Description of the AD-CHP-N-recovery system

Content: This document describes the anaerobic digestion (AD), combined heat and power (CHP) plant, and nitrogen recovery (N-rec) processes analysed in the comparative LCA study. A description of each process step is provided as well as a detailed mass and energy balance of the AD-CHP-N-rec system. These information served as a basis to define allocation factors to perform the LCA study of the integrated SpiralG biorefinery and AD-CHP-N-recovery system. This document is linked to the Excel files presenting the parameters of the AD-CHP-Nrec model that were computed in Python as well as the spreadsheet calculator model used in this study and published by Wu et al. [20].

Contents

1 General overview of the system

1.1 Feedstock for anaerobic digestion

The anaerobic digestion (AD) plant is located in Arborea (Italy), approximately 150 m away from the Spirulina cultivation and biomass pre-processing facilities (see Fig. 1). According to our knowledge and the information provided by Attene et al. [1], the four digesters operate under mesophilic conditions using grass silage and cattle slurry as a feedstock. The dimensions of the four digesters (e.g. diameter, height, volume) as well as the quantities of grass silage and cattle slurry used are unknown. The aerial view of the digesters allowed the measurement of their diameter. A value of 17.9 m was measured for the AD plant located in Arborea (see Fig. 2a). This value was compared with the diameter of the AD plant described by Beausang, McDonnell, and Murphy [2] (i.e. 18.8 m). Since the sizes of the digesters are comparable and the feedstocks similar, the data collected for the AD plant in Grange (Ireland) were used as a proxy to model the AD system in this study (for which no primary data could be collected on-site). Detailed information on the feedstock for AD is provided by Himanshu et al. [10].

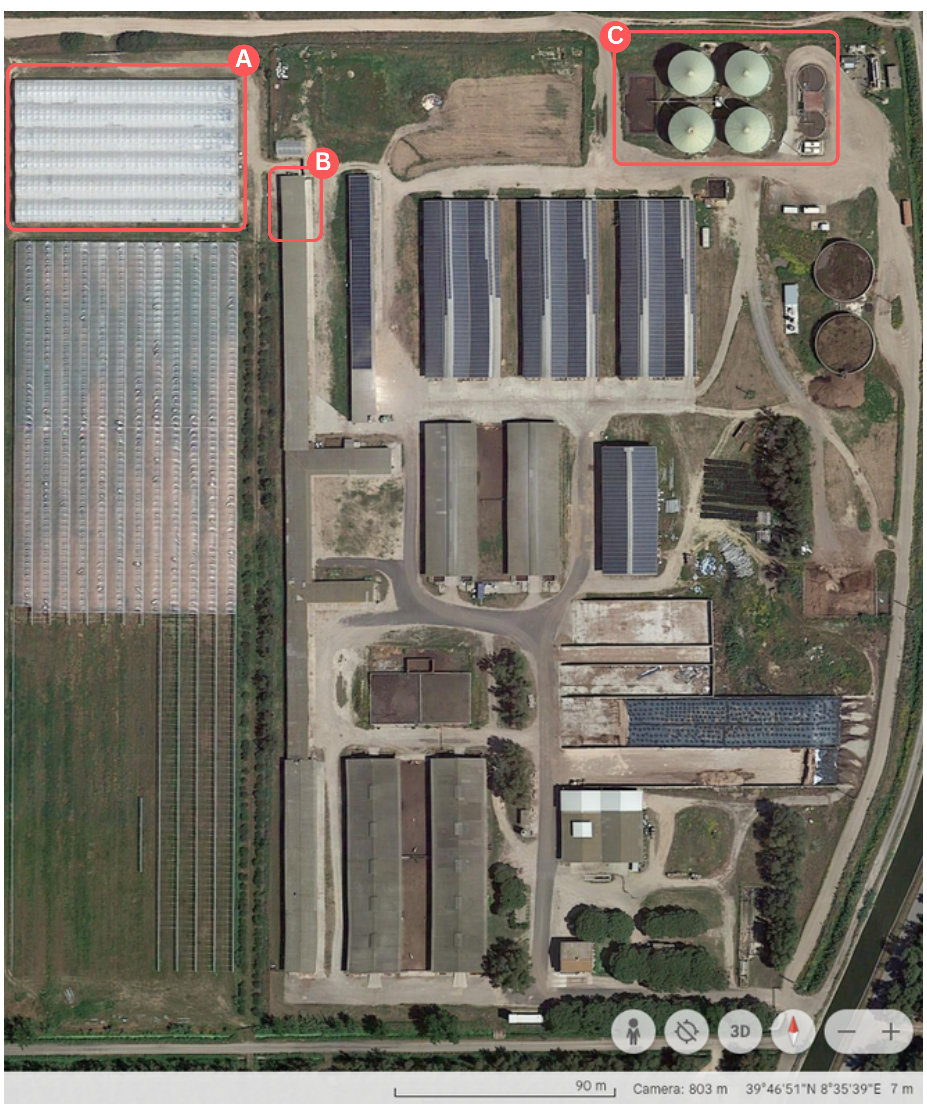


Figure 1: Map of the co-located Spirulina cultivation and biomass pre-processing facilities and anaerobic digestion plant in Arborea (Italy). The map highlights the greenhouse sheltering the six open raceway ponds (A), the Spirulina biomass pre-processing facility (B), and the anaerobic digestion plant consisting of four digesters (C). The rest of the map corresponds to farm buildings (e.g., cattle stables, warehouses). The map was extracted from Google Earth(accessed 09 February 2024).

(a) Anaerobic digestion plant consisting of four digesters located in Arborea (Italy).

(b) Anaerobic digestion plant consisting of one digester located in Grange (Ireland).

Figure 2: Aerial view of the anaerobic digestion plants located in Arborea (Italy) and Grange (Ireland). The pictures were extracted from Google Maps, available at: http://maps.google.com (accessed 05 February 2023). **(a)** Anaerobic digestion plant co-located with the Spirulina cultivation and biomass pre-processing facilities in Arborea (Italy). The diameter of the digesters was measured from the picture and corresponds to 17.9 m approximately. **(b)** Anaerobic digestion plant analysed by Beausang, McDonnell, and Murphy [2] and located at the Grange research centre in Ireland. The diameter of the digester was measured from the picture and corresponds to 18.8 m approximately.

1.1.1 Grass silage

The characteristics of the grass silage considered in this study were extracted from Himanshu et al. [10] and Beausang, McDonnell, and Murphy [2]. The grass silage was assumed to be produced in the region of Arborea and the transportation distance between the fields and the AD plant was set to an average of 20 km. The grass was grown between two cropping seasons and therefore did not compete with any other crops. The digestate produced from the co-digestion of grass silage and cattle slurry was assumed to be used as an organic fertiliser in the grass fields.

In this study, the model for grass silage production was not included in the foreground system. The ecoinvent 3.6 cut-off dataset “grass silage production, organic (CH)” was used as a proxy since we assumed that organic sources of nitrogen (N) and phosphorous (P) were supplied to the fields (i.e. from digestate). The location “CH” corresponds to Switzerland and the inventory is scaled to the production of one kilogram dry weight equivalent (DW-eq) of grass silage. Although the meteorological conditions observed in Switzerland and Sardinia are significantly different, the dataset was not adjusted to account for a higher water requirement for irrigation in the later. Switzerland was used as a proxy and it was assumed that the liquid digestate spred on the fields would provide extra water to ensure the growth of grass.

According to Himanshu et al. [10], the dry matter (DM) content of grass silage was set to 23% and the total solid (TS) yield to 6.65 tons TS/ha, i.e. 8.64 tons/ha of fresh grass silage which is close to the value described in the ecoinvent 3.6 dataset. We considered that the TS, volatile solids (VS), and specific methane yield (SMY) of grass silage equalled 230 g/kg, 920 g/kg TS, and 358 L CH_4/kg VS, respectively (see Table 1). The proportion of methane in the biogas produced from grass silage was assumed to be 55% CH_4 (vol/vol). Finally, each digester was assumed to have a capacity of 5,000 tons/year of fresh grass silage.

1.1.2 Cattle slurry

The cattle slurry was assumed to be produced in the farm in which the AD plant is located (see Fig. 1). Following Beausang, McDonnell, and Murphy [2], the cattle slurry was considered to be collected in reservoirs beneath the slatted-floors of the cattle stables. The manure is stored in two open tanks of unknown dimensions (see Fig. 2a). The TS, VS, and SMY were assumed to reach 88 g/kg, 776 g/kg TS, and 186 L CH_4/kg VS, respectively (see Table 1). The methane content of the biogas produced from cattle slurry was estimated at 64.5%. Each digester was assumed to have a capacity of 7,300 tons slurry/year.

In this study, the farm was excluded from the system boundaries and no environmental burdens were associated with the production of cattle slurry. No transportation from the farm to the AD plant was considered since the facilities are co-located (see Fig. 1). The environmental impacts associated with the construction and operation of the storage tank was considered and based on the ecoinvent 3.6 cut-off dataset "liquid manure storage and processing facility construction (CH)". The emissions associated with the storage of cattle slurry in open tanks were calculated according to Beausang, McDonnell, and Murphy [2] (see Box 1).

Box 1: Direct emissions from the storage of cattle slurry

The CH_4, N_2O, and NH_3 emissions originating from the storage of cattle slurry in open tanks are calculated using the formulas from Beausang, McDonnell, and Murphy [2].

