
Urea—CH_4N_2O	20.00	46.70	-	-	33.30	2.00
Superphosphate—$Ca_3(PO_4)_2$	-	-	19.50	-	80.50	1.00
Potash—KOH	-	-	-	63.00	37.00	8.00
Pig manure [91]	1.15	0.32	0.08	0.10	98.35	67.60

[a] db dry basis; [b] wb wet basis

2.5. Methods

Based on the literature [49–59], the C/y ratios reported in Table 4 are assumed as technical factors to be respected to maximize the biogas production in an $LSAD$.

Figure 2 provides a schematic of the system with all the masses used to perform the balance on the digester.

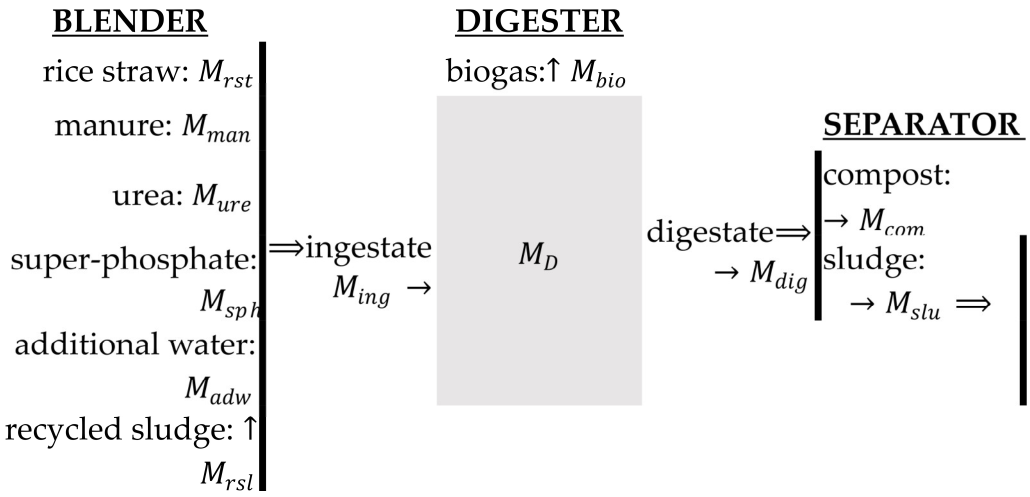


Figure 2. Schematic of the system with the different wet masses.

The mass balances were performed by imposing the conservation of W and of the chemical species, in particular C, N, P and K.

In this study, each wet mass M_j (e.g., M_{rst}, M_{ure}, M_{com}, M_{dig}, etc.) was divided into two normalized fractions: one of water and one of dry matter. The latter was further subdivided into its constituents as shown in the following equation:

$$x_{W,j} + x_{DM,j} = x_{W,j} + \left(x_{C,j} + x_{N,j} + x_{P,j} + x_{K,j} + x_{Oth,j}\right) = 1, \quad (3)$$

where $x_{W,j}$ is the water content; $x_{DM,j}$ is the dry matter which is the sum of the fractions of $C(x_{C,j})$, $N(x_{N,j})$, $P(x_{P,j})$, $K(x_{K,j})$ and $Oth(x_{Oth,j})$.

These fractions (Table 6) for both rice straw and organic/inorganic conditioners are known because they can be determined from the data reported in Tables 1 and 5 by recalculating the percentages based on the wet mass of the substance instead of the dry mass.

Table 6. Mass fractions evaluated on a wet basis.

State		$x_{W,j}$	$x_{DM,j}$	$x_{C,j}$	$x_{N,j}$ [% wb [a]]	$x_{P,j}$	$x_{K,j}$	$x_{Oth,j}$
RS	USA	20.00	80.00	30.59	0.70	0.49	1.67	45.55
	THA			30.64	0.50	0.11	1.55	47.20
	MYS			28.41	0.42	0.22	1.36	49.59
	CHN			30.51	0.41	0.23	0.83	48.02
	IND			31.04	0.16	0.04	0.82	47.94
	ITA			32.46	0.80	0.09	0.77	45.38
Urea		2.00	98.00	19.60	45.77	-	-	32.63
Superphosphate		1.00	99.00	-	-	19.30	-	79.70
Potash		8.00	92.00	-	-	-	57.96	34.04
Pig manure		67.60	32.40	0.37	0.10	0.03	0.03	31.87

[a] wb: wet basis.

The proposed model considers that during the HRT (t_R = 30 days), neither the digestate (M_{dig}) nor the recycled sludge (M_{rsl}) are available. During this lapse of time, the composition of the ingestate (M_{ing}) changes continuously because at the beginning of each day, the mass inside the digester (M_D) must respect the C/y ratios shown in Table 4. Additional water (M_{adw}) must be added to the wet masses of substances to obtain inside the digester a DM of 7.3%. After HRT, the mass balance must also take into account M_{rsl} which affects both M_{adw} and the addition of nutrients.

