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## Article

# Biomethanation of Rice Straw: A Sustainable Perspective for the Valorisation of a Field Residue in the Energy Sector

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**Abstract:** Rice straw represents a field waste. Indeed, only 20% of the rice straw produced is used in the pulp and paper industry. The larger amount of this field residue is burned or left in the field, which has very important environmental consequences. Recently, analogous to a barrel of oil, a metric approach to rice straw, the rice straw barrel, was introduced in order to assign economic value to this waste. In this paper, potential annual biomethane production from anaerobic digestion is evaluated, resulting in a range of biomethane created for each rice straw barrel depending on volatile solid (VS) content as a percentage of total solid (TS) content and on biomethane yield: 23.36 m<sup>3</sup> (VS = 73.8% TS, 92 L kg<sub>VS</sub><sup>-1</sup>), 26.61 m<sup>3</sup> (VS = 84.08% TS, 186 L kg<sub>VS</sub><sup>-1</sup>), 29.27 m<sup>3</sup> (VS = 95.26% TS, 280 L kg<sub>VS</sub><sup>-1</sup>). The new concept of the rice straw barrel is improved based on a new indicator for sustainability, the Thermodynamic Human Development Index (THDI), which was introduced within the last three years. The improvement in sustainability by using rice straw barrels for different countries is analysed based on the THDI.



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**Keywords:** HDI; THDI; rice straw; biomethane; circular economy; thermoeconomy

## 1. Introduction

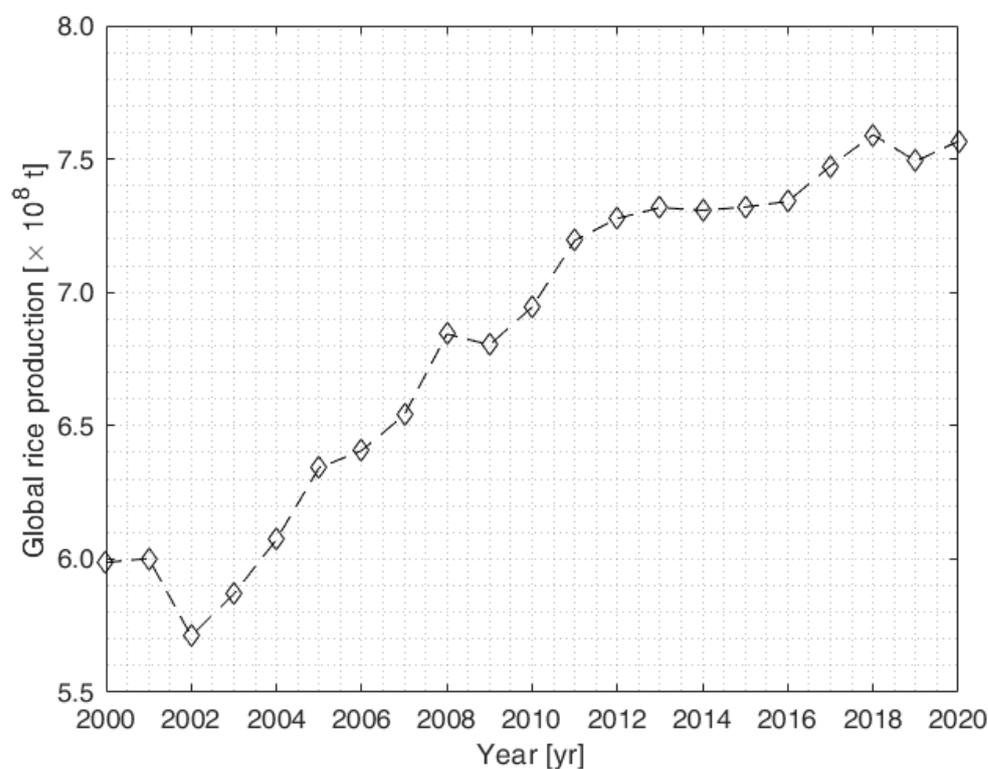
Energy represents a fundamental resource in industrial and modern society, and a consequent fundamental topic of investigation for sustainability. The increase in world population and the related improvement in economic activities determine the increase in energy demand, with related consequences for the Earth’s environment [1]. Indeed, the demand for energy is continuously increasing, with pressing problems for our societies including climate change, energy crises, and food security for a growing population [2]. Technical and socio-economic solutions are required for these challenges, with the aims of providing environmentally sustainable answers and cost-effectiveness for large-scale applications. In this context, waste-to-energy conversion of agricultural residues into renewable energy contribute to reduce global methane emissions and preserve valuable land resources for food production [3]. Thus, unused agricultural waste could represent one of the most stable sources of energy to support countries reaching a long-term energy strategy [3]: wheat straw and rice straw can play an important role in meeting growing energy demand based on a sustainable approach [4]; in this way, biomass, from field residue could become a resource in the energy sector.

Field residues are what remain after crop harvesting, whereas process residues are the waste of the crop after its harvesting [5]. In particular, rice straw is considered a field residue because it doesn’t find use in industry or agriculture. Every kg of harvested rice produces about 0.70–1.50 kg of rice straw [3,6]: 1.35 kg of rice straw for each kg of rice grain is considered the usual mean value for reference in technical studies [7–10]. Lignocellulosic

biomass can represent an economical and renewable substrate to process biofuels [5,11], particularly biogas and biomethane. Indeed, these products can be obtained by anaerobic microorganism digestion of lignocellulosic substrates [12]. Consequently, bioenergy production could represent an efficient approach to reduce waste generation [13]. Moreover, the related digestate can also be used as an organic fertiliser due to its phosphorus and nitrogen content [14]. In summary, valorisation of rice straw could reduce pollution related to its disposal and be used to produce second-generation biofuels and/or biodegradable plastics [15], specifically microbial polyesters, currently the biodegradable bio-based plastics most attractive for replacing fossil-fuel-based plastics [16–18].

### 1.1. Rice as an Agricultural Commodity

Rice is the third most popular agricultural crop grown in the world, after wheat and corn, with a total cultivated area estimated at 164.2 Mha and a gross grain yield production of  $756.7 \text{ Mt yr}^{-1}$  in 2020 [19,20]. Figure 1 shows total global rice production from 2000 to 2020. A continuous increase in global rice production can be highlighted during the 21st century: an overall increase of 26% from 2000 to 2020 is shown, increasing a total of 250% from 1961 to 2020.



**Figure 1.** Global rice production (tons) from 2000–2020 based on FAO data [20].

Table 1 reports the area, plant height, and rice yield in different regions in order to summarise global rice production.

**Table 1.** Area, plant height, and rice yield by region [20–25] for the year 2020. Rice yield is the ratio of overall rice grain production to harvested area.

Country	Area [Mha]	Plant Height [mm]	Yield [t ha <sup>-1</sup> ]
China	30.34	362–483	7.04
India	45.00	900–1300	3.96
Indonesia	10.66	701–998	5.13
Japan	1.46	1020–1170	6.64
Malaysia	0.65	631	3.60
Thailand	10.40	1000–6000	2.91
United States	1.21	950–1880	8.54
Vietnam	7.22	900–1750	5.92
World	164.19	n.d.	4.61

In Table 2, rice production for the year 2020 is summarised by continent. In Table 3, rice production of some of the largest rice-producing countries for different continents is reported from the years 2000 to 2020. In 2017, dry lignocellulosic biomass related to rice production was estimated to be 905 Mt yr<sup>-1</sup> [4,26].

**Table 2.** Rice production by macro-area for the year 2020 [20].

Continent	Rice Production [Mt yr <sup>-1</sup> ]
Africa	37.9
Asia	676.6
Australia	0.1
Central America	1.4
Europe	4.1
Northern America	10.3
Russian Federation	1.1
South America	25.0
World	756.5

**Table 3.** Rice production by some of the leading countries on different continents; data from Ref. [20].

Year	Rice Production									
	Bangladesh [ $\times 10^7$ t]	Brazil [ $\times 10^7$ t]	China [ $\times 10^8$ t]	India [ $\times 10^8$ t]	Italy [ $\times 10^6$ t]	Pakistan [ $\times 10^6$ t]	Spain [ $\times 10^5$ t]	Thailand [ $\times 10^7$ t]	USA [ $\times 10^7$ t]	Vietnam [ $\times 10^7$ t]
2000	3.76	1.11	1.90	1.27	1.23	7.20	8.27	2.58	0.87	3.25
2005	3.98	1.32	1.82	1.38	1.41	8.32	8.24	3.06	1.01	3.58
2010	5.01	1.12	1.97	1.44	1.52	7.23	9.28	3.57	1.10	4.00
2015	5.18	1.23	2.14	1.57	1.52	1.02	8.47	2.77	0.87	4.51
2020	5.49	1.11	2.14	1.78	1.51	8.42	7.39	3.02	1.03	4.28

### 1.2. Rice Straw: A Residual Waste of Rice Production—A Potential Energy Source

Rice is a crucial food crop, relevant to global food security and socio-economic stability [27]. However, rice cultivation creates pollution due to irrigation and fertilization methods. Indeed, during the growth phase of the rice plant, relevant amounts of CH<sub>4</sub> and N<sub>2</sub>O are emitted into the atmosphere [28,29]: methanogenesis is the result of the bacterial transformation of soil organic carbon under anaerobic conditions. Moreover, fertilisation also contributes to air pollution [30] because of the interaction between the fertilizer and the soil. Last, irrigation creates pollution [31].