CH_4 emissions:
CH_4 emitted (kg/day) = Amount of cattle slurry (tons/day) × DM content of the cattle slurry (% DW) × 0.8 × 0.24 × 0.67 × 0.10
Here: CH_4 emitted (kg/day) = 67.36 × 0.88 × 0.8 × 0.24 × 0.67 × 0.10 = 0.76 kg CH_4/day

N_2O emissions:
N_2O emitted (kg/day) = Amount of cattle slurry (tons/day) × DM content of the cattle slurry (% DW) × 40.7 × 0.005 × (44/28)
Here: N_2O emitted (kg/day) = 67.36 × 0.88 × 40.7 × 0.005 × (44/28) = 17.13 kg N_2O/day

NH_3 emissions:
The NH_3 emissions were calculated using linear scaling based on the values found by Beausang, McDonnell, and Murphy [2] (i.e. 7,098.52 kg NH_3 emitted for the storage of 5,557 tons of cattle slurry).
Here: NH_3 emitted (kg/day) = 67.36 × 7.098.52 / 5,557 = 86.05 kg NH_3/day

1.1.3 Mix of grass silage and cattle slurry

In this study, a 0.4:0.6 ratio of silage:slurry was considered based on the VS content, as described by Himanshu et al. [10] and Beausang, McDonnell, and Murphy [2]. The authors assumed no synergistic or antagonist co-digestion effects on methanogenesis. According to this ratio and the capacity of the digesters, the input of grass silage and cattle slurry was assumed to be 1,196 tons/year and 5,557 tons/year, respectively. These values correspond to fresh mass (FM). The potential biogas yield of the mix can be calculated from the CH_4 content of the biogas, assumed to be 59% and the SMY (see Box 2 and Section 1.2).

Table 1: Characteristics of the grass silage and cattle slurry used as feedstock for anaerobic digestion according to Himanshu et al. [10] and Beausang, McDonnell, and Murphy [2].

Parameter	Unit	Grass silage	Cattle slurry
Total solids (TS)	% total mass	23	8.8
Volatile solids (VS)	% TS	92	77.6
Specific methane yield (SMY)	m^3 CH_4/ton VS	358	186
Proportion of methane in biogas	%CH_4 in biogas	55	64.5
Capacity of the digester	tons/year fresh mass	5,000	7,300

Box 2: Potential biogas yield of the mix of grass silage and cattle slurry

Biogas yield per amount of volatile solids:

BY VS (m^3/ton VS) = SMY (m^3 CH_4/ton VS) × 100 / %CH_4 in biogas

Here: BY VS grass silage (m^3/ton VS) = 358 × 100 / 55 = 651 m^3/ton VS

BY VS cattle slurry (m^3/ton VS) = 186 × 100 / 64.5 = 288 m^3/ton VS

Biogas yield per amount of fresh mass:

BG FM (m^3/ton FM) = BY VS (m^3/ton VS) × %TS × %VS

Here: BG FM silage (m^3/ton FW) = 651 × 0.23 × 0.92 = 137.8 m^3/ton FM

BG FM slurry (m^3/ton FM) = 288 × 0.088 × 0.776 = 19.67 m^3/ton FM

1.2 Anaerobic co-digestion and combined heat and power production model

The anaerobic co-digestion and combined heat and power (AD-CHP) production model is based on the spreadsheet tool developed by Wu et al. [20] and the data extracted from Beausang, McDonnell, and Murphy [2] and Himanshu et al. [10].

1.2.1 Inputs and outputs of the model developed by Wu et al. [20]

The spreadsheet tool developed by Wu et al. [20] consists of two models, one to estimate the amount of biogas and digestate generated from AD and the other to quantify the operation costs and revenues. As described by the authors, the first model “estimates the biogas yield (the biogas produced per unit mass of a particular material) as a function of the retention time, operating temperature, dead time and a broad classification of the type of feedstock”. This tool, originally published as a Microsoft Excel spreadsheet, was translated into a Python script to be integrated with the SpiralG biorefinery model.

The input parameters of the AD-CHP model and associated outputs are described in Figure 3. The biogas production is estimated from the biogas yield, calculated using the volatile solids destruction (VSD) rate. VSD is presented as a function of retention time, temperature, dead time, and mixing profile. The equations used to calculate the intermediate and final outputs of the model are described below. The functions were distributed into three distinct groups to facilitate their computation. Each group corresponds to one of the boxes below: biogas potential (see Box 3), AD products (see Box 4), and digester properties (see Box 5). The values generated using the Python model were compared to the ones obtained from the spreadsheet for verification.

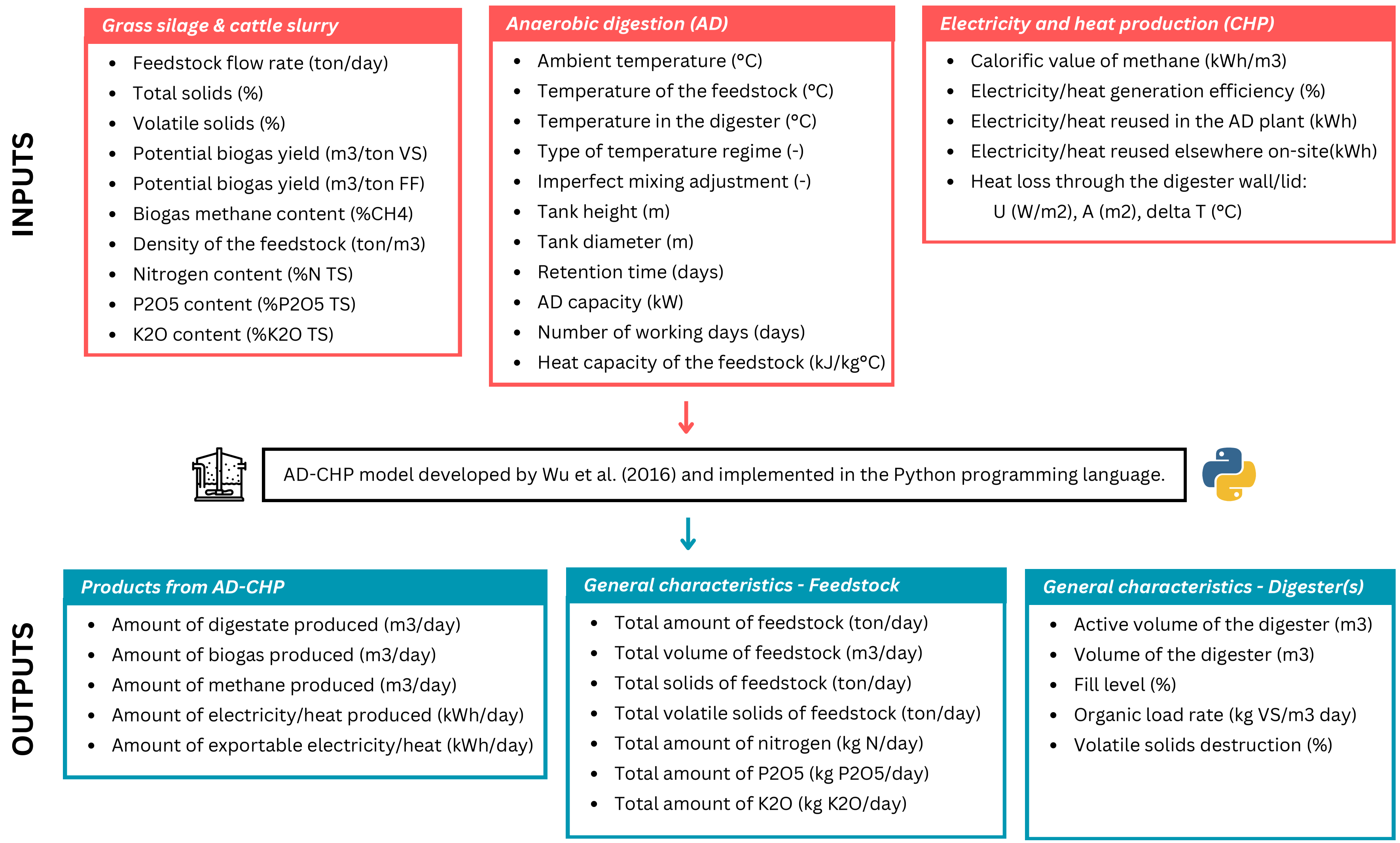


Figure 3: List of the inputs and outputs of the anaerobic digestion and combined heat and power plant model adapted from Wu et al. [20]

Box 3: Equations used to calculate the biogas production potential

The equations below were used to calculate the biogas production potential of the individual and mix of feedstocks according to Wu et al. [20].

Total solids:

TS (ton/day) = TS content of the feedstock (% TS) × Amount of feedstock (ton/day)

Volatile solids:

VS (ton/day) = VS content of the feedstock (% TS) × TS (ton/day)

Biogas potential volatile solids:

BG VF (m^3/day) = Biogas yield (m^3/ton) × VS (ton/day)

Biogas potential fresh feedstock:

BG FF (m^3/day) = Biogas yield (m^3/ton) × VS (ton/day)

If the values for BG VF and BG FF are different, the maximum between the two values is chosen as indicated in Wu et al. [20].

Methane production:

CH_4 (m^3/day) = CH_4 content of specific feedstock (%CH_4) × BG (m^3/day)

Amount of nitrogen:

N (kg/day) = Nitrogen content of the feedstock (%N) × TS

Amount of phosphorus:

P_2O_5 (kg/day) = P_2O_5 content of the feedstock (%P_2O_5) × TS

Amount of potassium:

K_2O (kg/day) = K_2O content of the feedstock (%K_2O) × TS

Box 4: Equations used to calculate the products obtained from AD-CHP

The equations below were used to calculate the products obtained by AD-CHP according to Wu et al. [20].