During t_R, the methane production follows the growth of methanogenic microorganisms described by the Gompertz distribution [85]. Based on this distribution, the volume $V(t)$ of biogas produced and the volumetric rate of production $dV(t)/dt$ are:

$$V(t) = V_\infty exp\left[ln\left(\frac{V_0}{V_\infty}\right) exp\left(-\frac{t}{t_C}\right)\right], \tag{4}$$

$$\frac{dV(t)}{dt} = -\frac{V(t)}{t_C}\ln\left[\frac{V(t)}{V_\infty}\right]$$
$$t = 0 \Longrightarrow \frac{dV(t)}{dt} = \frac{V_0}{t_C} ln\left(\frac{V_\infty}{V_0}\right); \quad t \longrightarrow \infty \Longrightarrow \frac{dV(t)}{dt} = 0, \tag{5}$$

where V_0 and V_∞ are the initial $(t = 0)$ and the maximum $(t \to \infty)$ volume of biogas produced. In the previous equations, t_C is a characteristic time dependent on the initial microbial population whose value determines the latency time (t_L) at which the production rate reaches its maximum value. Figure 3 reports a typical distribution of the rate of biogas production with $t_L = 7$ days. During the production of biogas, the carbon content in M_D proportionally decreases.

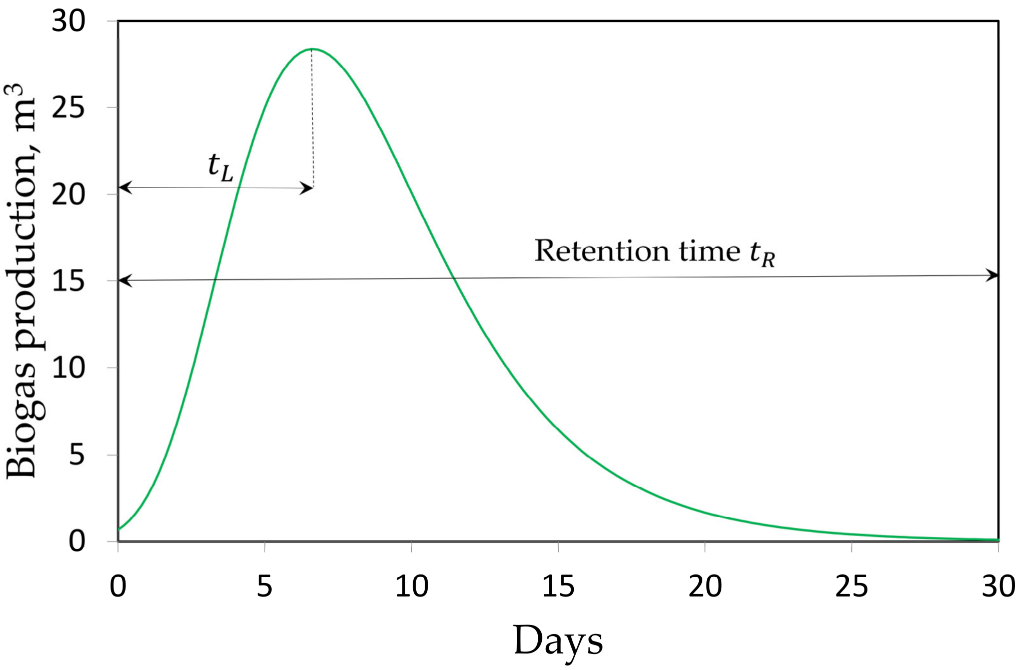


Figure 3. Daily rate of biogas produced per each ton of rice straw ($V_\infty = 270$ m^3, $V_0 = 0.35$ m^3, $t_C = 3.5$ days and retention time $t_R = 30$ days).

From the point of view of the mass balances, the digester, if accurately managed, reaches the steady state after $t_R = 30$ days. Over a generic time interval $\Delta t = t^k - t^{k-1}$, the mass balance on the digester is described by the following equation:

$$M_{ing}^k - M_{dig}^k - M_{bio}^k = \frac{M_D^k - M_D^{k-1}}{\Delta t}, \tag{6}$$

where $M_D^k - M_D^{k-1}$ is the mass change inside the digester during a day.

At the end of the generic day k, Equation (6) becomes:

$$M_D^k = M_D^{k-1} + M_{ing}^k - M_{dig}^k - M_{bio}^k, \tag{7}$$

where on the first day $(k = 1)$ $M_D^{k-1} = 0$. Table 7 shows the values used in Equations (6) and (7) on each of the k days.

Table 7. Numerical values and ranges for the masses entering and exiting the digester.

	$\boldsymbol{M_{rst}}$	$\boldsymbol{M_{man}}$	$\boldsymbol{M_{ure}}$	$\boldsymbol{M_{sph}}$	$\boldsymbol{M_{dig}}$	$\boldsymbol{M_{rsl}}$
$k \leq 30$	1000	100	≥ 0	≥ 0	0	0
$k > 30$	1000	0	≥ 0	≥ 0	> 0	$0 \leq M_{rsl} \leq M_{sld}$

The DM in the digester changes day by day because of both the biogas production (M_{bio}^{k}) and DM contained in the ingestate ($M_{DM,ing}^{k}$):

$$M_{DM,D}^{k} = M_{DM,D}^{k-1} + M_{DM,ing}^{k} - M_{DM,dig}^{k} - M_{bio}^{k}, \tag{8}$$

where $M_{DM,ing}^{k}$ is:

$$M_{DM,ing}^{k} = x_{DM,rst}M_{rst}^{k} + x_{DM,man}M_{man}^{k} + x_{DM,ure}M_{ure}^{k} + x_{DM,sph}M_{sph}^{k} + x_{DM,rsl}M_{rsl}^{k}. \tag{9}$$