As the result of rice cultivation, husk, chaff, and rice straw are produced in the following average quantities depending on the variety of rice:

- Husk: 20% by weight of the rice;
- Chaff: 10% by weight of the rice;
- Rice straw: 700–1500 kg for every ton of rice grain.

However, husk and chaff have economic value due to their use in some industrial sectors, such as energy, food, and pharmaceuticals, while only 20% of the rice straw can be used as a raw material for the pulp and paper industry, especially if it is collected without machinery [21]. Consequently, rice straw is considered a field waste due to its high silica (SiO<sub>2</sub>) content (around 13% by weight). Usually, there are two disposal methods for rice straw, estimated to be responsible for around 10–15% of worldwide anthropogenic emissions [3]:

- Open-field burning— at least 50% of total rice straw is burned globally [21], generating atmospheric pollution equivalent to approximately 11 t ha<sup>-1</sup> yr<sup>-1</sup> of CO<sub>2</sub> [32];
- Incorporation by the soil (up to 12 t ha<sup>-1</sup> yr<sup>-1</sup>) increases CH<sub>4</sub> and N<sub>2</sub>O emissions [33].

On the other hand, these disposal methods allow the reintroduction of elementary substances into the lithosphere (C, K, N, P, etc.) and eliminate weeds from the soil, with the favourable result of avoiding compromising the quality of the next harvest [34]. However, rice straw removal from flooded rice fields has been shown to not reduce the level of soil organic matter [35].

Here, consideration of carbon dioxide emissions due to open-field burning of the biomass must be introduced. Indeed, biomass is considered carbon neutral [36,37] due to the biospheric carbon cycle, i.e., the carbon that is released during combustion is the same that had been sequestered by the plant during its life cycle. However, based on exergetic analysis, a resource (including energy) presents a quality [38,39], which consists of the number of uses to which it can be subjected before becoming waste. Thus, rice straw open-field burning generates heat, pollution, and CO<sub>2</sub> emissions that are dissipated into the environment [40]. Heat, pollution, and CO<sub>2</sub> emissions represent exergetic losses. On the contrary, if the rice straw is converted into biofuels (or other useful by-products), it becomes a resource to obtain useful work; consequently, an equal amount of CO<sub>2</sub> emissions and heat are released, but with the production of useful work. In this second process, the rice straw presents a higher quality (i.e., exergy) because, though it still produces carbon dioxide and heat, it now also generates useful work.

In energy terms, one of the fundamental properties of biomasses is its heating value, which depends on its composition. Table 4 reports the heating value of rice straw from different countries.

**Table 4.** Calorific values of rice straw from different countries [21].

Country	Calorific Value [10 <sup>6</sup> J kg <sup>-1</sup> ]
China	18.0
India	12.3–28.5
Malaysia	15.1
Thailand	11.7–16.3
United States	11.5–15.3

Bioenergy production from crop residues can be done by thermal conversion (combustion, pyrolysis, and gasification) or by biochemical conversion (anaerobic digestion or co-digestion, fermentation, and transesterification) [1]. In particular, the organic substrate can be degraded into biogas and digestate by using anaerobic digestion [41]. Rice straw could represent a low-cost choice for the bio-based economy because it is a field residue of rice cultivation that would otherwise be burned or left in the soil without any economic value. However, its use in the energy sector has recently been highlighted, along with techniques for its collection and baling [42].

Anaerobic digestion of rice straw is considered the best route to exploit its energy potential [43]. The composition of rice straw can be summarised as follows [4,43]:

- Cellulose ( $C_6H_{10}O_5$ )<sub>x</sub>: the main constituent (29–80%) of lignocellulosic biomass. It is a polysaccharide consisting of a linear chain of D-glucose linked by  $\beta$  bonds. The cellulose strains are associated to make cellulose fibrils. Cellulose fibres are linked by intra-molecular and inter-molecular hydrogen bonds. Cellulose is insoluble in water and most organic solvents;
- Hemicelluloses ( $C_5H_8O_4$ )<sub>m</sub> (10–45%): heterogeneous branched biopolymers, relatively easy to hydrolyze due to their amorphous and branched structure, with short lateral chains, and their lower molecular weight;
- Lignin [ $C_9H_{10}O_3(OCH_3)_{0.9-1.7}$ ]<sub>n</sub> (5–25%): an aromatic polymer.

In particular, lignin cannot easily be digested by microbes [44]. To overcome this difficulty, lignocellulosic residues must be mechanically, thermally, biologically, and/or chemically pretreated [45]. Notably, mechanical pretreatments reduce the biomass into particles, increasing porosity, which improves degradation by anaerobic bacteria [34]. Table 5 summarises the densities of different forms of processed rice straw [21].

**Table 5.** Densities of different forms of processed rice straw [21].

Form	Density [kg m <sup>-3</sup> ]
Baled	110–200
Chopped	40–80
Cubed	320–640
Hammer milled	40–100
Loose	20–40
Pelleted	560–720

Moreover, high lignin content slows anaerobic digestion of lignocellulosic biomass waste. Indeed, this increases the time required for degradation. Consequently, the efficiency of the process must be improved in order to decrease the cost to use biomass [46]. Cellulose, hemicellulose, and lignin are the fundamental components of rice straw, and their proportions affect the rate of degradation of the substrate [5]: in aerobic decomposition, cellulose is depolymerized to produce glucose, which is then oxidized into CO<sub>2</sub> and H<sub>2</sub>O. Consequently, the biomass is reduced over time: rice straw in the soil has been estimated to have a half-life of two years, and around the 80–90% of it is decomposed during the first year [3].

Thus, in a recent analysis of the Novara district [42], following the concept of oil barrel, cylindrical bales of rice straw were suggested as a metric unit for the use of rice straw for energy [42]. The barrel of rice straw was proposed based on having the same energy potential as a barrel of oil.

In relation to the analogy between the rice straw barrel and the oil barrel, it is important to highlight that rice straw is composed of polysaccharides and lignin, and it is relatively easily degradable, with the consequence that at the end of the season around 80–90% of the added rice straw disappears [47]: this natural degradation points out the difficulty of using rice straw barrels as energy storage, making it suitable for local, quick use. Indeed, rice straw has lower energy and density than fossil fuels; consequently, more biomass is required to obtain the same amount of energy [48]. Moreover, the economic feasibility of solid biomass transport limits rice straw use to distances within 200 km of the source [49].

At present, great attention is given to the anaerobic conversion of lignocellulosic biomass in bio-methane, with particular regards to the kinetic characteristics of the digestion process, related to the lag phase, hydrolysis rate, methane production rate, and methane yield [1]. Moreover, from this energy route, it is possible to obtain fertilizer as by-product [50].

### 1.3. Anaerobic Digestion

Anaerobic digestion of biomass is one of the viable conversion processes of rice straw into energy. Indeed, it has been highlighted to be the most favourable route to use the rice straw energy potential [43]. Anaerobic digestion is a natural process in which specific microorganisms degrade organic matter into intermediate products that are converted into methane (CH<sub>4</sub>). Based on the concentration of total solids (TS), anaerobic digestion can be wet (total solid concentration less than 15%), semi-dry (total solid concentration from 15–20%), or dry (total solid concentration greater than 20%) [3]. In [51], advantages and disadvantages of different biomass pretreatments and anaerobic straw digestion processes are highlighted. Anaerobic digestion of rice straw occurs faster in wet conditions, even though the related methane yield is approximately the same in any condition [52]. Wet systems have advantages related to decreased water use, elimination of wastewater disposal, and reuse of the solid residue as fertilizers [3]

Biomethanation is a complex biological process composed of four phases [41]:

- Hydrolysis phase: During this phase, cellulose and other carbohydrates, proteins, and fats are broken down into monomers by hydrolase enzymes of anaerobic bacteria; this takes from a few hours for the hydrolysis of carbohydrates, to several days for the hydrolysis of proteins and lipids;
- Acidogenic phase: The results of hydrolysis are monomers, which can be degraded into short-chain organic acids, alcohols, hydrogen, and carbon dioxide by anaerobic bacteria;
- Acetogenic phase: The results of the acidogenic process become the substrates for bacteria in the acetogenic phase, which uses H<sub>2</sub> and CO<sub>2</sub> to form acetic acid. Methanogenic bacteria grow concurrently with acetogenic bacteria. Acetate production decreases if hydrogen partial pressure is great enough;
- Methanogenic phase: Methane is generated in anaerobic conditions; based on the substrate, methanogenesis can be divided into the following categories [41]:
  - Acetoclastic Methanogenesis: Acetate → CH<sub>4</sub> + CO<sub>2</sub>
  - Hydrogenotrophic Methanogenesis: H<sub>2</sub> + CO<sub>2</sub> → CH<sub>4</sub>
  - Methyltrophic Methanogenesis: Methanol → CH<sub>4</sub> + H<sub>2</sub>O

Anaerobic digestion results in biogas composed of 50–65% biomethane (CH<sub>4</sub>) and 35–40% carbon dioxide (CO<sub>2</sub>), with the balance consisting of nitrogen (N<sub>2</sub>) and trace amounts of hydrogen sulphide (H<sub>2</sub>S) and water vapour (H<sub>2</sub>O).