Operating type:

Mesophilic: k4 = 0.49, k5 = 0.07, k6 = 23.81, k7= 0, k8 = 0.32

Thermophilic: k4 = 22.77, k5 = 0.11, k6 = 58.62, k7= 20.96, k8 = 0.11

Temperature and activity factor (B):

B = k4 × exp (k5 × (T - k6)) - k7 × exp (k8 × (T - k6))

T/B = Operating temperature () / B

VSD based on the retention time:

VSDiRT = k1 × HRT / (1 + k1 × HRT)

VSDiRT,T = B × k1 × (RT - DT) / (1 + B × k1 × (RT - DT))

Or:

VSDiRT = k2 × ln (RT + k3) / 100%

VSDiRT = k2 × ln (B × [RT-DT] + k3) / 100% V

Adjustment for imperfect mixing:

VSDi = k9 × VSDi0.5×RT,T + k10 × VSDi2×RT,T + (1 - k9 - k10) × VSDiRT,T

Weighted VSD = k11 × VSDi,method 1 + (1 - k11) × VSDi, method 2

Amount of electricity/heat produced by CHP:

Electricity/heat production (kWh/day) = Calorific value of CH_4 (kWh/m^3) × Total amount of CH_4 produced × Electricity generation efficiency (%) / 100

Amount of exportable electricity/heat:

Exportable electricity/heat (kWh/day) = Total electricity/heat produced by CHP (kWh/day) - Total amount of electricity/heat reused in the AD plant (kWh/day)

The calculations of the amount of exportable heat accounts for losses of heat through the walls and the lid of the digester.

Box 5: Equations used to calculate the properties of the digester(s)

The equations below were used to calculate the properties of the digester according to Wu et al. [20].

Feedstock flow:

Vfeed (m^3/day) = Amount of feedstock (ton/day) / Density of the feedstock (ton/m^3)

Active volume of the digester(s):

V_active_dig (m^3) = Total feedstock flow (m^3/day) × Retention time (day)

Volume of the digester(s)

V_dig_tank (m^3) = Tank height (m) × π × Tank diameter^2 (m) / 4

Fill level:

fill_level = V_active_dig (m^3) / V_dig_tank (m^3) × 100

Organic load rate:

OLR (kg VS / m^3 day) = Total VS (kg/day) × 1,000 V_active_dig (m^3)

1.2.2 Production of heat, electricity, and digestate

The outputs of the model developed by Wu et al. [20] include, among others, the daily amount of biogas and digestatre produced by AD and energy (heat and electricity) generated by CHP. All the values are expressed for one digester and per day, considering that the AD plant operates 330 days per year (i.e. the same time period as the Spirulina cultivation and pre-processing facility). Theoretically, the values could be multiplied by four to obtain the total amount of heat, electricity, and digestate produced in the AD plant located in Arborea (Italy) since it consists of four distinct digesters.

The total amount of grass silage and cattle slurry supplied to each digester was calculated from the data provided by Beausang, McDonnell, and Murphy [2], i.e. 3.62 and 16.8 tons FM/day, respectively. The characteristics of the feedstocks (e.g. TS, VS, CH_4 content, biogas yield) were defined in Sections 1.1.1 and 1.1.2. The yearly average temperature in Arborea (Italy) was set to 16.5°C (see Table 2). The density of grass silage and cattle slurry were rated at 0.5 ton/m^3 and 0.99 ton/m^3, respectively based on Wu et al. [20]. The temperature of the feedstock was considered to be the same as the ambient temperature i.e. 16.5°C. The temperature of the digester was fixed to 37°C which corresponds to the mesophilic conditions described by Beausang, McDonnell, and Murphy [2].

The dimension of the digester was determined from the aerial view of the AD plant and the diameter was fixed to 17.9 m (see Section 1.1). Since the digester studied by Beausang, McDonnell, and Murphy [2] has a volume of 1,500 m^3, the height of the digester was set to 6 m in order to reach the same volume approximately (considering a diameter of 17.9 m). Beausang, McDonnell, and Murphy [2] defined a retention time of 75 days. However, the use of this value led to a fill level of the digester greater than 100%. Therefore, the retention time was reduced to 55 days and a digester tank fill level of 88% was reached. The digester active volume corresponded to 1,300 m^3. The volume of the digester reached 1,510 m^3, the closest value to 1,500 m^3 obtained by varying the height of the digester. An organic load of 1.4 kg VS/m^3/day was calculated from the input data while Beausang, McDonnell, and Murphy [2] used a value of 1.16 with the same 0.4:0.6 mix of grass silage and cattle slurry. The plant capacity was set to 150 kW according to Beausang, McDonnell, and Murphy [2]. The volatile solid destroyed (VSD) was calculated from the model and a value of 87% was obtained.

Table 2: Average meteorological data for Arborea (Italy) from 1991 to 2021. **Abbreviations.** Av.: average temperature (°C); Min.: minimum temperature (°C); Max.: maximum temperature (°C); Prec.: precipitations (mm); Hum.: humidity (%); Rain: number of rainy days (d); Sunlight: average hours of sunlight (h). Data extracted from Climate Data(accessed 09 February 2024).

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Av.
Av. (°C)	9.1	9.1	11.4	14.1	17.8	22.3	24.9	25.1	21.7	18.4	13.7	10.4	16.5
Min. (°C)	5.7	5.5	7.4	9.8	13	16.9	19.5	19.7	17.3	14.5	10.6	7.2	12.3
Max. (°C)	12.5	12.7	15.4	18.3	22.3	27.1	30	30.3	26.1	22.7	17.2	13.7	20.7
Prec. (mm)	74	73	63	66	43	16	3	9	39	71	112	94	55.3
Hum.(%)	81	78	76	75	70	62	59	60	67	74	79	80	71.8
Rain (d)	8	7	6	7	4	2	1	1	4	7	10	9	5.5
Sunlight (h)	5.5	6.5	8.1	9.7	11	12.3	12.4	11.6	9.8	8.3	6.5	5.7	9.0

1.2.3 Mass and energy balance of the AD-CHP system

A total volume of 840 m^3 of biogas with a CH_4 content of 59% and 18.4 m^3 of digestate are is produced daily. The electricity and heat generation efficiency from CHP were set to 37% and 53%, respectively, as defined in the ecoinvent 3.6 dataset “heat and power co-generation, biogas, gas engine (IT)”. According to the AD-CHP model, 1,766 and 2,529 kWh of electricity and heat are produced daily, respectively. Part of the electricity is reused in the AD plant to support the operation of pumps and mixers. In addition, part of the heat is used to warm up the feedstock and part is lost through the walls of the digester and the lid. The model developed by Wang, Xu, and Li [19] estimates both, the amount of heat required to warm up the feedstock and the parasitic heat losses. The exportable electricity and heat corresponds the difference between the amount of each produced by AD-CHP and the amount reused or lost. According to Beausang, McDonnell, and Murphy [2], 10% of the electricity is reused in the AD plant, which corresponds to 176.6 kWh. The amount of heat reused is calculated via the model: 20.3 kW of heat are required to warm up the feedstock and 12.1 kW are lost through the walls and the lid of the digester i.e. a total of 32.4 kW (33% of the total heat generated or 827.7 kWh). Therefore, 1,589.4 kWh and 1,701.3 kWh of electricity and heat can be exported, respectively.

While the VSD was estimated at 87% in the model, no specific information regarding the dry matter (DM) content of the digestate was provided. In this study, the characteristics of the digestate were extracted from the study of Tambone et al. [17] (see Section 1.3). The DM content of the digestate was estimated at 5.8% (which also corresponds to the TS). Based on this value and the VSD, the VS was calculated by assuming the conservation of mass of the inorganic solids (IS) and using the formulas described by Koch [12] (see Box 6). A value of 64% of VSD was calculated by considering a DM of 5.8% which is lower than the 87% obtained from the model. Due to a lack of data, we used the information from Tambone et al. [17] in the rest of the study and acknowledge the assumptions made.

Box 6: Characteristics of the digestate produced by co-digestion

Characteristics of the feedstock:

Total fresh mass: FM mix = FM silage + FM slurry

Total TS: TS mix = TS silage + TS slurry

Total IS: IS mix = TS mix - VS mix

Here: FM mix = 1,196 + 5,557 = 6,753 tons/year

TS mix = 275 + 489 = 764 tons TS/year

VS mix = 253 + 379 = 632 tons VS/year

IS mix = 764 - 632 = 132 tons/year

Characteristics of the digestate:

Conservation of IS: IS digestate (tons/year) = IS mix (tons/year)

TS digestate (tons/year) = amount digestate (tons/year) × %TS digestate VS digestate (tons/year) = TS digestate - IS digestate

%VSD = (VS mix - VS digestate) / VS mix × 100

Here: IS digestate = 0.4 tons/day

TS digestate (m^3/day) = 18.5 (m^3/day) × 0.058 = 1.073 (m^3/day)

density digestate = 1 m^3/ton

VS digestate (tons/day) = 1.073 - 0.4 = 0.673 tons/day

%VSD = (1.92 - 0.693) / 1.92 × 100 = 64%

Box 7: emissions from biogas production and digestate storage

The CH_4, NH_3, and N_2O emissions originating from the co-digestion of grass silage and cattle slurry and storage of digestate in open tanks are calculated using the formulas described by [2].

CH_4 emissions:

According to [2], the fugitive emissions of CH_4 account for 2.4% of the methane produced. They also include the CH_4 emissions related to the storage of digestate in open tanks.

CH_4 emitted (kg/day) = 0.024 x amount CH_4 produced (m^3/day)

Here: CH_4 emitted (kg/day) = 0.024 x 1,699 = 40.78 kg CH_4/day

NH_3 emissions:

The NH_3 emissions were calculated by simple cross multiplication using the values found by [2] (i.e. 1,451.65 kg NH_3 emitted for the storage of digestate obtained from 5,557 and 1,196 tons/day of cattle slurry and grass silage, respectively).

Here: NH_3 emitted (kg/day) = 67.36 x 1,451.65 / 5,557 = 17.60 kg NH_3/day

N_2O emissions:

N_2O emitted (kg/day) = NH_3 emitted (kg/day) x 0.01 x (44/28)

Here: N_2O emitted (kg/day) = 17.60 x 0.01 x (44/28) = 0.28 kg N_2O/day.