The terms in Equation (9) can assume different values based on k according to Table 7. At the beginning of each day, to obtain inside the digester the desired C/N and C/P (Table 4), the quantities of inorganic additives (M_{ure}^{k} and M_{sph}^{k}) must be determined starting from the equations:

$$\frac{C}{N} = \frac{x_{C,rst}M_{rst}^{k} + x_{C,man}M_{man}^{k} + x_{C,ure}M_{ure}^{k} + x_{C,D}^{k-1}M_{D}^{k-1} - x_{C,D}^{k-1}M_{dig}^{k} + x_{C,sld}^{k-1}M_{rsl}^{k}}{x_{N,rst}M_{rst}^{k} + x_{N,man}M_{man}^{k} + x_{N,ure}M_{ure}^{k} + x_{N,D}^{k-1}M_{D}^{k-1} - x_{N,D}^{k-1}M_{dig}^{k} + x_{N,sld}^{k-1}M_{rsl}^{k}}, \tag{10}$$

$$\frac{C}{P} = \frac{x_{C,rst}M_{rst}^{k} + x_{C,man}M_{man}^{k} + x_{C,ure}M_{ure}^{k} + x_{C,D}^{k-1}M_{D}^{k-1} - x_{C,D}^{k-1}M_{dig}^{k} + x_{C,sld}^{k-1}M_{rsl}^{k}}{x_{P,rst}M_{rst}^{k} + x_{P,man}M_{man}^{k} + x_{P,sph}M_{sph}^{k} + x_{P,D}^{k-1}M_{D}^{k-1} - x_{P,D}^{k-1}M_{dig}^{k} + x_{P,sld}^{k-1}M_{rsl}^{k}}, \tag{11}$$

where the mass fractions for the different substances in the ingestate are those reported in Table 6 and the mass M_{D}^{k-1} is known because it was determined on the previous day. The mass fractions of carbon and of the $i-th$ constituent ($i = N, P, K, Oth$) already present inside the digester, and so in the digestate, on a generic k day are:

$$x_{C,D}^{k} = \frac{x_{C,rst}M_{rst}^{k} + x_{C,man}M_{man}^{k} + x_{C,ure}M_{ure}^{k} - x_{C,bio}M_{bio}^{k} + x_{C,D}^{k-1}M_{D}^{k-1} - x_{C,D}^{k-1}M_{dig}^{k} + x_{C,sld}^{k-1}M_{rsl}^{k}}{M_{D}^{k}}, \tag{12}$$

$$x_{i,D}^{k} = \frac{x_{i,rst}M_{rst}^{k} + x_{i,man}M_{man}^{k} + x_{i,ure}M_{ure}^{k} + x_{i,sph}M_{sph}^{k} + x_{i,D}^{k-1}M_{D}^{k-1} - x_{i,D}^{k-1}M_{dig}^{k} + x_{i,sld}^{k-1}M_{rsl}^{k}}{M_{D}^{k}}. \tag{13}$$

In the four previous equations, from Equations (10) to (13), the mass fractions for the sludge can be determined starting from the characteristic of the digestate and applying the coefficients reported in Table 3. Positive values for M_{ure}^{k} and M_{sph}^{k} in Equations (10) and (11) mean that an addition of conditioners is required while negative values highlight an excess of N and P inside the digester.

On the same day, the mass fractions of DM and W in the digester are:

$$x_{DM,D}^{k} = \frac{x_{DM,rst}M_{rst}^{k} + x_{DM,man}M_{man}^{k} + x_{DM,ure}M_{ure}^{k} + x_{DM,sph}M_{sph}^{k} - M_{bio}^{k} + x_{DM,D}^{k-1}M_{D}^{k-1} - x_{DM,D}^{k-1}M_{dig}^{k} + x_{DM,sld}^{k-1}M_{rsl}^{k}}{M_{D}^{k}}, \tag{14}$$

$$x_{W,D}^{k} = \frac{x_{W,rst}M_{rst}^{k} + x_{W,man}M_{man}^{k} + x_{W,ure}M_{ure}^{k} + x_{W,sph}M_{sph}^{k} + x_{W,D}^{k-1}M_{D}^{k-1} - x_{W,D}^{k-1}M_{dig}^{k} + x_{W,sld}^{k-1}M_{rsl}^{k}}{M_{D}^{k}}. \tag{15}$$

In the considered $LSAD$, the ratio (W/DM) between water and dry matter is 12.7 ($DM\%$ = 7.3). Once the $M_{DM,D}^{k}$ has been determined, through Equation (8), the total mass of water ($M_{W,D}^{k}$) is:

$$M_{W,D}^{k} = M_{DM,D}^{k} \cdot \left(\frac{W}{DM}\right). \tag{16}$$

Consequently, on the same day, the mass of water to be added (M_{adw}^{k}) is:

$$M_{adw}^{k} = M_{W,D}^{k} - M_{W,D}^{k-1} + x_{W,D}^{k-1} M_{dig}^{k} - \left(x_{W,rst} M_{rst}^{k} + x_{W,man} M_{man}^{k} + x_{W,ure} M_{ure}^{k} + x_{W,sph} M_{sph}^{k} + x_{W,sld}^{k-1} M_{rsl}^{k}\right), \quad (17)$$

and the total mass in the digester (M_D^k) is:

$$M_D^k = M_{DM,D}^k + M_{W,D}^k. \quad (18)$$

When $k = 30$, M_D^k reaches its maximum allowed value with reference to the digester capacity. Starting from $k > 30$, $M_{dig}^k \neq 0$ (Figure 2 and Table 7) and M_{slu}^k (Table 3) is available. The recycled sludge (M_{rsl}^k) is useful to adjust the C/y in the digester and allows for no further addition of manure ($M_{man}^k = 0$) because of its bacterial charge.