Anaerobic digestion systems are designed in two possible configurations [3]:

- Batch reactors, in which all the substrate/inocula mixture is added at the beginning: They are much simpler and 40% less expensive, but with larger volume requirements and a related larger footprint for the reactors;
- Continuously-fed reactors, in which the substrate/inocula mixture is added incrementally over time.

### 1.4. The Aim of the Paper

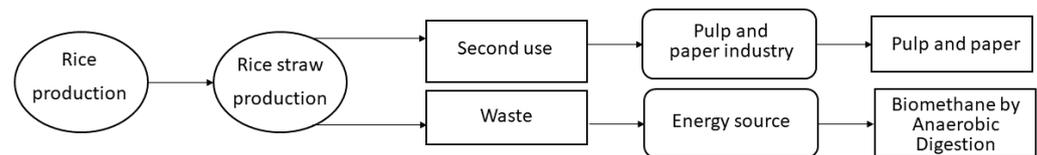
In this paper, we develop a first analysis of rice straw as a resource for energy use by considering the concept of the rice straw barrel, recently developed by Bressan et al. [42]. Afterwards, some considerations on the sustainable use of rice straw based on the Thermodynamic Human Development Index (THDI) will be introduced. A comparison is developed between the present issue of open-field rice straw burning and biomethane production *via* anaerobic digestion. In this context, potential biomethane production is estimated.

## 2. Materials and Methods

In this section, we introduce all of the elements required to evaluate the number of rice straw barrels, the potential biomethane production, and all the fundamental quantities to assess the sustainability of biomethanation from anaerobic digestion. To do this, we introduce the Thermodynamic Human Development Index (THDI).

First, we obtain the amount of rice straw available for energy use, evaluated in terms of rice straw barrels. Moreover, it has been considered that only 20% of the total amount of rice straw is usually used for other purposes, such as the pulp and paper industry [21]; consequently, we considered only 80% of the total amount of rice straw as available.

Once the average number of rice straw barrels is obtained and the proportion dedicated to other uses is deducted, the amount of biomethane produced from anaerobic digestion can be evaluated. Figure 2 shows the flow of the processes considered.



**Figure 2.** Schematic assumptions used in our analysis, considering rice production, the related average rice straw production, its possible second use in the pulp and paper industry (20% by weight) and the remainder (for which the available RSB are evaluated) that can be anaerobically digested in order to obtain biomethane.

Lastly, the effect of using at least 50% of the total amount of rice straw for anaerobic digestion is compared with the current practice of open-field burning. To develop this comparison, an indicator of sustainability, THDI, is introduced.

### 2.1. Rice Straw Availability

In order to evaluate the total amount of rice straw available on fields prior to bailing,  $m_{rs}$ , we consider that it is proportional to the amount of milled rice,  $m_r$ , produced in a specific region:

$$m_{rs} = k m_r \quad (1)$$

where  $m$  denotes the mass, and the subscripts  $rs$  and  $r$  are, respectively, rice straw and rice,  $k$  is the empirical coefficient that gives the amount of rice straw with respect to the amount of rice.

### 2.2. The Rice Straw Barrel

This study considers the concept of rice straw barrels, recently introduced by Bressan et al. [42], in order to evaluate the potential use of rice straw to produce by-products such as methane and the related digestate.

To do so, the first step is to analyse the rice straw barrel as introduced in [42], improving this approach by using recently developed thermoconomics [53–57].

The rice straw barrel has been introduced in the analysis of rice production in the Novara district, Italy. This district has an area of 134,025 ha, with a temperate climate characterised by cold winters (minimum temperatures often below 0 °C between December and February) and quite hot summers (frequently 30 °C). Mean rainfall amounts to approximately 1000 mm yr<sup>-1</sup>, characterised by two maximums (148.9 mm in November and 110.7 mm in May) and two minimums (52.5 mm in July and 56.5 mm in January). Winter averages approximately 35 cm of snow. According to Torrión Quartara Geophysical Observatory data [58] (meteorological archive dating back to August 1999), the average annual temperature during the 21st century is 13.9 °C [59]. In this area, the rice variety mostly cultivated is Baldo: it is characterised by round, thick, hard grains; the cultivation season is from January to October; it is carried out by submersion and high levels of agricultural mechanization [42]: all agricultural processes are carried out by medium-power tractors and specific equipment, and the fields are flooded using water irrigation canals [42].

The rice straw barrel contains the rice straw, which is removed as soon as its moisture content has dropped from 50% to below 20% in order to prevent fermentation [42]: usually, rice straw is removed 3–4 days after harvest, depending on the local climate [7]. The

biomass left in the field decomposes, which decreases available biomass. The reduction in biomass can be evaluated as follows [60]:

$$m(t) = m_r + m_d \cdot e^{-kt} \quad (2)$$

where  $m(t)$  is the mass of the rice straw over time,  $m_r$  is the remaining mass after time  $t$ ,  $m_d$  is the difference between the initial mass  $m_0 = m_r + m_d$  and the remaining mass  $m_r$ ,  $t$  is the time in month,  $k$  is the decomposition rate ( $\text{month}^{-1}$ ). The values of the coefficients for the case study in Novara are summarised in Table 6: the value of the exponent in Equation (2) for Novara district for rice straw removal after 4 days or 1 month is  $m = m_r + 0.024 m_d \approx 5765.4 \text{ kg ha}^{-1}$  or  $4177.3 \text{ kg ha}^{-1}$ , respectively.

**Table 6.** Numerical values of the coefficients in Equation (2) for Novara area during rice harvesting [42].

Quantity	Value	Unit of Measurement
$m_r$	1828.8	$\text{kg ha}^{-1}$
$m_d$	4262.2	$\text{kg ha}^{-1}$
$k$	0.596	$\text{month}^{-1}$

The barrel considered is a cylinder 1.8 m in diameter and 1.2 m in height, wrapped in a nylon film, weighing 430 kg and having a density of  $141 \text{ kg m}^{-3}$ —which is in agreement with the values reported in Table 5—and with an energy content of around 6020 MJ.

In Northern Italy, the major environmental impact from cultivation has been estimated to be related to field emissions for 68.0%, to fertilizers for 9.2%, to transportation for 6.1%, to refining and packing for 4.7%, and to field operations for 3.6% [3]. Consequently, removing rice straw will contribute to environmental mitigation of the cultivating process.

In order to obtain the number of rice straw barrels available to be used as energy, the average decrease in moisture content is considered to be from 50% to 20%. This must occur prior to baling and excludes the 20% of the total amount of rice straw that can be used for the pulp and paper industry. Thus, the characteristics of the barrel have been adopted as introduced in [42]. We assume to use the total number of barrels for anaerobic digestion to obtain biomethane.

### 2.3. Biomethanation

Here, the evaluation of biomethane production by rice straw is developed. To do so, the results of Meraj et al. [1] are considered. Rice straw substrates were air-dried and mechanically pretreated in order to reduce their size to 0.1 mm, and then put in anaerobic bioreactors maintained at a temperature of  $(35 \pm 1) \text{ }^\circ\text{C}$  and pH in the range of 7.0–7.5 [1]. Table 7 shows cellulose content based on particle size.

**Table 7.** Cellulose content in relation to particle size [1].

Size [mm]	Cellulose Content [%]
<0.15	84
0.15–0.18	83
0.18–0.21	76
0.21–0.25	68
0.25–0.30	61
0.30–0.42	56
>0.42	50

Meraj et al. [1] proved experimentally that biogas production kinetics are well-modelled by the Logistic Function Model [61]:

$$m(t) = \frac{m_0}{1 + \exp\left(2 + \frac{4 \dot{m}_{max} (\ell - t)}{m_0}\right)} \quad (3)$$

where  $m(t)$  is methane mass production ( $\text{mL g}_{VS}^{-1}$ ),  $VS$  means volatile solids,  $m_0$  is the methane yield potential ( $\text{mL g}_{VS}^{-1}$ ),  $\ell$  is the lag phase (d), which is the minimum time required for methane production,  $t$  is the time (d), and  $\dot{m}_{max}$  is the maximum methane production rate ( $\text{mL g}_{VS}^{-1} \text{d}^{-1}$ ) [1]. The amount of methane yield in terms of total solids (TS) was evaluated to be in the range of 193–240 L  $\text{kg}_{TS}^{-1}$ , while Table 8 summarises methane yield based on volatile solids (VS) for different pretreatments [3].