1.3 Separation of the solid and liquid fractions by screw press

Tambone et al. [17] analysed the influence of the solid-liquid separation of digestate from AD on the dry matter (DM), total kjeldhal nitrogen (TKN), total ammonia nitrogen (TAN), and total P_2O_5 of the solid fraction (SF) and liquid fraction (LF). The authors studied 13 AD plants located in Italy for which a screw press was used to separate the LF and SF of the digestate. The four AD plants using cattle slurry and energy corps as feedstock (i.e. AD plants no. 6, 9, 11, and 13) were used as a reference in this study. TAN usually refers to the sum of ammonia nitrogen (N-NH_3) and ammonium nitrogen (N-NH_4^+) [19]. However, Tambone et al. [17] mention N-NH_4^+ only. Due to a lack of data, it was assumed in this study that TAN corresponds to N-NH_4^+ only. In addition, TKN includes organic N plus N-NH_3 and N-NH_4^+ (see Fig. 6). P_2O_5 corresponds to the total phosphorous content of the digestate.

Figure 4: Mass balance of the anaerobic digestion process for one digester

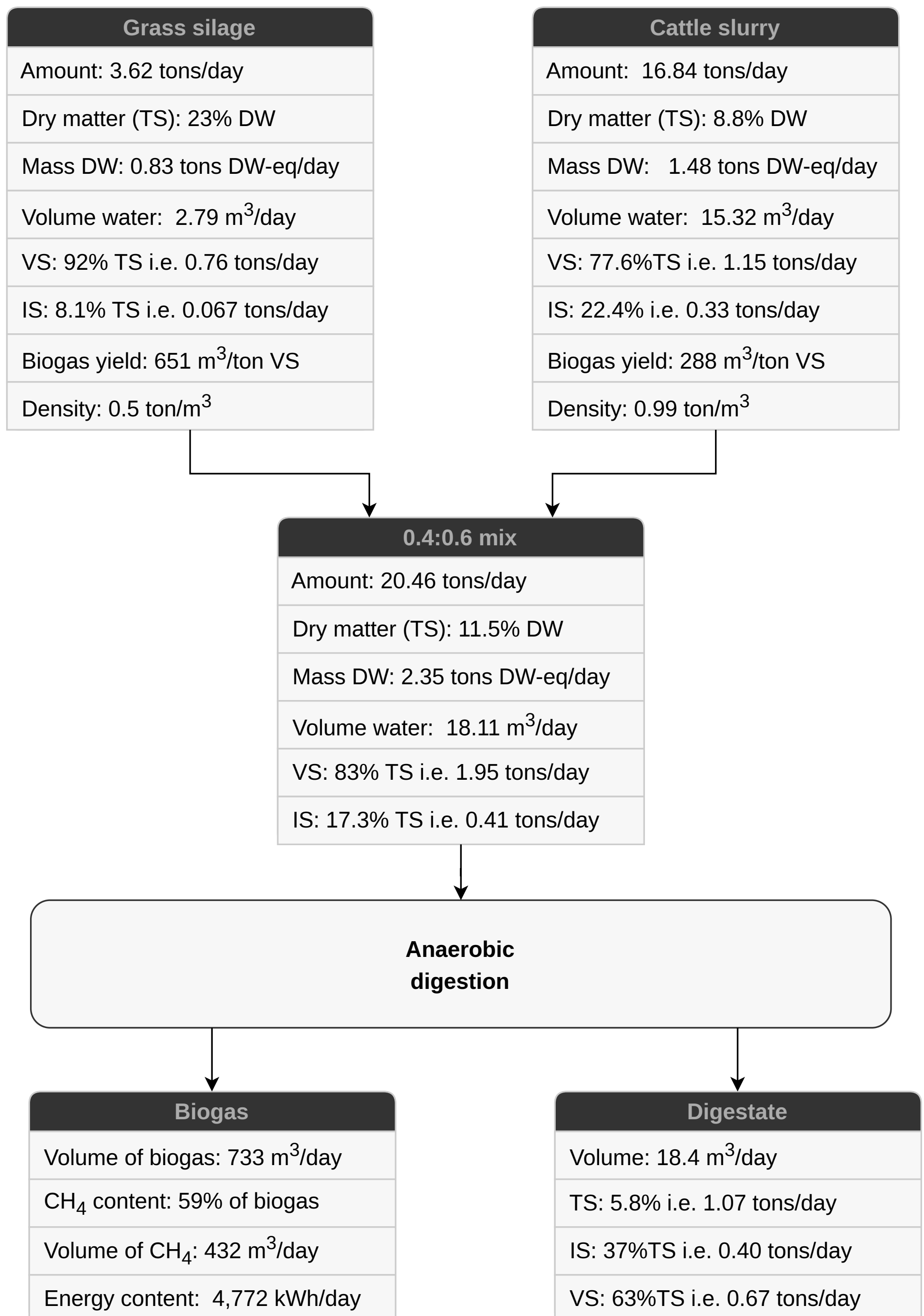


Figure 5: Energy balance of the combined heat and power generation process.

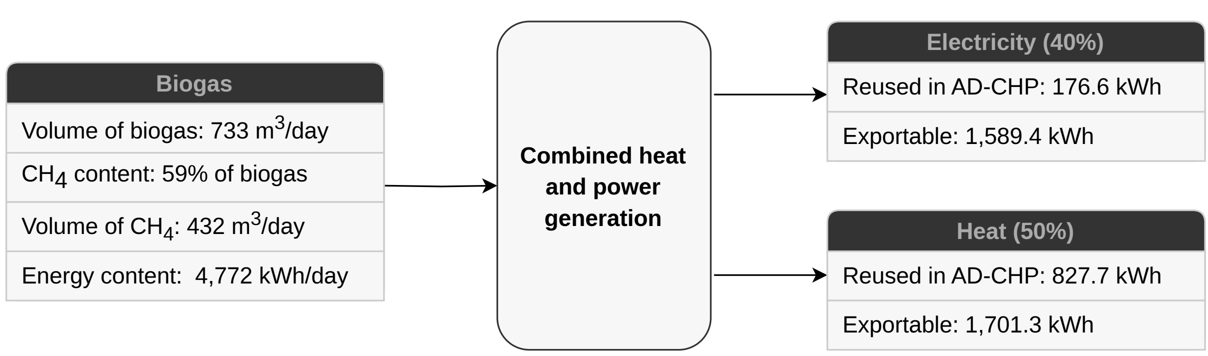


Figure 6: Differences between total nitrogen, total ammonia nitrogen, and total Kjeldhal nitrogen.

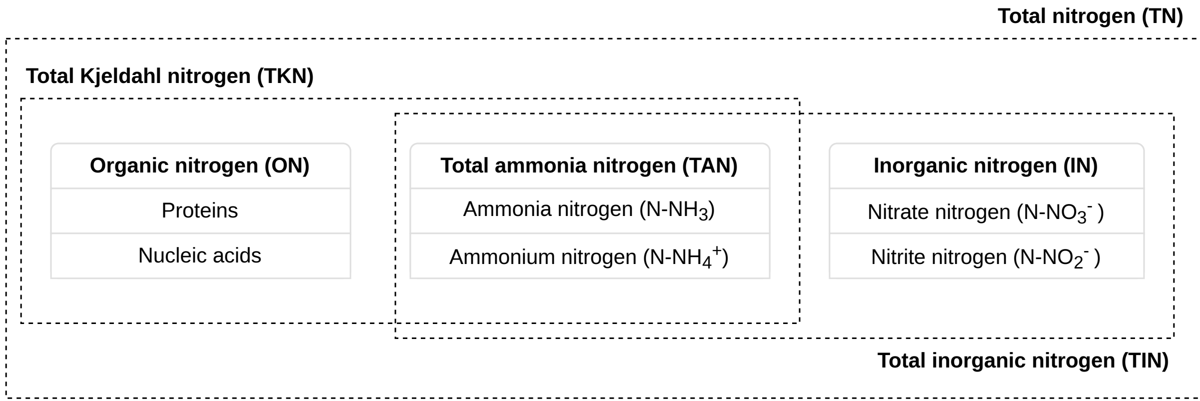


Table 3: Characteristics of the samples of digestate, liquid and solid fractions for four anaerobic digestions plants analysed by Tambone et al. [17]. *Abbreviations.* DM: dry matter; TKN: total Kjeldhal nitrogen; TAN: total ammonia nitrogen, here considered as $N\text{-}NH_4^+$; P_2O_5: total phosphorous; SF: solid fraction; LF: liquid fraction.

AD	Samples	DM (g/kg DW)	TKN (g/kg DW)	TAN (g/kg DW)	P_2O_5 (g/kg DW)
6	D	57.3	67.4	36.7	33.5
6	LF	42.9	85.1	49.7	34.8
6	SF	228	22.4	8.42	39.2
9	D	50.1	61.2	29.1	25.1
9	LF	35.8	78.3	38.7	31.2
9	SF	161	25.4	8.65	12.8
11	D	68.1	64.2	31.9	31.4
11	LF	48.6	81.4	46.4	29.5
11	SF	189	34.3	10.3	34.6
13	D	55.1	70.1	36.7	29
13	LF	42.3	83.2	45.6	24.7
13	SF	227	26.9	6.8	27.9
Av.	D	57.65	65.725	33.6	29.75
Av.	LF	42.4	82	45.1	30.05
Av.	SF	201.25	27.25	8.5425	28.625

This study is based on the results obtained by Attene et al. [1] which originate from experiences conducted with the digestate from the AD plant located in Arborea (Italy). The authors give information on the LF of the digestate only, i.e. after separation. Therefore, the data regarding the composition of the digestate exiting the digesters (i.e. before separation) and the SF were extracted from Tambone et al. [17]. The values of DM, TKN, TAN, and P_2O_5 obtained for the AD plants no. 6, 9, 11, and 13 were averaged (see Table 3). The digestate produced by AD was assumed to have a DM content of 5.8% DW. Therefore, the volume of 18.4 m^3 of digestate produced daily corresponds to 1,067 kg DW-eq. In addition, 29% and 71% of the DM were transferred into the SF and LF, respectively (see Table 4). We assumed that LF has a DM content of 4.2% and SF 20.1%.