The proposed model, through an iterative calculation of M_{dig}^k, aims to obtain in the digester a steady-state condition ($M_D^k \cong M_D^{k-1}$) paying attention to the C/y ratios. Since, among the C/y ratios, the one that has the greatest influence on biogas production is C/N, its value was assumed as a reference for the whole process. The iterative process was repeated for all the integer values of C/N in the range 20–30 looking for the value, which allows minimizing both the addition of chemical conditioners and water. After, the C/P and C/K ratio were calculated to highlight the need for conditioning.

The main steps of the iterative procedure can be summarized as follows:

- A value for M_{dig}^k is chosen and M_{slu}^k is calculated;
- The mass of recycled sludge (M_{rsl}^k) required to obtain the desired C/N ratio is evaluated using Equation (10), initially setting $M_{ure}^k = 0$;
- If $M_{rsl}^k > M_{slu}^k$, a mass M_{ure}^k must be added. M_{ure}^k is determined using again Equation (10);
- The dry mass inside the digester $M_{DM,D}^k$ is calculated using Equation (8) where $M_{DM,ing}^k$ is obtained applying Equation (9), setting $M_{man}^k = 0$ and M_{sph}^k=0;
- The mass of water $M_{W,D}^k$ and of additional water M_{adw}^k are determined using Equations (16) and (17), respectively;
- A check is performed to verify if the steady state is reached:

$$\left|M_{AD}^k - M_{AD}^{k-1}\right| < \varepsilon, \quad (19)$$

where ε is the maximum accepted deviation set at 0.01 kg. If this tolerance is not respected, a new value for M_{dig}^k is chosen.

The most critical aspect of this method concerns the management of the digester when $k \leq 30$ because the required amounts of water and nutrient change day by day. For this reason, using the previous results, another approach was also investigated in which, during the first 30 days, the daily quantities of inorganic additives and additional water are freely chosen, postponing the verification of C/N, C/P and W/DM. Furthermore, when $k > 30$, the M_{dig}^k value was fixed to the value previously calculated at the end of day $k = 30$.

When M_{dig}^k is fixed, the masses of compost (M_{com}^k) and sludge (M_{slu}^k) are:

$$M_{com}^k = S_f M_{dig}^k, \quad (20)$$

$$M_{slu}^k = \left(1 - S_f\right) M_{dig}^k. \quad (21)$$

If the steady-state condition is imposed for the digester, the outgoing masses (M_{com}^k, M_{dsl}^k, M_{bio}^k) will be equal to the incoming masses (M_{rst}^k, M_{ure}^k, M_{sph}^k, M_{adw}^k):

$$M_{com}^k + M_{dsl}^k + M_{bio}^k = M_{rst}^k + M_{ure}^k + M_{sph}^k + M_{adw}^k. \quad (22)$$

The discharged sludge (M_{dsl}^k) is a fraction of M_{slu}^k which is not recirculated and which , can be calculated using Equation (22) while M_{rsl}^k is:

$$M_{rsl}^k = M_{dig}^k - \left(M_{com}^k + M_{dsl}^k\right). \quad (23)$$

3. Results and Discussion

The assumptions reported in Tables 1–7 were applied to the method proposed in this study and the results discussed in this paragraph are strictly related to these assumptions.

The daily trend of biogas production calculated using Equation (4) (V_{∞} = 270 m^3, about 310 kg of biogas) is shown in Figure 4.

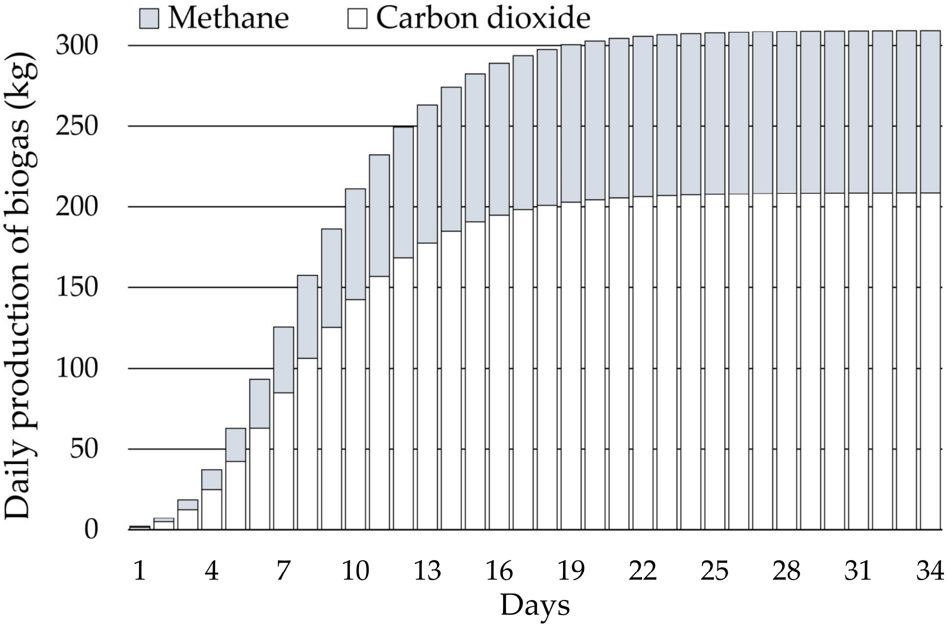


Figure 4. Daily biogas production.