**Table 8.** Methane yield in term of volatile solids for different pretreatments [3,62].

Type of Pretreatment	Methane Yield [ $10^{-3} \text{m}^3 \text{kg}_{VS}^{-1}$ ]	Digestion Temperature [°C]	Time Period [d]
Cut (3–5 mm)	280	22	120
Pulverized	215	35	120
Extrusion (<50 mm)	227	35	45
2% $\text{NH}_3$	190	35	24

Starting from these considerations, we evaluate the average amount of total solids (TS) and volatile solids (VS) available in relation to an RSB. These quantities allow us to assess annual biomethane potential. To do so, we consider the average values of the proximate analysis of rice straw, summarised in [43] and biomethane yields,  $\dot{V}_{\text{CH}_4}$ , summarised in [3]. These average values depend on different inocula, pretreatments, and working temperatures. The values considered in this paper are summarised in Table 9.

**Table 9.** Values used to perform the calculations: empirical coefficient  $k$  (Equation (1)), amount of volatile solids (VS) with respect to total solids (%TS), biomethane yield ( $\dot{V}_{\text{CH}_4}$ ).

Quantity	Minimum	Average	Maximum	References
$k$	0.70	1.35	1.50	[3,6–10]
VS (%TS)	73.80	84.08	95.26	[43]
$\dot{V}_{\text{CH}_4}$ ( $\times 10^{-3} \text{m}^3 \text{kg}_{VS}^{-1}$ )	92	186	280	[3]

#### 2.4. Open-Field Burning

At least 50% of the rice straw produced is open-field burned, with notorious negative impacts both on the environment due to atmospheric pollution and agronomy through reduced soil quality [63]. However, open-field burning is a cheap disposal method; thus, it is the one most adopted by farmers around the world [7]. This disposal method is a major contributor to damaging levels of air pollution, with related health issues, and a high contributor to greenhouse gas emissions, especially in Asia countries [64]. Hence, research is ongoing for the development of alternative uses of rice straw, turning it into a commodity with sustainable value chains to benefit rural people [64].

In order to evaluate the effects of emissions due to open field burning versus anaerobic digestion and biomethanation, we considered the results of Refs. [43,65]. The emissions for each 1000 kg of rice straw can be summarised as follows [43]:

- Open field burning:
  - 1460.00 kg  $\text{CO}_2$  (carbon dioxide);
  - 34.70 kg CO (carbon monoxide);
  - 13.00 kg PM (particulate matter);

- 3.10 kg NO<sub>x</sub> (oxides of nitrogen);
- 2.00 kg SO<sub>2</sub> (sulphur dioxide);
- 1.20 kg CH<sub>4</sub> (methane).
- Anaerobic digestion:
  - 2.05 kg CO<sub>2</sub> (carbon dioxide);
  - 0.67 kg CO (carbon monoxide);
  - 0.01 kg H<sub>2</sub>S (hydrogen sulphide);
  - 0.04 kg NO<sub>x</sub> (oxides of nitrogen);
  - 1.07 kg CH<sub>4</sub> (methane).

### 2.5. The Thermoeconomic Approach

Here, we introduce a recently developed thermodynamic index in order to analyse the sustainable use of rice straw barrels by considering biomethane production by anaerobic digestion.

The indicator, introduced to quantify a country's conditions, is an improvement of the United Nations Human Development Index (*HDI*), which is based on three quantities: Education Index, *EI*, Income Index *II*, and Life Expectancy Index, *LEI*. Thus, *HDI* quantifies the development level and well-being of a country with regards to education, health, and earnings [66]. It is the geometric mean of three normalised indices that are representative of each dimension [67], and its analytical definition is [68]:

$$HDI = (LEI \cdot EI \cdot II)^{1/3} \quad (4)$$

with *LEI* being the Life Expectancy Index, while *EI* represents the Education Index, and *II* stands for the Income Index.

The Life Expectancy Index *LEI* is expressed as [68]:

$$LEI = \frac{LE - 20}{85 - 20} \quad (5)$$

where *LE* denotes the Life Expectancy at birth, indicative of the overall mortality level of a country, and it corresponds to the years that a newborn is expected to live at current mortality rates [69]. The UN has set its minimum and maximum values to 20 and 85 years, respectively [70].

The *Education Index*, *EI*, has been defined by the United Nations Development Program (UNDP) as follows [68]:

$$EI = \frac{MYSI + EYSI}{2} \quad (6)$$

where *MYSI* = *MYS*/15 is the Mean Years of Schooling Index and *EYSI* = *ESI*/18 is the Expected Years of Schooling Index [68].

The United Nations defined the Normalised Income Index *II* as:

$$II = \frac{\ln(GNI_{pc}/100)}{\ln(75,000/100)} \quad (7)$$

where *GNI<sub>pc</sub>* is the gross national income per capita at purchasing power parity (PPP), with minimum and maximum values set by the UN [68] as USD 100 and USD 75,000.

However, the *HDI* does not take into account the country's technological level and the environmental impact of the country. Aiming to incorporate the technological stage, an improvement of the *HDI* [71] was recently introduced, which puts forward an irreversible thermodynamic approach [53,57] as follows:

$$THDI = \left( \frac{LEI \cdot EI}{I_T} \right)^{1/3} \quad (8)$$

where [54]:

$$I_T = \frac{T_0 \dot{S}_g}{\dot{W} \cdot GNI_{pc}} = 0.01 \cdot \frac{T_0 \dot{S}_g}{\dot{W}} \cdot 750^{-II} \quad (9)$$

and [55,72–74]:

$$T_0 \dot{S}_g = T_0 \dot{m}_{CO_2} s_g \quad (10)$$

where  $\dot{m}_{CO_2}$  is the  $CO_2$  mass flow rate emitted for obtaining the required effect  $\dot{W}$ , and  $s_g$  is the specific entropy generation.

In relation to these considerations, it is possible to evaluate the thermodynamic indicator THDI [75] in the case of rice straw  $THDI_{rs,ad}$  used for biomethane production and the present-condition THDI. This ratio results:

$$\frac{THDI_{rs,ad}}{THDI} = \sqrt[3]{\frac{m_{CO_2}}{m_{CO_2} - m_{CO_2rs}} \cdot 750^{-(II_{rs}-II)}} \quad (11)$$

where  $m_{CO_2rs}$  is the amount of  $CO_2$  saved by production of biomethane from rice straw.

Thus, we analyse the effect on sustainability derived from substituting the current practice of burning rice straw on open fields with anaerobic digestion and biomethanation by using the THDI Equation (11), considering the results of [43,65].

### 3. Results

The analysis is first focused on the Novara district and then extended to Italy. The Italian values are compared to those of other major rice producing countries (Bangladesh, Brazil, China, India, Pakistan, Spain, Thailand, United States of America, and Vietnam). The rice production for those countries is shown in Table 3.

#### 3.1. The Novara Case and the Italian Context

In 2020, 220,000 t of rice were harvested in the Novara area; representing approximately 15% of total Italian rice production.

Starting from rice quantity, it is possible to obtain the mass of rice straw available for energy ( $m_{rs,AD}$ ), the number of rice straw barrels available ( $RSB$ ), the total amount of volatile solids (total solids minus ash content) in the biomass ( $m_{VS}$ ), and the annual biomethane yield ( $\dot{V}_{CH_4}$ ). The numerical values of these quantities are reported in Table 10. In the worst case (the amount of rice straw around 70% of the mass of the rice grain collected,  $k = 0.70$ ), 200,558 rice straw barrels ( $RSB$ ) are theoretically available for energy. This corresponds to an annual biomethane yield ranging from  $(1.09\text{--}3.32) \times 10^7 \text{ m}^3$ . Considering  $k = 1.50$ ,  $RSB$  equals 429,767, with a potential annual biomethane yield of  $(2.93\text{--}8.90) \times 10^7 \text{ m}^3$ .

**Table 10.** Results for the Novara area in the year 2020. The minimum, average, and maximum values are based on data from Table 9. Subscripts *A*, *B*, and *C* in  $\dot{V}_{CH_4}$  refer to biomethane yields of 92, 186, and 280 L  $kg_{VS}^{-1}$ , respectively.

Quantity		Min.	Avg.	Max.
$m_{rs,AD}$	(t)	86,240	166,320	184,800
$RSB$	( $\times 10^5$ )	2.01	3.87	4.30
$m_{VS}$	(t)	118,410	260,171	317,959
$\dot{V}_{CH_4,A}$	( $\times 10^7 \text{ m}^3 \text{ yr}^{-1}$ )	1.09	2.39	2.93
$\dot{V}_{CH_4,B}$	( $\times 10^7 \text{ m}^3 \text{ yr}^{-1}$ )	2.20	4.84	5.91
$\dot{V}_{CH_4,C}$	( $\times 10^7 \text{ m}^3 \text{ yr}^{-1}$ )	3.32	7.28	8.90

If we expand these results to the entirety of Italian, the total amount of  $RSB$  and the related potential amount of biomethane from rice straw can be obtained. The time period considered is from the years 2000 to 2020, as summarised in Table 3. Table 11 shows the minimum, average, and maximum values for Italy based on data from Table 9. The average annual biomethane yield is in the range of  $(0.71\text{--}2.15) \times 10^8 \text{ m}^3$ . The rice straw

yield of 1.35 is based on milled rice in the year 2020. In 2019, in Italy, the total amount of biomethane produced from agricultural and zootechnical effluents has been estimated to be  $2.2 \times 10^9 \text{ m}^3$ , producing a gross of 987 MW electrical power across 1629 different power plants [76]. The agricultural and zootechnical sectors represents around 82% of electrical production from biogas.