The mass balance of the solid/liquid separation of the digestate was adjusted based on the data extracted from Tambone et al. [17]. The volume of digestate produced daily was calculated from the model of Wu et al. [20] (see Section **??**) and its DM content was fixed to 5.8% DW as described above. The mass balance was based on the proportion of DM transferred to SF and LF which allows the calculation of the amount of dry matter (kg DW-eq) in the two fractions. The DM content of the SF was fixed to 20.1% DW. The DM content of the LF was calculated by subtracting the total amount of fresh SF (6,192 kg) to the total amount of fresh digestate (74 m^3). Figure 7 shows the mass balance of the SL separation process used in this study.

Table 4: Repartition of the dry matter, total nitrogen, and total phosphorous between the solid and liquid fractions of digestate according to Tambone et al. [17]. *Abbreviations.* DM: dry matter; TKN: total Kjeldhal nitrogen; P_2O_5: total phosphorous; SF: solid fraction; LF: liquid fraction..

AD	SF (%DM)	LF (%DM)	SF (%TKN)	LF (%TKN)	SF (% P_2O_5)	LF (% P_2O_5)
6	31.29	68.71	10.7	89.3	33.9	66.1
9	21.37	78.63	8.1	91.9	10.03	89.97
11	34.44	65.56	18.12	81.88	38.12	61.88
13	29.37	70.63	11.85	88.15	31.96	68.04
Av.	29.12	70.88	12.19	87.81	28.50	71.50

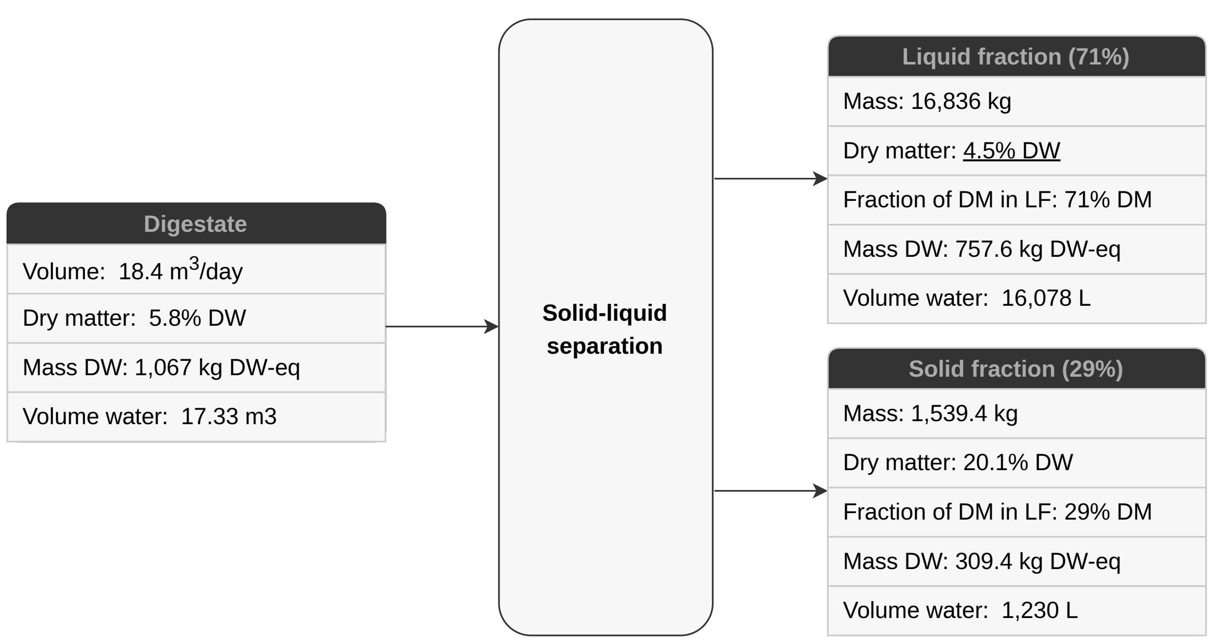


Figure 7: Mass balance of the solid-liquid separation of the digestate from anaerobic digestion. The underlined value was adjusted from 4.2 to 4.5% DW to close the mass and water balance of the process.

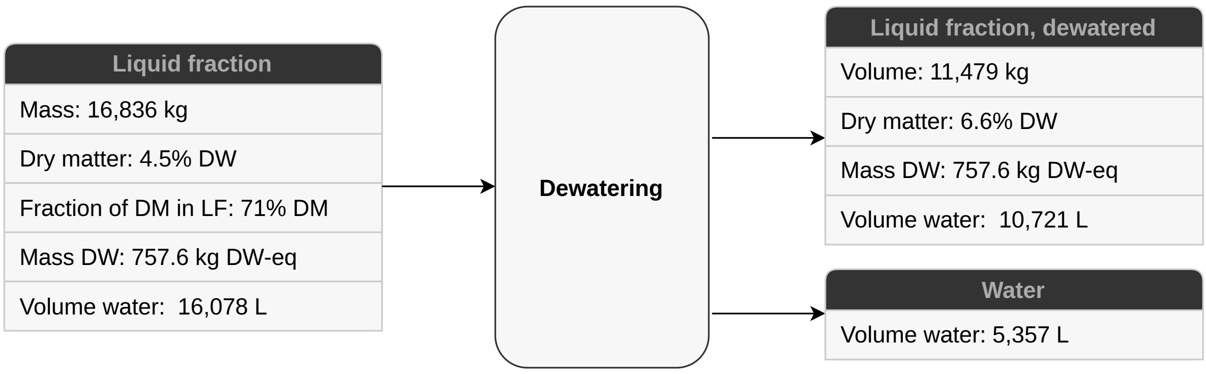


Figure 8: Mass balance of the dewatering of the liquid fraction of the digestate from anaerobic digestion.

Feiz et al. [8] analysed the impacts of different solid/liquid separation techniques on climate change using three types of digestates. In this study, the inventory data associated with the use of a screw press (labelled as “SP”) for manure-based digestate (indicated as “M”) were used as a proxy. The class M consists of cow, pig, and poultry manure. The average DM content of this category corresponds to 7.4% DW. The authors present inventory data for the solid/liquid separation of 1 ton of raw digestate. The direct emissions of CH_4, NH_3, and N_2O corresponded to 0.03, 0.12, and 0.02 kg/ton digestate at 7.4%. It was assumed that the direct emissions would be the same for a DM of 5.8%. Therefore, a total amount of 0.552, 2.208, and 0.368 kg of CH_4, NH_3, and N_2O would be emitted daily considering the processing of 18.4 m^3 of digestate at a density of 1 kg/L. In addition, the processing of 1 ton of digestate at 7.4% was considered to require 2.2 MJ of electricity (i.e. 0.61 kWh) and 36.4 MJ of fuel. A total amount of 11.22 kWh is used in the SL separation process as well as 669.76 MJ of fuel. In this study, the amount of energy required for solid/liquid separation was considered to be included in the total amount of heat and electricity recirculated to the AD plant (see Section **??**). According to Cathcart et al. [4], a screw press consumes between 0.4 and 0.6 kWh per ton of raw biogas digestate, which ranges in the same order of magnitude than the value calculated in this study.

1.4 Nitrogen recovery by stripping and absorption

The nitrogen recovery (N-rec) process was modeled from the laboratory experiments conducted by Attene et al. [1] on the digestate produced by the AD plant in Arborea (Italy). The authors measured an initial concentration of 1.345 kg $N\text{-}NH_4^+/m^3$ in the LF of the digestate. A DM content of 6.6% was noted. This value is significantly higher than the 4.5% calculated from the mass balance of the SL separation process (see Fig. 7). In order to bridge the gap between the two DM contents, a dewatering step was added in the process chain. The DM content of the dewatered LF was fixed to 6.6% DW and the amount of DM in the LF and dewatered LF was assumed identical (i.e. conservation of mass). According to the mass balance, a total volume of 5.36 m^3 of water was removed from the LF fraction to increase the DM content from 4.5% to 6.6% (see Fig. 8).

In their study, Attene et al. [1] compared different experimental conditions of N-recovery from the dewatered LF. Citric acid and sulfuric acid were used to recover $N\text{-}NH_3$ via a stripping/absorption process. LF contains two forms of nitrogen in equilibrium: ammonium nitrogen ($N\text{-}NH_4^+$) and unionised (free) ammonia nitrogen ($N\text{-}NH_3$) [19]. The equilibrium (see Box 8) depends on the pH and temperature of the LF. An increase in temperature and/or pH moves the equilibrium from soluble NH_4^+ to gaseous NH_3, i.e. “strippable ammonia” [16]. In this study, it was considered that N is present in the LF in the form of $N\text{-}NH_4^+$ and that the experimental conditions applied by Attene et al. [1] (i.e. 50°C and pH 8) increase the free ammonium fraction and favour its stripping and absorption. The authors measured the concentration of N-NH_4^+ in the digestate before the start and at the end of the process from which they calculated the percentage of N-NH_4^+ stripped, recovered, and lost.

Box 8: Equilibrium between NH_4^+ and NH_3 in liquid digestate

$$\mathrm{NH_3}(g) \rightleftharpoons \mathrm{NH_3}(aq.) + \mathrm{H_2O}(aq.) \rightleftharpoons \mathrm{NH_4}^+(aq.) + \mathrm{HO}-(aq.)$$

N-NH_3 is stripped from the digestate, transferred to the gaseous phase, and absorbed in the acid solution (i.e. citric acid or sulfuric acid). The resulting solution of ammonium citrate/sulfate is enriched in N. In this study, it was assumed that from the initial amount of N-NH_4^+ in LF, 71% were recovered in the ammonium salts solution, 75% were stripped from the LF, and 4% were lost during the process (i.e. 96% of N-NH_4^+ was found in the N-stripped digestate and ammonium salts solution at the end of the process). These values correspond to the average of the calculations performed by Attene et al. [1] for citric acid and sulfuric acid. At the end of their study, the authors envisioned using this experimental approach at larger scale, to supply the daily N requirement to Spirulina grown in the six open raceway ponds (ORPs) in Arborea (Italy).