Figure 4 shows that the mass of CO_2 produced is significantly higher than the mass of CH_4 but this is not worrying for some different reasons. First, if reference is made to Table 2, it is possible to note that the volumetric production of CH_4 and CO_2 is approximately the same. Furthermore, AD as an alternative to SI reduces the emission of CH_4, which has a global warming potential 28 times higher than CO_2 [92]. In addition, the amount of CO_2 produced during AD is lower than that which the plant has absorbed during its growth cycle [28].

Table 8 reports the quantities of by-products and of conditioners used to obtain the indicated C/N and C/P. The results for $k \leq 30$ represent the total quantities accumulated in the digester over the entire period, while for $k > 30$, the values refer to the daily requirement. Examining Table 8, it is possible to observe that during the first 30 days, the quantity of M_{ure} is in the range 350 kg–390 kg except for ITA and the USA, for which the need of urea is close to 250 kg due to the fact the initial C/N is lower.

Table 8. Main incoming/outgoing digester masses reported by country.

		USA	**THA**	**MYS**	**CHI**	**IND**	**ITA**
C/N		20	20	20	21	30	20
C/P		≤200	≤200	≤200	≤200	≤200	≤200
M_{adw}	$k \leq 30$	226.3 t	226.7 t	226.7 t	228.2 t	228.8 t	226.9 t
	$k > 30$	4.2 t/d	2.1 t/d	2.0 t/d	1.5 t/d	1.5 t/d	4.3 t/d
M_{ure}	$k \leq 30$	252.0 kg	353.6 kg	380.2 kg	388.8 kg	371.8 kg	244.5 kg
	$k > 30$	n.r. [a]	n.r.	n.r.	n.r.	3.0 kg/d	n.r.
M_{sph}	$k \leq 30$	n.r.	13.4 kg	n.r.	n.r.	101.8 kg	46.0 kg
	$k > 30$	n.r.	n.r.	n.r.	n.r.	1.6 kg/d	0.3 kg/d
M_{dig}	$k > 30$	8.4 t/d	10.3 t/d	10.4 t/d	10.9 t/d	11.0 t/d	8.3 t/d
M_{rsl}	$k > 30$	3.6 t/d	7.5 t/d	7.7 t/d	8.7 t/d	8.8 t/d	3.3 t/d

M_{dsl}	$k > 30$	3.2 t/d	0.8 t/d	0.6 t/d	0 t/d	0 t/d	3.3 t/d
M_{com}	$k > 30$	1.7 t/d	2.0 t/d	2.1 t/d	2.2 t/d	2.2 t/d	1.7 t/d

[a] n.r.: not required.

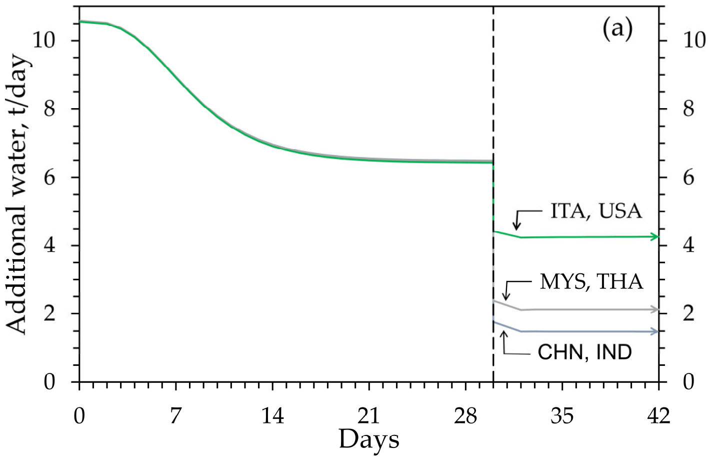
For all the countries, up to $k \leq 30$, the total mass of water (M_{adw}) to be added to the digester is approximately the same because the same initial water content (20%) is assumed for all straws. When $k > 30$, a mass of sludge rich in water is available and consequently, the daily water requirements change based on the fraction of sludge recirculated.

The nutrients carried by the sludge if returned to the digester can decrease the amount of conditioners needed. For the straw of Chinese and Indian origin, the sludge can be totally recirculated because of the low content in N and P of the straw (Table 1). Recirculating the sludge for IND, the daily amounts of urea and superphosphate reduce to 3 kg/d and 1.6 kg/d, respectively, while for CHI, no addition of conditioners is needed. At the same time, for these two countries, the daily requirement of M_{adw} is only 1.5 m^3/d.