**Table 11.** Rice straw barrels (*RSB*) and potential annual biomethane production ( $\dot{V}_{\text{CH}_4}$ ) in Italy. Subscripts *A*, *B*, and *C* refer to biomethane yields of 92, 186, and 280 L  $\text{kg}_{\text{VS}}^{-1}$ , respectively.

Quantity	Year														
	2000			2005			2010			2015			2020		
	Min.	Avg.	Max.												
<i>RSB</i> ( $\times 10^6$ )	1.12	2.16	2.40	1.29	2.48	2.76	1.38	2.67	2.96	1.38	2.67	2.97	1.37	2.65	2.94
$\dot{V}_{\text{CH}_4,A}$ ( $\times 10^7 \text{ m}^3 \text{ yr}^{-1}$ )	2.62	5.75	7.03	3.01	6.61	8.08	3.23	7.09	8.67	3.23	7.10	8.68	3.21	7.05	8.62
$\dot{V}_{\text{CH}_4,B}$ ( $\times 10^8 \text{ m}^3 \text{ yr}^{-1}$ )	0.53	1.16	1.42	0.61	1.34	1.63	0.65	1.43	1.75	0.65	1.44	1.75	0.65	1.43	1.74
$\dot{V}_{\text{CH}_4,C}$ ( $\times 10^8 \text{ m}^3 \text{ yr}^{-1}$ )	0.80	1.75	2.14	0.92	2.01	2.46	0.98	2.16	2.64	0.98	2.16	2.64	0.98	2.15	2.62

Thus, biogas from rice straw can improve the production of biogas, which is useful for green energy production. This can be facilitated by increasing the number of anaerobic digestion plants within 200 km of rice crops. This can improve the circular economic framework by using field waste without a second use and preventing its burning on fields. Moreover, the digestate obtained from anaerobic digestion can be employed as a fertilizer [3].

### 3.2. Some of the Major Rice-Producing Countries

Table 12 shows the results of the previous approach extended to some of the major rice-producing countries for the period 2000–2020. The total number of *RSB* and the potential biomethane yield per year are shown. The minimum, average, and maximum biomethane yields are based on the literature and are, respectively, 92, 186, and 280 L  $\text{kg}_{\text{VS}}^{-1}$  [3].

Several studies have reported higher biomethane yields (e.g., 325.76 L  $\text{kg}_{\text{VS}}^{-1}$  [77]). The difference between the data used in the present paper and the literature is due only to different pretreatments (in this paper only mechanical pretreatments are considered).

#### Improvements in Sustainability Due to Avoiding Rice Straw Burning on Field

In this paper, biomethanation by anaerobic digestion has been considered as a sustainable alternative to burning rice straw on field. Thus, the related possible  $\text{CO}_{2,eq}$  reduction has been analysed by considering the data summarised in [43,65] together with the AR5 Global Warming Potentials (*GWP*). Then, the sustainability of the biomethanation was analysed by introducing the THDI indicator. This index has been evaluated using Equations (8) and (9).

We must highlight that the countries considered presented different trends in carbon dioxide equivalent emissions,  $\text{CO}_{2,eq}$ , during the period 2000–2018, as shown in Figure 3. Indeed, if we consider the overall ratio  $(\text{CO}_{2,eq} 2018 - \text{CO}_{2,eq} 2000) / \text{CO}_{2,eq} 2000$ , the values are positive (increased emissions) for most developing countries, such as: Bangladesh +64%, China +175%, India +123%, Pakistan +86%, Thailand +61%, and Vietnam +477%, while it is negative (decreased emissions) for the following countries: Brazil −21%, Italy −21%, Spain −4%, and U.S.A. −10%.

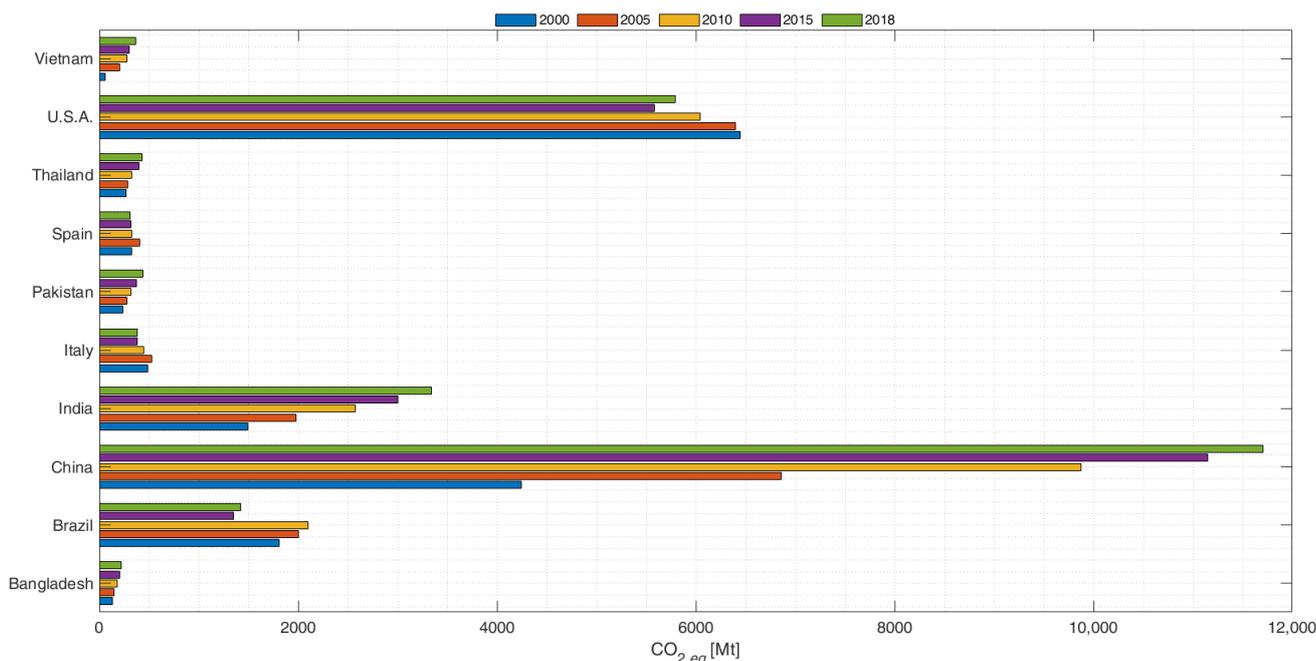
**Table 12.** Rice straw barrels (*RSB*) and potential annual biomethane production ( $\dot{V}_{CH_4}$ ) for major rice-producing countries. Subscripts *A*, *B*, and *C* refer to biomethane yields of 92, 186, and 280 L kg<sup>-1</sup><sub>VS</sub>, respectively.