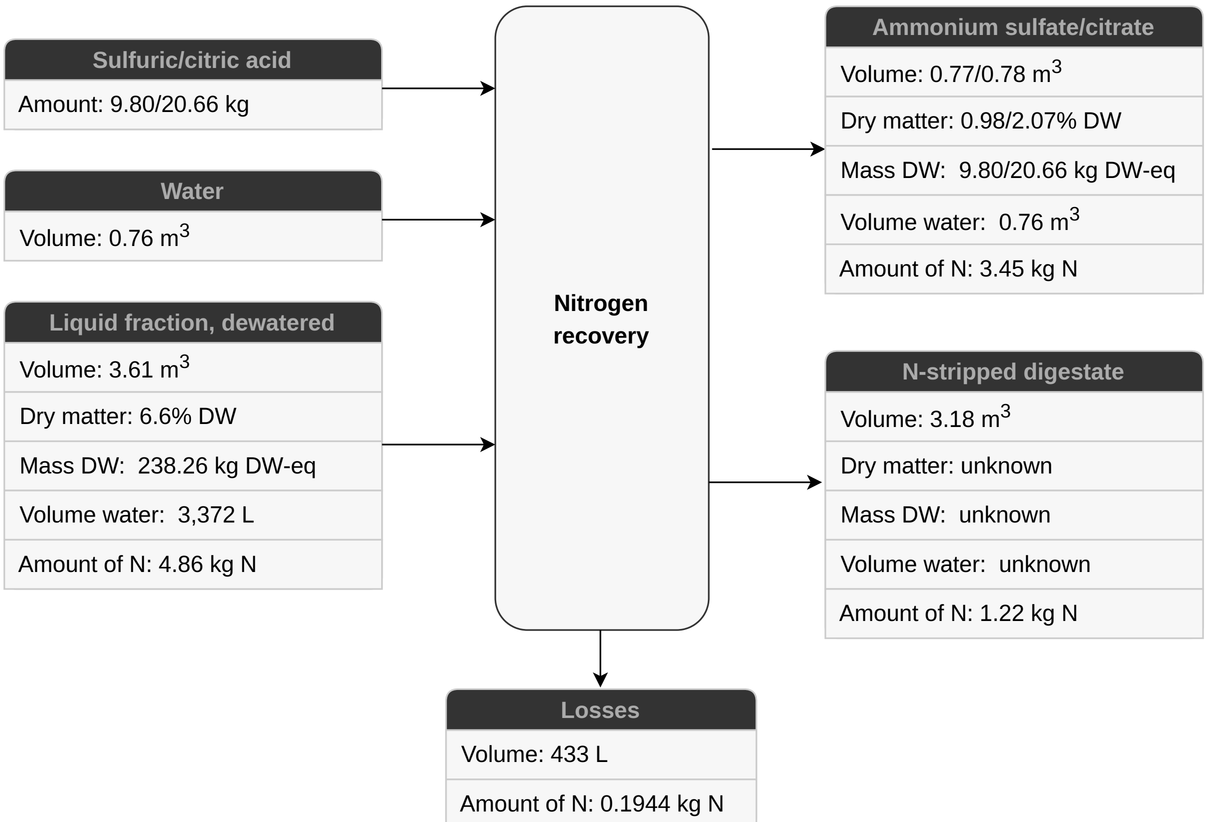
The amount of digestate to be treated in order to recover a sufficient amount of N to meet Spirulina growth requirements was calculated based on the N composition of the cyanobacterium, its N absorption efficiency (i.e. amount of N uptaken by Spirulina from the culture medium), and amount of dry biomass produced daily. In accordance with the rest of the study (i.e. data regarding the Spirulina biorefinery), we assumed that 28.78 kg DW-eq of dry Spirulina spaghettini were produced daily. The N content of Spirulina biomass was fixed to 10% [1]. In the literature, N absorption efficiencies range between 60 to 100% [13, 6, 11]. Considering an uptake rate of 80%, 3.45 kg N/day should be supplied to the ORPs to meet the daily N requirement for Spirulina growth (i.e. 2.878 kg N/day). The organic N from ammonium citrate/sulfate replaces the use of N from potassium nitrate (KNO_3).

The amount of citric acid, sulfuric acid, water, and heat required for the N-recovery process were calculated from the literature. Following Attene et al. [1], we considered that the LF is transferred to a storage tank warm up at a temperature of 50°C using heat from AD. Air is bubbled to facilitate mixing and NH_3 stripping. The stripped gas is injected into a second tank containing the acid mixed with water, also kept at 50°C. An accumulation tank is used to collect the ammonium solution at the end of the process. Considering a recovery rate of 71%, a total amount of 4.86 kg N should be initially present in the LF which corresponds to a volume of 3.61 m^3/day (assuming an initial concentration of 1.345 kg N-NH_4^+/m^3 in LF).

The volume of digestate decreased by 12% during the process [1]. Therefore, the final volume of N-stripped digestate corresponded to 3.18 m^3. The 433 L removed (i.e. 12% of the initial volume) were assumed to be lost via evaporation. Considering that 75% of N was stripped from LF, 1.22 kg N remained in the N-stripped LF at the end of the process. In addition, 0.1944 kg N were lost (i.e. 4% of initial N) (see Fig. 9). The volume of the solution of ammonium citrate/sulfate was determined from the volume of water added initially. According to Attene et al. [1], we consider that 0.76 m^3 of water were required to prepare the solutions of acid. In addition, we calculated that 9.80 kg of sulfuric acid and 20.66 kg citric acid are used based on the 3.61 m^3 of digestate to be treated.

No details regarding the amount of energy required for the N-recovery process were given by Attene et al. [1]. We assumed that 5 kWh of energy was consumed per kg N stripped from

Figure 9: Mass balance of the nitrogen recovery process.



the digestate [3]. We calculated the total amount of energy required based on the amount of N stripped from the LF (i.e. including the losses). Since 3.64 kg N were stripped from the 3.61 m^3 of LF (i.e. 75% stripping efficiency), a total amount of 18.22 kWh were used in the process, provided by heat from AD [1].

1.5 Mass and energy balance of the AD-CHP-Nrec system

2 Mass and economic allocation factors

The Spirulina biorefinery uses three products from the AD-CHP-N-recovery system: the heat and electricity from CHP as well as the solution of ammonium citrate (or sulfate) from the N-recovery process. In this study, the environmental impacts associated with the production of each stream are assigned using allocation based on the mass balance, economic value, and exergy content of the products.

2.1 Economic allocation factors for biogas and digestate from co-digestion

2.1.1 Economic value of biogas

The economic value of the biogas produced in the AD plant located in Arborea (Italy) was determined from its CH_4 content and energy value, based on the average price of natural gas between 2016 and 2023 (i.e. 54.00 €/MWh) (see Fig. 11). The energy content of natural gas and CH_4 were assumed to be 11 kWh/m^3 and 10 kWh/m^3, respectively. In this study, the CH_4 content of biogas was set to 59% (see Section 1.2). The biogas produced by the one digester contained 432.5 m^3 of CH_4 which represent 4,325 kWh of energy. Since the price of biogas was estimated at 0.054 €/kWh, the economic value of the daily production of biogas was estimated