For THA and MYS, even if a fraction of sludge lower than 10% is discharged, increasing the need for additional water to about 2 m^3/d, the addition of conditioners is not required. In the case of ITA and the USA, to avoid an excess of nutrients in the digester, M_{dsl} is about 50% of M_{slu} and consequently, the additional water is about three times greater than for IND and CHI.

The mass of compost, which is determined by the separator (Table 3), varies up to 23% if the minimum (ITA, USA) and maximum (CHI, IND) amounts are compared.

Figure 5 shows how M_{adw}, M_{ure} and M_{sph} change over time. In the figure, it is possible to observe how the trends of these needs are, as long as $k \leq 30$, closely correlated to the decrease of C in the digester due to the increase in biogas production (Figure 4). The area below the different curves for the first 30 days represents the total amounts of M_{adw}, M_{ure} and M_{sph} reported in Table 8 for $k \leq 30$.



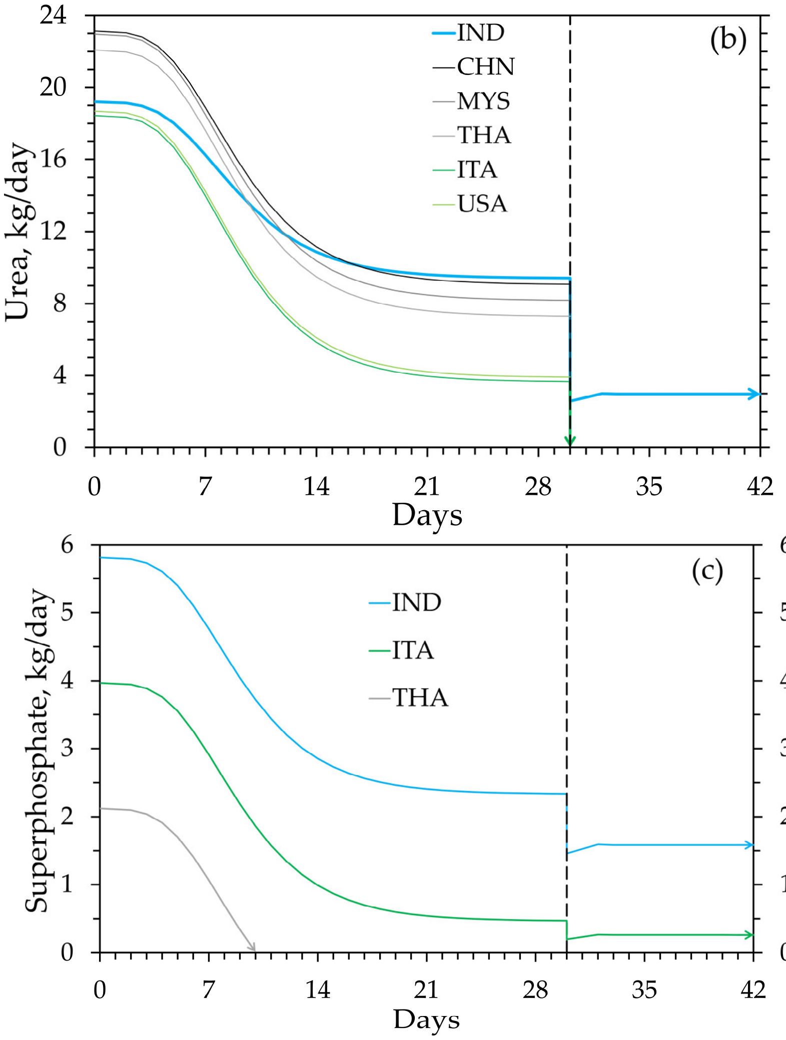


Figure 5. Time trends for additional water (**a**), urea (**b**) and superphosphate (**c**).

After, these aforementioned needs stabilize, sometimes becoming zero, as the daily biogas production becomes constant. In Figure 5, the trends for M_{adw}, M_{ure} and M_{sph} show how the steady-state condition is reached shortly after the retention time. When the quantities of M_{adw}, M_{ure} and M_{sph} become constant, M_{dig}, M_{com} and M_{rsl} also stabilize, because they are strictly correlated to the previous three masses.

During the first 30 days, M_{adw} shows the same trend (Figure 5a) for all the examined countries while when $k > 30$, the trends become different due to the different amounts of M_{rsl}. The lower the quantity of N and P in the RS (Table 1), the higher the amount of recycled sludge (Table 8) and the lower the M_{adw} required.

Figure 5b shows the different needs of M_{ure} for the different countries, which vary up to 37% if CHI is compared with ITA. When $k > 30$, it is no longer required to add urea except for IND. As written above for USA, MYS and CHN, a mass of superphosphate is never required. Figure 5c shows that for IND and ITA, a mass of superphosphate is always required but when the steady state is reached, the need is reduced by 50% (IND) and 80% (ITA) compared to the average value of the first 30 days. A particular trend is shown for THA for which the superphosphate is required only during the first 10 days.

As previously mentioned, one of the advantages of AD compared to other uses of rice straw is the availability of compost and sometimes of a drained fraction of sludge, which can be used in rice cultivation as soil amendments due to the nutrients contained. For both of them, the ratio of water to dry matter is determined by the separator (Table 3) and is approximately 28 for sludge and 3.4 for compost.