Quantity	2000			2005			Year 2010			2015			2020		
	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.
<b>Bangladesh</b>															
<i>RSB</i> ( $\times 10^7$ )	3.43	6.62	7.35	3.63	7.00	7.77	4.56	8.80	9.78	4.72	9.11	10.12	5.01	9.65	10.75
$\dot{V}_{CH_4,A}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.80	1.76	2.15	0.85	1.86	2.28	1.07	2.34	2.86	1.10	2.42	2.96	1.17	2.57	3.14
$\dot{V}_{CH_4,B}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	1.62	3.56	4.35	1.71	3.76	4.60	2.15	4.73	5.79	2.23	4.90	5.99	2.36	5.19	6.35
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	2.44	5.36	6.55	2.58	5.67	6.92	3.24	7.13	8.71	3.36	7.38	9.01	3.56	7.82	9.55
<b>Brazil</b>															
<i>RSB</i> ( $\times 10^7$ )	1.02	1.96	2.18	1.20	2.32	2.58	1.02	1.98	2.19	1.12	2.16	2.40	1.01	1.95	2.17
$\dot{V}_{CH_4,A}$ ( $\times 10^8$ m <sup>3</sup> yr <sup>-1</sup> )	2.37	5.21	6.37	2.81	6.17	7.54	2.39	5.26	6.42	2.62	5.75	7.03	2.36	5.19	6.34
$\dot{V}_{CH_4,B}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.48	1.05	1.29	0.57	1.25	1.52	0.48	1.06	1.30	0.53	1.16	1.42	0.48	1.05	1.28
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.72	1.59	1.94	0.86	1.88	2.30	0.73	1.60	1.96	0.80	1.75	2.14	0.72	1.58	1.93
<b>China</b>															
<i>RSB</i> ( $\times 10^8$ )	1.73	3.34	3.71	1.66	3.20	3.56	1.80	3.47	3.85	1.95	3.76	4.18	1.95	3.76	4.17
$\dot{V}_{CH_4,A}$ ( $\times 10^{10}$ m <sup>3</sup> yr <sup>-1</sup> )	0.40	0.89	1.09	0.39	0.85	1.04	0.42	0.92	1.13	0.46	1.00	1.22	0.46	1.00	1.22
$\dot{V}_{CH_4,B}$ ( $\times 10^{10}$ m <sup>3</sup> yr <sup>-1</sup> )	0.82	1.80	2.19	0.78	1.72	2.10	0.85	1.87	2.28	0.92	2.02	2.47	0.92	2.02	2.47
$\dot{V}_{CH_4,C}$ ( $\times 10^{10}$ m <sup>3</sup> yr <sup>-1</sup> )	1.23	2.70	3.30	1.18	2.59	3.17	1.28	2.81	3.43	1.38	3.04	3.72	1.38	3.04	3.72
<b>India</b>															
<i>RSB</i> ( $\times 10^8$ )	1.16	2.24	2.49	1.26	2.42	2.69	1.31	2.53	2.81	1.43	2.75	3.06	1.63	3.13	3.48
$\dot{V}_{CH_4,A}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	2.71	5.96	7.29	2.93	6.44	7.87	3.07	6.74	8.23	3.33	7.32	8.95	3.80	8.34	10.20
$\dot{V}_{CH_4,B}$ ( $\times 10^{10}$ m <sup>3</sup> yr <sup>-1</sup> )	0.56	1.21	1.47	0.59	1.30	1.59	0.62	1.36	1.66	0.67	1.48	1.81	0.77	1.69	2.06
$\dot{V}_{CH_4,C}$ ( $\times 10^{10}$ m <sup>3</sup> yr <sup>-1</sup> )	0.83	1.81	2.22	0.89	1.96	2.40	0.93	2.05	2.51	1.01	2.23	2.72	1.16	2.54	3.10
<b>Pakistan</b>															
<i>RSB</i> ( $\times 10^7$ )	0.66	1.27	1.41	0.76	1.46	1.63	0.66	1.27	1.41	0.93	1.79	1.99	0.77	1.48	1.64
$\dot{V}_{CH_4,A}$ ( $\times 10^8$ m <sup>3</sup> yr <sup>-1</sup> )	1.53	3.37	4.12	1.77	3.89	4.76	1.54	3.38	4.14	2.17	4.77	5.83	1.79	3.94	4.81
$\dot{V}_{CH_4,B}$ ( $\times 10^8$ m <sup>3</sup> yr <sup>-1</sup> )	3.10	6.81	8.33	3.58	7.87	9.62	3.11	6.84	8.36	4.39	9.65	11.84	3.62	7.96	9.73
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.47	1.03	1.25	0.54	1.18	1.45	0.47	1.03	1.26	0.66	1.45	1.78	0.55	1.20	1.47
<b>Spain</b>															
<i>RSB</i> ( $\times 10^6$ )	0.75	1.45	1.62	0.75	1.45	1.61	0.86	1.63	1.81	0.77	1.49	1.65	0.67	1.30	1.44
$\dot{V}_{CH_4,A}$ ( $\times 10^7$ m <sup>3</sup> yr <sup>-1</sup> )	1.76	3.87	4.73	1.75	3.86	4.71	1.98	4.34	5.30	1.80	3.96	4.84	1.57	3.46	4.23
$\dot{V}_{CH_4,B}$ ( $\times 10^7$ m <sup>3</sup> yr <sup>-1</sup> )	3.56	7.82	9.56	3.55	7.79	9.53	3.99	8.78	10.70	3.65	8.01	9.79	3.18	6.99	8.54
$\dot{V}_{CH_4,C}$ ( $\times 10^8$ m <sup>3</sup> yr <sup>-1</sup> )	0.54	1.18	1.44	0.53	1.17	1.43	0.60	1.32	1.61	0.55	1.21	1.47	0.48	1.05	1.29
<b>Thailand</b>															
<i>RSB</i> ( $\times 10^7$ )	2.36	4.54	5.05	2.79	5.39	5.99	3.25	6.28	6.97	2.53	4.87	5.41	2.76	5.32	5.91
$\dot{V}_{CH_4,A}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.55	1.21	1.48	0.65	1.43	1.75	0.76	1.67	2.04	0.59	1.30	1.58	0.64	1.41	1.73
$\dot{V}_{CH_4,B}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	1.11	2.44	2.99	1.32	2.90	3.54	1.54	3.38	4.13	1.19	2.62	3.20	1.30	2.86	3.49
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	1.67	3.68	4.50	1.99	4.36	5.33	2.31	5.08	6.21	1.80	3.94	4.82	1.96	4.30	5.26
<b>U.S.A.</b>															
<i>RSB</i> ( $\times 10^7$ )	0.79	1.52	1.69	0.92	1.78	1.97	1.01	1.94	2.15	0.80	1.53	1.70	0.94	1.81	2.02
$\dot{V}_{CH_4,A}$ ( $\times 10^8$ m <sup>3</sup> yr <sup>-1</sup> )	1.84	4.05	4.95	2.15	4.73	5.78	2.35	5.16	6.30	1.86	4.08	4.99	2.20	4.83	5.90
$\dot{V}_{CH_4,B}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.37	0.82	1.00	0.44	0.96	1.17	0.48	1.04	1.27	0.48	0.83	1.01	0.44	0.98	1.19
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.561	1.23	1.51	0.66	1.44	1.76	0.72	1.57	1.92	0.57	1.24	1.52	0.67	1.47	1.80
<b>Vietnam</b>															
<i>RSB</i> ( $\times 10^7$ )	2.97	5.72	6.35	3.27	6.30	7.00	3.65	7.03	7.82	4.11	7.93	8.81	3.90	7.52	8.35
$\dot{V}_{CH_4,A}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	0.69	1.52	1.86	0.76	1.68	2.05	0.85	1.87	2.29	0.96	2.11	2.58	0.91	2.00	2.44
$\dot{V}_{CH_4,B}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	1.40	3.08	3.76	1.54	3.39	4.14	1.72	3.78	4.62	1.94	4.26	5.21	1.84	4.04	4.94
$\dot{V}_{CH_4,C}$ ( $\times 10^9$ m <sup>3</sup> yr <sup>-1</sup> )	2.11	4.63	5.66	2.32	5.10	6.24	2.59	5.70	6.96	2.92	6.42	7.85	2.77	6.09	7.44

On the other hand, all the countries improved their Life Expectancy Index (*LEI*), Income Index (*II*), and Educational Index (*EI*) during the time period considered, as shown in Table 13.

**Table 13.** Variation of the indicators *LEI*, *II*, and *EI* during the period 2000–2018. The percentage variation was evaluated by  $(I_{2018} - I_{2000})/I_{2000}$  [%].

Indicator <i>I</i>	Variation in the Period 2000–2018 [%]									
	Bangladesh	Brazil	China	India	Italy	Pakistan	Spain	Thailand	USA	Vietnam
<i>LEI</i>	38	21	16	31	12	18	11	14	7	10
<i>II</i>	43	7	89	46	3	15	7	22	7	56
<i>EI</i>	111	50	62	78	32	96	41	76	7	81