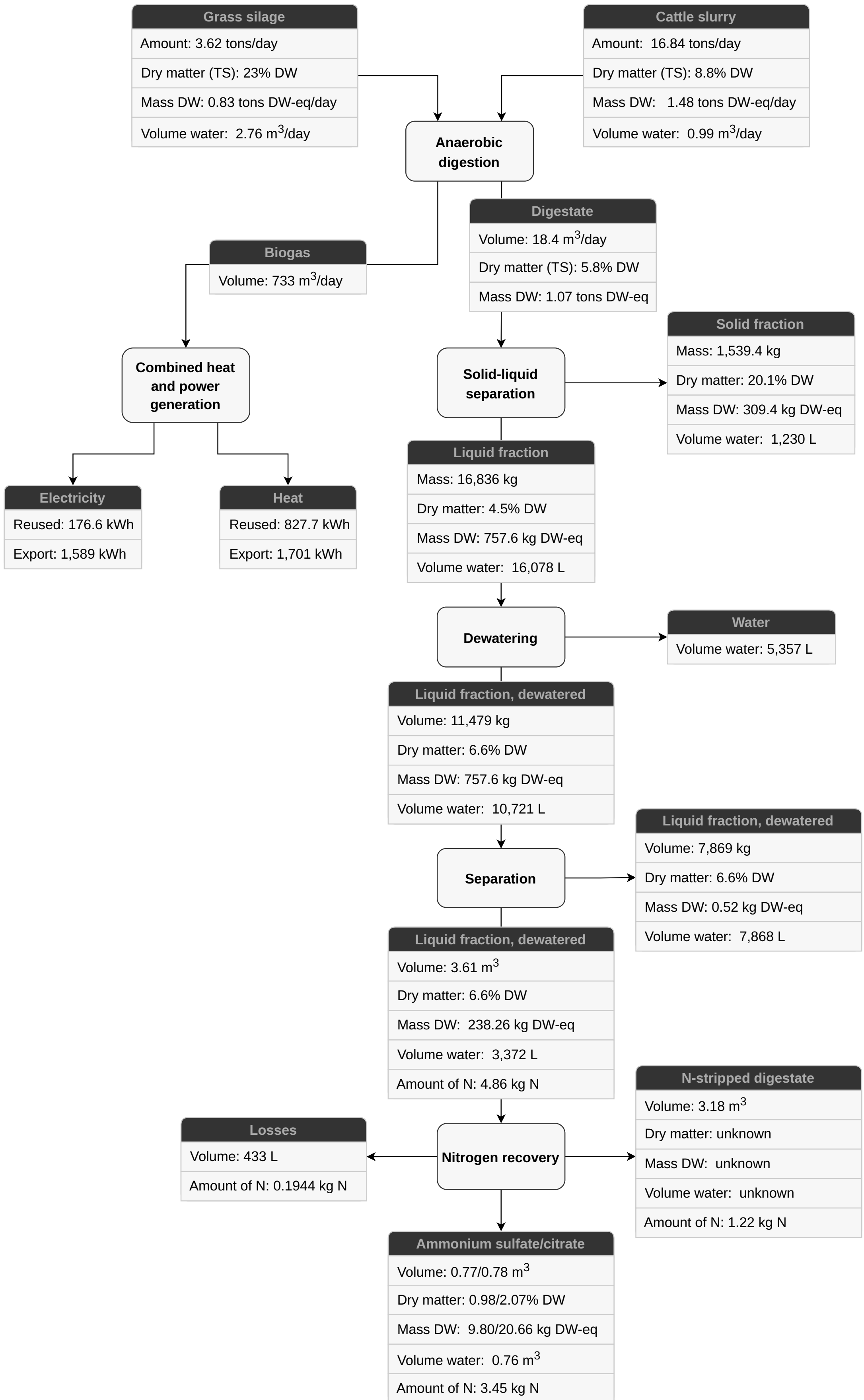


Figure 10: Mass and energy balance of the AD-CHP-N-recovery system.

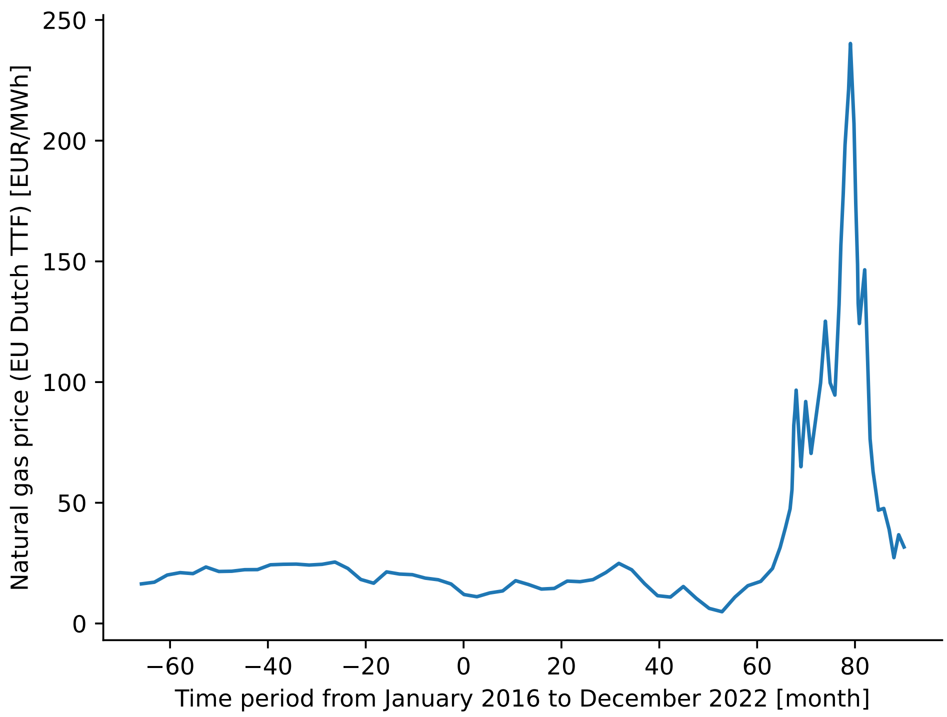


Figure 11: Evolution of the market price for natural gas between 2016 and 2023.

at 233.6 €/day.

2.1.2 Economic value of digestate

The economic value of the digestate from AD was estimated from the market prices of diammonium phosphate (DAP), muriate, and urea, three common agricultural fertilisers used as a source of P, K, and N, respectively. Similar to natural gas, the market prices of DAP, muriate, and urea varied considerably between 2019 and 2023 (see Fig. 12). In this study, the average prices over this time period were considered as proxy to estimate the price of the digestate.

The concept of "willingness to pay" described in a report of the European project called "Systemic" was used to estimate the economic value of the digestate based on the market prices mentioned above [9]. In that report, the authors evaluated the preferences of primary stakeholders (e.g. farmers, horticultural producers, private garden owners) regarding the use of fertilisers containing recovered nutrients (e.g. N and P from digestate). The results show that these alternative sources of essential nutrients can replace inorganic fertilisers to a certain extent only. The acceptance of organic fertilisers depends on the composition and quality of the product, ease of use, and price. In particular, the authors highlighted the need to consider the cost of the application technique (e.g. land spreading) and maximum amount that can be applied to the soils per growing season in the estimation of their price. Several authors suggest that the price of alternative organic fertilisers should be 10% lower than the price of inorganic fertilisers and application costs. Others consider that farmers would not pay more than 50% of the price of mineral fertilisers.

Urea, DAP, and muriate wereassumed to contain 46% N, 46% P, and 60% K, respectively. Based on the average price of the inorganic fertilisers between 2016 and 2023 as well as their composition, the price of each nutrient was estimated at 0.26 €/kg N, 0.29 €/kg P, and 0.23 €/kg K (see Fig. 13). The amount of N, P, and K present in the digestate was calculated from the model developed by Wu et al. [20] (see Section 1.2). The 18.4 m^3 of digestate generated by AD contain 85.17 kg N, 43.51 kg P, and 167.46 kg K (see Fig. 15). The maximum economic

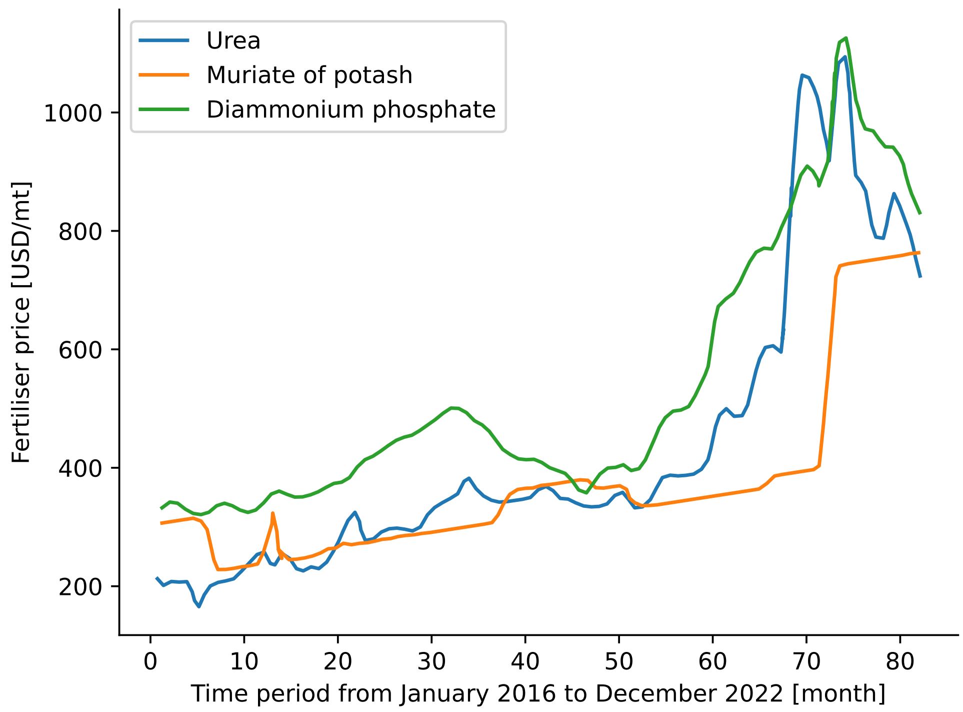


Figure 12: Evolution of the market price for diammonium phosphate, muriate, and urea between 2016 and 2023.

value of the digestate was calculated by summing the values of NPK, i.e. 22.14 €/day, 12.62 €/day, and 38.52 €/day. A total value of 73.28 €/day was found.

In this study, the price of organic NPK from the digestate was considered to be 50% lower than the price of inorganic NPK from urea, DAP, and muriate, respectively. Therefore, the economic value of digestate was considered to be 36.64 €/day. When considering the assumption of 10% of the price of inorganic NPK, a value of 7.33 €/day was found.

2.1.3 Determination of the allocation factors

The allocation factors for biogas and digestate were determined from the economic values calculated in Sections 2.1.1 and 2.1.2 i.e. 233.6 €/day and 36.64 €/day for biogas and digestate, respectively (i.e. total value of 270.24 €/day). The allocation factors corresponded to 86.44% for biogas and 13.56% for digestate using the average market prices of conventional products (e.g. natural gas, DAP, muriate, and urea) between 2016 and 2023 (see Fig. 16). The reduction of the allocation factors for biogas in 2022 corresponds to the increase of the market prices for inorganic NPK which also results in an increase of the economic value of digestate.