Table 9 shows the mass fractions of the chemical elements of interest in the sludge and compost evaluated referring to the DM, while Table 10 shows the carbon to nutrient ratios of both the by-products. Table 9 shows that the sludge has a higher content of nutrients than the compost while the compost is richer in C than the sludge. For this reason, the discharged sludge, if available ($M_{dsl} \neq 0$ in Table 8), favors soil fertilization while the compost reintroduces chemically stabilized C into the soil which will not be converted into methane.

Table 9. Mass fractions (dry basis) of the chemical elements of interest in the sludge and compost.

$\boldsymbol{DM}$ **Composition**	**USA**	**THA**	**MYS**	**CHI**	**IND**	**ITA**
	$\boldsymbol{M_{slu} - M_{com}}$					
	[%]					
$C_{\text{cellulose}}$	15.4–17.0	15.2–16.8	12.3–13.6	14.9–16.5	15.5–17.1	18.6–20.6
C_{lignine}	17.3–19.1	17.0–18.8	15.7–17.4	16.8–18.7	17.1–18.9	18.7–20.7
N	8.2–2.0	3.1–0.9	2.7–0.8	3.0–0.8	2.1–0.6	3.6–1.0
P	1.3–0.9	0.3–0.2	0.7–0.4	0.7–0.5	0.2–0.1	0.3–0.2
K	3.3–0.9	11.1–2.7	10.0–2.4	6.9–1.7	6.7–1.6	3.7–0.9
Oth	54.5–60.0	53.3–60.0	58.6–65.4	57.7–61.8	58.4–61.7	55.1–56.6

Table 10. Carbon to nutrients ratios for sludge and compost.

$\boldsymbol{C/y}$	**USA**	**THA**	**MYS**	**CHI**	**IND**	**ITA**
	$\boldsymbol{M_{slu} - M_{com}}$					
	[kg/kg]					
C/N	10.2–40.1	10.2–40.1	10.2–40.0	10.7–42.1	15.4–60.2	10.3–40.2
C/P	24.2–40.9	95.1–160.6	42.7–72.2	44.7–75.5	144.8–244.5	145.1–245.1
C/K	4.0–18.1	2.9–13.2	2.8–12.8	4.6–21.0	4.8–22.1	10.0–45.6

To simplify the management of the digester, the second approach described above was applied to the scenarios related to IND and ITA, which are to be considered the most complex, as they require the addition of inorganic additives also when $k > 30$. Table 11 shows a possible pattern for the feeding mixture (M_{adw}, M_{ure} and M_{sph}), the constant value for M_{dig} evaluated with the previous model at the end of the day $k = 30$, the values for both M_{rsl} and M_{dsl} that minimize the addition of water and conditioners and the mass M_{com} determined using Equation (20).

Table 11. Data used for IND and ITA scenarios.

	$\boldsymbol{IND}$			$\boldsymbol{ITA}$		
	$k \leq 15$	$15 < k \leq 30$	$k > 30$	$k \leq 10$	$10 < k \leq 30$	$k > 30$
M_{adw} (t/d)	7.6	7.6	1.5	7.6	7.6	4.3
M_{ure}(kg/d)	24.8	3.0	3.0	8.4	8.4	n.r.
M_{sph}(kg/d)	6.8	1.6	1.6	4.6	0.3	0.3
M_{dig}(t/d)	-	-	11.0	-	-	8.3
M_{rsl}(t/d)	-	-	8.8	-	-	3.3
M_{dsl}(t/d)	-	-	-	-	-	3.3
M_{com}(t/d)	-	-	2.2	-	-	1.7

Figure 6 elucidates the time progression of the *C*/*N*, *C*/*P* and *W*/*DM* ratios over a 90-day span that is obtained using the data in Table 11. The figure shows that the *C*/*N* and *C*/*P* ratios vary daily but remain consistently within the allowable limits and stabilize by day 90 at the latest. The implemented water supply methodology ensures that the water to dry matter ratio in the digestate remains within the applicability range of Equation (2).