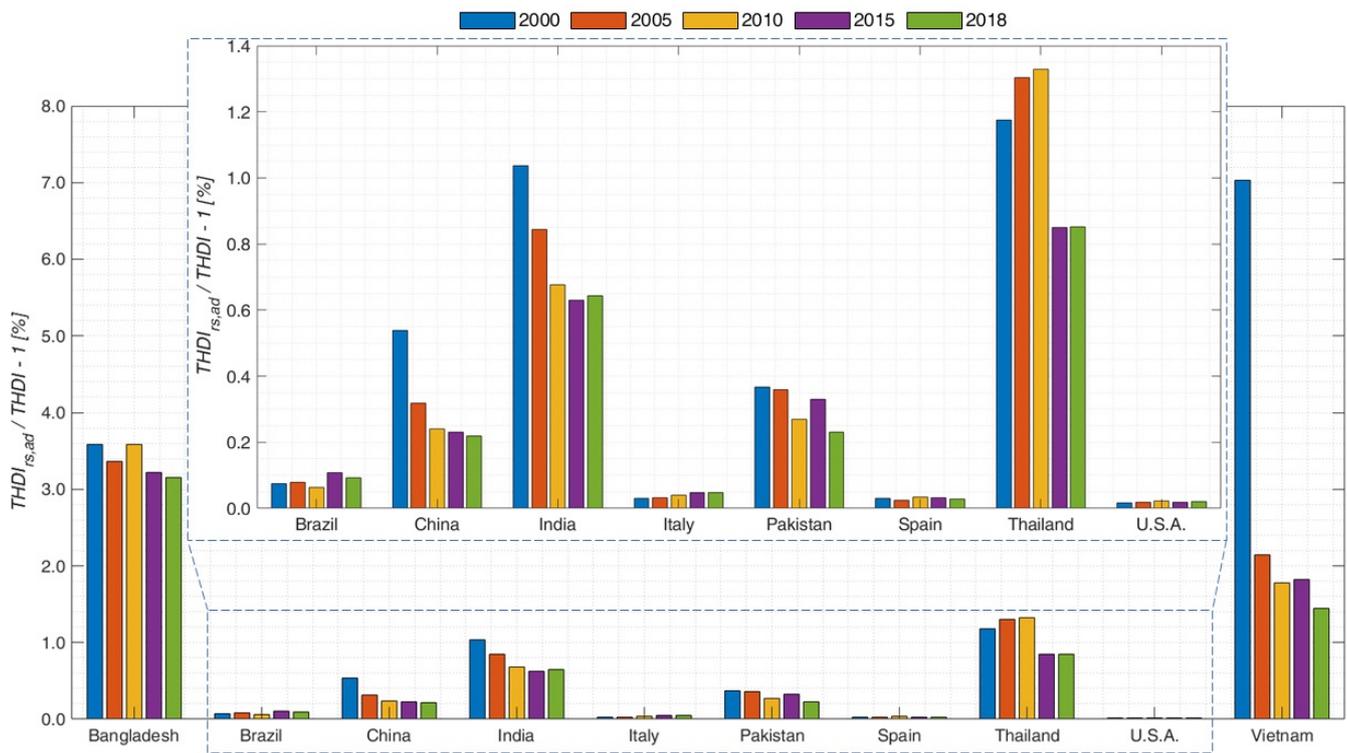


**Figure 3.** Carbon dioxide equivalent emissions  $CO_{2,eq}$  (Mt) in Bangladesh, Brazil, China, India, Italy, Pakistan, Spain, Thailand, United States of America, and Vietnam from 2000 (bottom bar for each country, red colour) to 2018 (top bar for each country, green colour); data from [78].

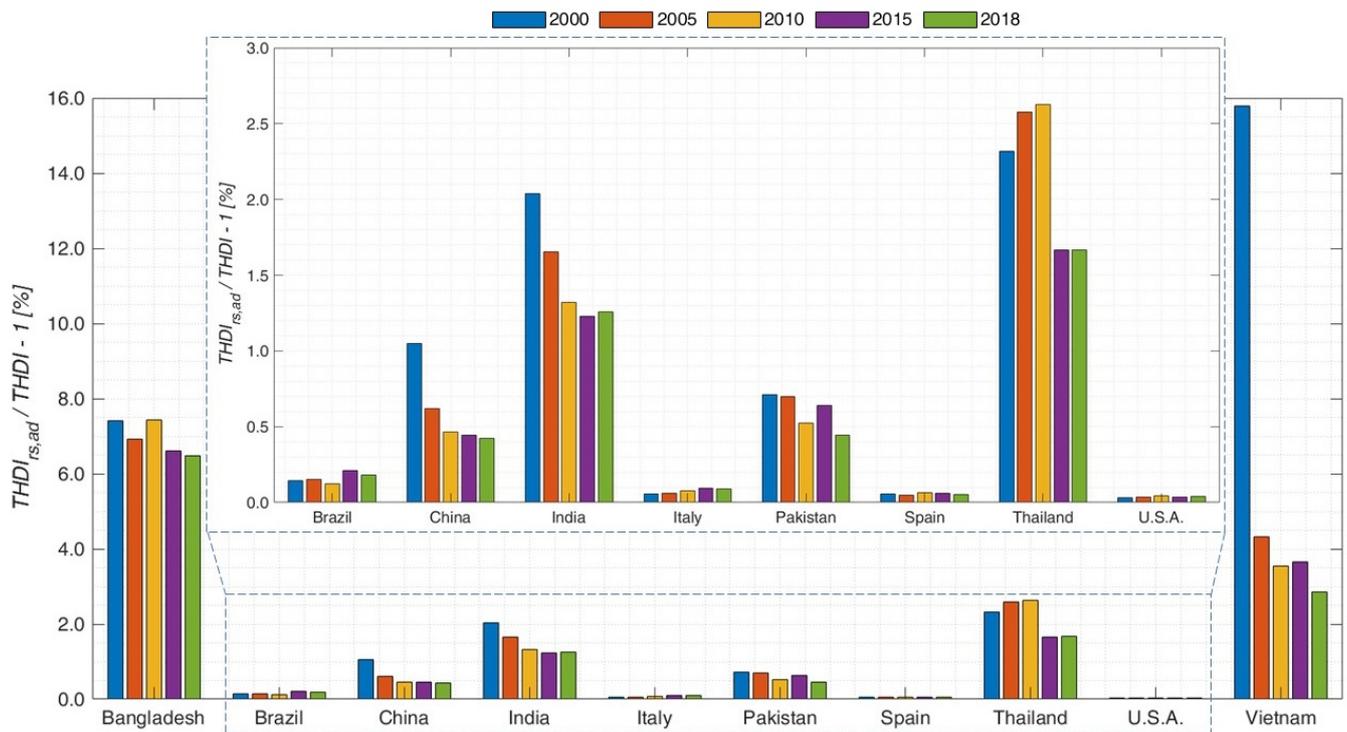
Thus, we calculated the THDI (Equation (11)) in order to quantify the effect on sustainability of biomethanation by anaerobic digestion. The amount of rice straw considered was half that available in each country, which corresponds to the amount actually burned in open fields. In Figures 4–6, the ratio  $(THDI_{rs} - THDI)/THDI$  is reported, considering, respectively, the previous  $k$  coefficient values (from Equation (1)) of 0.70, 1.35, and 1.50. THDI was evaluated only in relation to the reduction in carbon dioxide equivalent emissions due to anaerobic digestion of rice straw; indeed, at first approximation, the socio-economic effect of biomethane production from anaerobic digestion of rice straw should result in income redistribution. Rice straw barrels represent a new source of income for farmers and a reduction in sales of fossil-fuel-derived methane. Consequently, in this introductory approach the income index is considered unchanged for all the continents.

A more detailed analysis requires designing the biomethane production chain, which can be developed by a local techno-economic analysis because agricultural processes are different across continents and are locally dependent. For instance, in Italy, biomethane production from agricultural and zootechnic wastes has been estimated to have generated approximately 12,000 new jobs through the year 2019 [76].

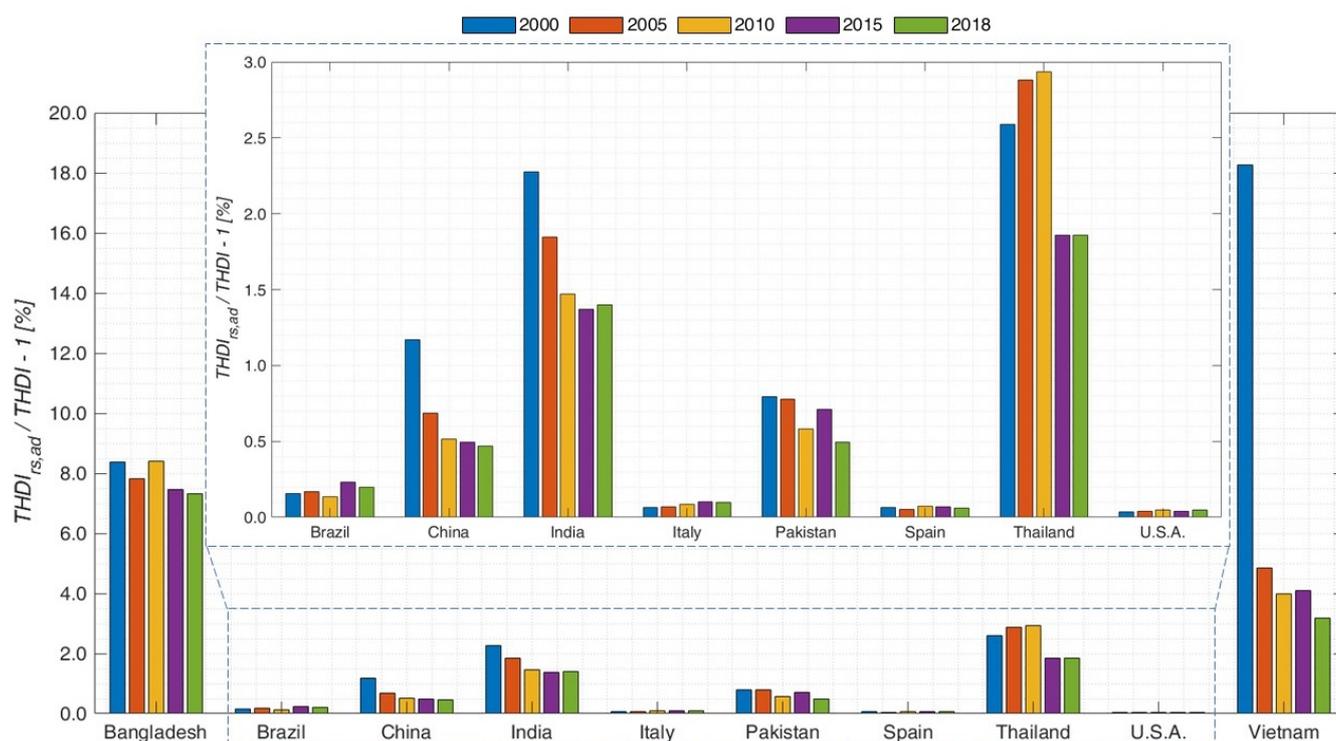
The results highlight how the use of rice straw could be very interesting from a sustainable viewpoint, but also from a socio-economic one. However, we are unable to estimate the economic value of rice straw barrels due to cost fluctuations in the energy market. This could be the next step, but it must be based on local energy market constraints.