In a sensitivity analysis, the LCA results obtained for the "50%" approach were compared with the ones obtained for "100%" (the price of organic NPK is similar to inorganic NPK), "10%" (the price of organic NPK corresponds to 10% of the price of inorganic NPK), and "0%" (organic NPK has no economic value i.e. digestate is considered as a waste). In all cases, only a limited part of the impacts were allocated to the digestate based on the average values between 2016 and 2023: 73%, 84%, 96%, and 100% of the environmental impacts are allocated to biogas for the "100%", "50%", "10%", and "0%" strategies, respectively. In contrast, [18] used high economic values for N, P, and K from digestate, allocating 64-71% of the impacts to the digestate and 29-32% to biogas depending on the amount of biogas and digestate produced in the different scenarios. When applying a mass allocation approach, the authors attributed 5% to biogas and 95% to the digestate based on the mass balance of the process. The authors compared these

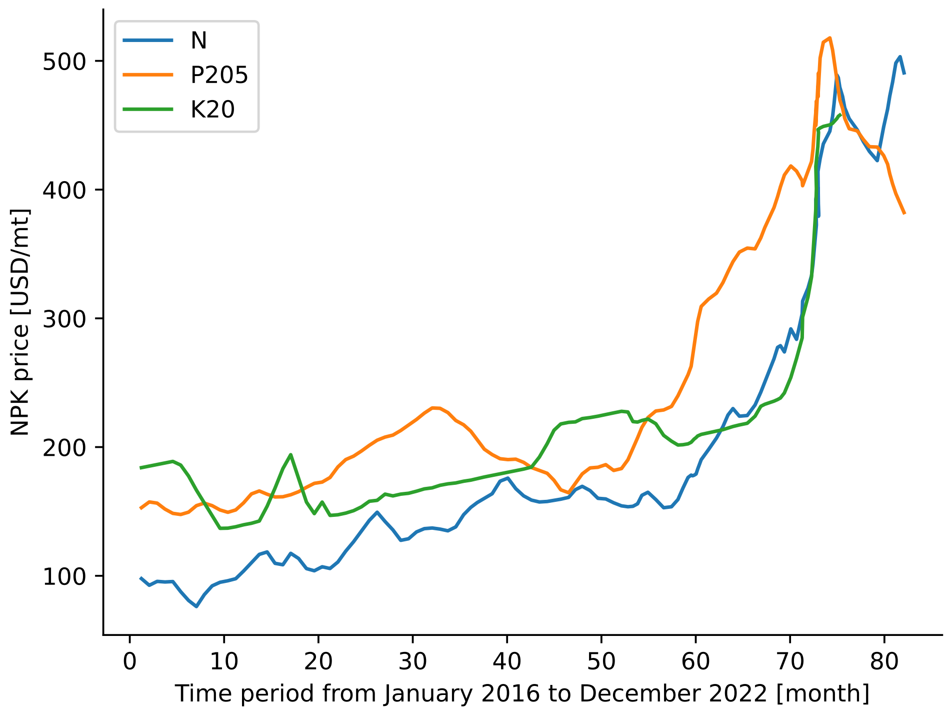


Figure 13: Evolution of the market price for nitrogen, phosphorous, and potassium between 2016 and 2023.

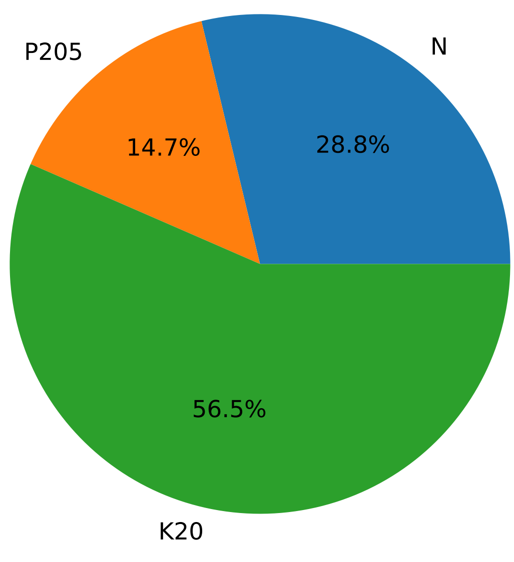


Figure 14: Composition of the digestate produced by anaerobic digestion.

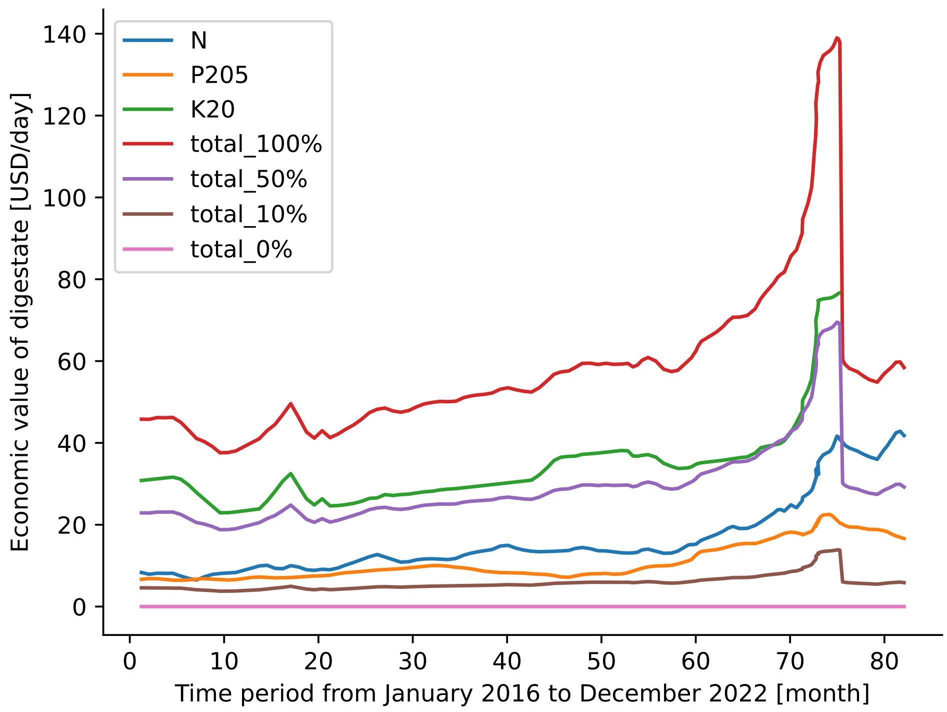


Figure 15: Economic value of the digestate considering a fixed NPK content.

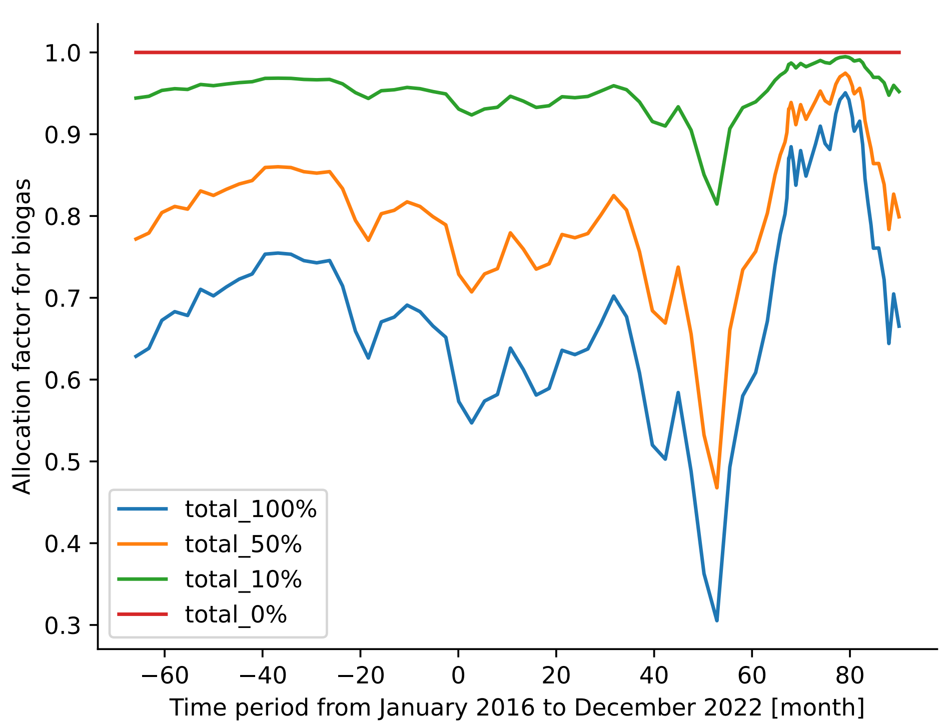


Figure 16: Evolution of the economic allocation factors for biogas between 2016 and 2023 considering different approaches.

two methods with using the calorific value of the biogas and digestate, attributing almost all the impacts to biogas.

2.2 Economic allocation factors for the electricity and heat from CHP

Due to a lack of data regarding the prices of district heat in Europe from 2019 to 2022, an exergy-based allocation procedure was applied to electricity and heat from CHP. This method is used in the ecoinvent v.3 database to distribute the environmental impacts between the two energy streams [7]. The exergy method was identified as the "most appropriate from a thermodynamic point of view" [5]. The exergy content of an energy carrier (e.g. electricity, heat) is a measure of the maximum useful work which can be performed by the stream (i.e. work potential) [14]. The electricity generated by CHP is associated with an exergy content of 1.0 i.e. 100% of the electricity produced can be converted into energy. However, heat is rated with an exergy factor of 0.17 i.e. only 17% of heat can be transformed into energy. According to the ecoinvent 3.6 dataset "heat and power co-generation, biogas, gas engine (IT)", we assumed that the thermal and electrical efficiencies corresponded to 37% and 53%, respectively (see Section 1.2). In addition, exergy factors of 1.0 and 0.17 for electricity and heat, respectively, were considered [15]. Allocation factors of 80.4% and 19.6% were attributed to electricity and heat, respectively.

2.3 Mass allocation factors for the solid and liquid fractions of the digestate

The allocation factors for the solid and liquid fractions of the digestate were determined based on the mass balance of the screw press separation step (see Section 1.3). According to [17], 71% of the DM of the digestate is transferred to the liquid fraction after separation. Therefore, allocation factors of 71% and 29% were attributed to the liquid and solid fractions, respectively.

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