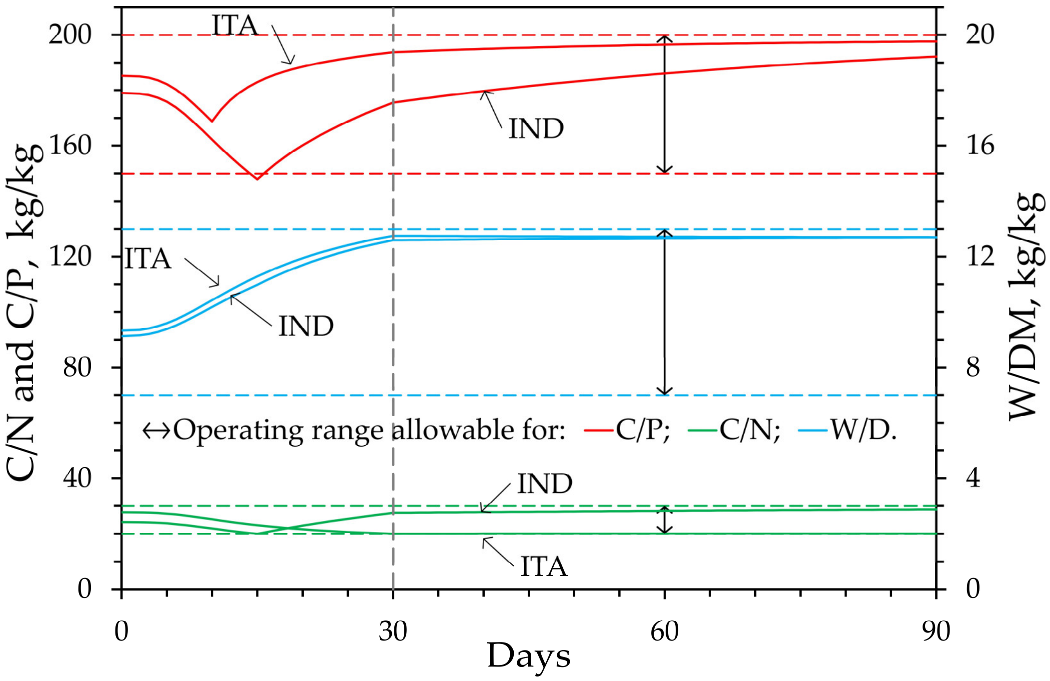


Figure 6. Carbon to nutrient ratios and water to dry matter ratios in the digester versus time shown by solid lines. Dashed lines define the allowed ranges for these ratios.

Figures 7 and 8 reveal that the resulting dry matter composition in both sludge and compost is practically in line with the previous analysis results reported in Table 9.

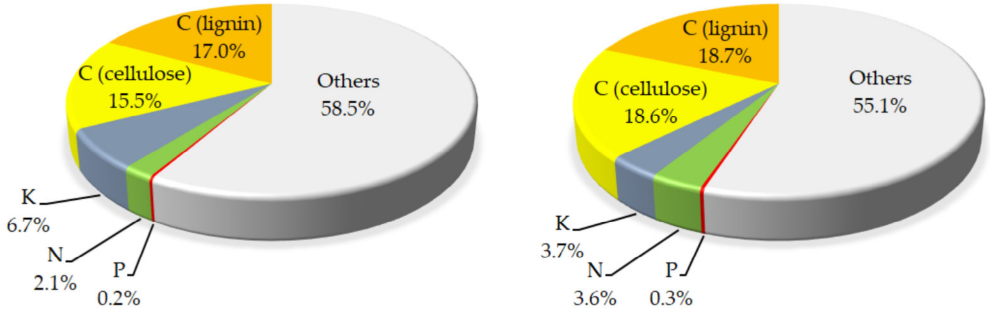


Figure 7. Mass fractions of main components in the dry matter of the sludge: IND (**left**) and ITA (**right**).

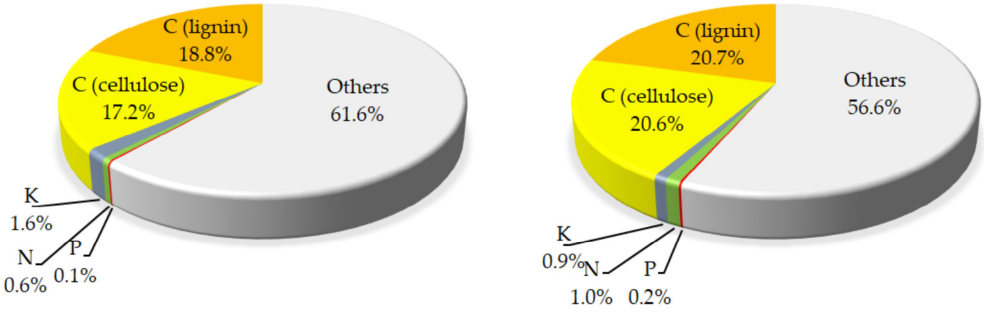


Figure 8. Mass fractions of main components in the dry matter of the compost: IND (**left**) and ITA (**right**).

The results obtained, although not general because they are strictly related to the assumptions introduced, show that by adopting a forecasting method, it is possible to manage the digester which allows minimizing the consumption of water and chemical additives. The benefits of such an approach are measurable both in terms of biogas produced and in terms of chemical additives saved. There is also evidence that using an analytical approach to digester management allows steady state to be achieved in a short time.

4. Conclusions

This research provides an exploration into the anaerobic digestion of rice straw originating from disparate geographical regions, underscoring the necessity of enhancing methane production via judicious water resource management and appropriate conditioning. The mass conservation-oriented method proposed herein offers precision in predicting and minimizing the requisite volumes of water and conditioners. It is evident from our investigation that, during the digester's initial phase, water usage remains relatively consistent across all scrutinized countries, yet presents substantial variations in subsequent stages. The requirement for nitrogen supplementation was observed as a consistent factor, while the necessity of phosphorus supplementation was determined to be context specific. Importantly, our study establishes that despite exceeding the ideal values, potassium concentrations do not appreciably impact methane production.

The quantifiable results of this research bolster the progress towards devising efficient, sustainable strategies for the management of rice straw in a multitude of global contexts. This furthers the potential of this prolific agricultural by-product as a significant resource for renewable energy generation.

In conclusion, the effective transformation of rice straw into renewable energy via anaerobic digestion not only addresses the disposal predicament but also propounds an environmentally conscious pathway towards a sustainable future in the agricultural industry. The broader implications of these findings could greatly impact our understanding of waste management and energy production, driving a shift towards more sustainable practices worldwide.

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