**Figure 4.** Yearly annual variation of the sustainability indicator THDI using Equation (11) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane using  $k = 0.70$  in Equation (1).



**Figure 5.** Yearly annual variation of the sustainability indicator THDI by using Equation (11) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane, using  $k = 1.35$  in Equation (1).



**Figure 6.** Yearly annual variation of the sustainability indicator THDI by using Equation (11) to compare the current situation (50% of total rice straw burned on field) with anaerobic digestion of the same amount of rice straw to obtain biomethane, using  $k = 1.50$  in Equation (1).

#### 4. Discussion

Biofuels from renewable organic biomass could represent an interesting resource to decrease the use of fossil fuels and greenhouse gas emissions (particularly related to transportation) and to improve local economies [79]; the production of sustainable fuels has been estimated to eliminate the 68% of the global warming potential [3]. Recently, great effort has been put into research to establish biofuel production from not only second-generation biomass, but also third-generation biomass. In this context, straw or wood residues represent field residue [80].

Rice is the most important staple food, providing nutrition and calories for over half of the world's human population [81]. Consequently, rice straw could represent an ideal resource for biofuel production because it is a waste product of food production; consequently, it does not compete with food availability [82]. Indeed, in 2009, 915 Mt of rice straw were produced [3]; this amount represents great potential for bio-methane, biofuel, and bioplastic production. In some areas of the world, the surplus of rice straw is frequently removed from fields by open-field burning, which consequently increases environmental pollution, even if it is economically convenient for the farmer.

Thus, biofuel production from rice straw is a way to assign economic value to this residue, allowing farmers to use it in a more sustainable way. In this context, the rice straw barrel [42] could represent a metric for the financial market, analogous to a barrel of oil for fossil fuels.

Waste rice straw can be converted into biofuels by biological processes that use bacteria to convert the biomass into biofuel in anaerobic digestion conditions for methane production or fermentation of sugars for ethanol generation [3]. In particular, anaerobic digestion is a useful technology to treat animal and agro-industrial wastes and municipal sludge containing high organic content [5]. During anaerobic degradation of organic substrates,  $\text{CO}_2$  and  $\text{CH}_4$  are obtained as end products, with biomethane productivity depending on the reduced amount of organic carbon [83]. Among the variety of field residues available,

rice straw presents an interesting capability for conversion into biomethane [12]. However, anaerobic digestion is conditioned by some constraints, as outlined in [84,85]:

- The high C/N ratio of rice straw: This is a favourable nutrient balance both for anaerobic bacteria and for maintaining a steady environment. The C/N ratio can be in the range of 20–30 for anaerobic digestion and methanogenesis, 16–45 for hydrolysis, and 20–30 for methanogenesis [86];
- The lignin, hemicellulose, and cellulose percentages of rice straw affect the microorganisms effects on the substrate;
- The volatile fatty acids, temperature, and the pH. Volatile fatty acids (acetic acid, propionic acid, butyric acid, valeric acid, lactic acid, and formic acid) represent the most crucial intermediaries produced in anaerobic digestion and affect its stability [85]. They are generated when acids produced from hydrolysis and acidification cannot be consumed by methanogenic bacteria (for example *Clostridium thermosuccinogenes* and *Clostridium cellulovorans* [3]), resulting in a pH decrease and process destabilisation [5]. Indeed, the pH range for anaerobic digestion is from 6.8–7.2, with 6.5–7.3 providing the best results, 7.0 required for methanogenesis [3], and hydrolysis and acidogenesis occurring in the range of 5.5–6.5 [87]. Temperature affects the reaction velocity, the transport phenomena (diffusion), and chemical dissociation. Acceptable temperature ranges for digestion by anaerobic microorganism are 10–20 °C for psychrophilic, 30–40 °C for mesophilic, and 50–60 °C for thermophilic microorganisms, with thermophilic conditions preferred to inactivate pathogenic populations [5];
- The quality of inoculum, the feedstock-to-inoculum ratio, and the organic loading rate;
- The pretreatment involved, mainly classified as: physical pretreatments (e.g., particle size reduction [3]), chemical pretreatments (e.g., alkaline pretreatment [50]), and biological pretreatments (e.g., fungal pretreatment [88]).

Thus, due to the complex organic structure of rice straw, it requires different catalytic activities by several enzymes to be broken down. The efficiency of cellulose degradation can be improved by symbiotic cooperation between cellulolytic and noncellulolytic bacteria [89]. In this context, it has been experimentally proven that microbial communities cultivated in mixtures of rice straw, chicken feces, pig feces, cattle feces, and sugar cane dregs are able to degrade more than 60% of the rice straw within four days [90]. The bacterium able to initiate degradation have been identified by polymerase chain reaction *Clostridium thermosuccinogenes*. It is a strict anaerobe that lives in manure, beet pulp, soil, and mud [3]. A synergist effect has been shown during the degradation of rice straw by *Clostridium cellulovorans* involving both cellulosome and non-cellulosome enzymes working under mesophilic conditions [89]. The result of this symbiotic cooperation is the degradation of the rice straw in around 10 days without any type of pretreatment [3].

In order to improve anaerobic digestion, novel two-stage digesters have been developed [50], such as a novel, continuous anaerobic digester that uses hyacinth water as feedstock [91]. Moreover, some analytical models have been developed to optimise and control the anaerobic digestion process [92].

Rice straw conversion into biofuels has a long history, dating back to the 1930s when Richards and Norman [93] analysed the factors influencing anaerobic decomposition of rice straw, and Acharya [94] improved the study of anaerobic decomposition of rice straw. However, the current growing interest in anaerobic rice straw digestion is driven by the requirements of a more efficient use of renewable energy sources in order to reduce greenhouse gas emissions and to mitigate climate change. Indeed, rice straw can be utilized to produce biofuels (e.g., a potential of 205 GL yr<sup>-1</sup> of ethanol to replace 147 GL yr<sup>-1</sup> of gasoline [3]) and bioplastics, but it requires pretreatment in order to alter the interactions of cellulose, hemicellulose, and lignin and to increase the accessibility of cellulose, to remove the lignin–carbohydrates complexes, and to reduce the cellulose crystallinity.

Lastly, we wish to highlight that the sustainable use of rice straw must consider the needs of some countries where 20% of the rice straw is used for the pulp and paper industry: this rice straw cannot be used for energy because of the social and economic needs of people

in these countries. For example, in rural China, out of a total of 740 Mt of rice straw in 2006, an estimated 47% was used for household cooking and heating [3]. When rice straw is stolen from these people, preferable access to sustainable energy systems should be ensured for them.

## 5. Conclusions

Methanization of rice straw is considered one of the most environmentally friendly processes to convert this biomass into biofuels, as it reduces greenhouse gas emissions and mitigates climate change. Indeed, less energy input is required compared to other conversion or feedstock processes [3].

In this paper, we evaluated the number of rice straw barrels available from defined areas. Then, we calculated the total annual biomethane yield for these areas by considering the specific biomethane yield potential in the range of 92–280 L kg<sup>-1</sup><sub>VS</sub> (depending on different inocula, pretreatments, and working temperature) [3].

For each straw barrel, depending on the specific biomethane yield, we obtained the following quantities: 23.36 m<sup>3</sup> ( $VS = 73.8\% TS$ , 92 L kg<sup>-1</sup><sub>VS</sub>), 26.61 m<sup>3</sup> ( $VS = 84.08\% TS$ , 186 L kg<sup>-1</sup><sub>VS</sub>), and 29.27 m<sup>3</sup> ( $VS = 95.26\% TS$ , 280 L kg<sup>-1</sup><sub>VS</sub>). Moreover, equivalent carbon dioxide emissions can be reduced by approximately 754 kg for each RSB by substituting the current practice of burning rice straw in open fields with methanation *via* anaerobic digestion. In this context, the THDI index was introduced in order to evaluate the effect on sustainability of converting rice straw into biomethane instead of its open-field burning for the major rice producing countries.

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## Abbreviations

The following abbreviations and quantities are used in this manuscript:

AD	Anaerobic Digestion
EI	Educational Index
GWP	Global Warming Potential
HDI	Human Development Index
II	Income Index
<i>k</i>	Coefficient
LEI	Life Expectancy Index
<i>m</i>	Mass (kg)
<i>r</i>	Rice
<i>rs</i>	Rice Straw
RSB	Rice Straw Barrel
THDI	Thermodynamic Human Development Index

TS	Total Solids
$\dot{V}_{\text{CH}_4}$	Annual biomethane potential yield ( $\text{m}^3 \text{yr}^{-1}$ )
VS	Volatile Solids

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