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Systematic Review

Bridging the Gap between Biowaste and Biomethane Production: A Systematic Review Meta-Analysis Methodological Approach

Charalampos Toufexis [1], Dimitrios-Orfeas Makris [1], Christos Vlachokostas [1,*], Alexandra V. Michailidou [1], Christos Mertzanakis [1] and Athanasia Vachtsiavanou [2]

[1] Sustainability Engineering Laboratory, School of Mechanical Engineering, Aristotle University of Thessaloniki, P.O. Box 483, 54124 Thessaloniki, Greece; cptoufex@meng.auth.gr (C.T.); makrdimi@meng.auth.gr (D.-O.M.); amicha@meng.auth.gr (A.V.M.); cmertzan@meng.auth.gr (C.M.)

[2] Department of Procurement, Services and Projects, Waste Management of Western Macedonia Region, General Commercial Registry G.E.MI.: 122074536000, 6th km Kozani-Ptolemaida Rd., 50150 Kozani, Greece; vachtsiavanou@diadyma.gr

* Correspondence: vlahoco@meng.auth.gr

Abstract: Anaerobic digestion (AD) is a promising biowaste valorization technology for sustainable energy, circular economy, local energy community growth, and supporting local authorities' environmental goals. This paper presents a systematic review meta-analysis methodology for biomethane estimation, using over 600 values of volatile solids (VS) content and biochemical methane potential (BMP) of six different waste streams, collected from 240 scientific studies. The waste streams include cow manure (CM), sheep/goat manure (SGM), wheat straw (WS), household waste (HW), organic fraction of municipal solid waste (OFMSW), and sewage sludge (SS). The statistical analysis showed a mean VS content of 11.9% (CM), 37.3% (SGM), 83.1% (WS), 20.8% (HW), 19.4% (OFMSW), and 10.6% (SS), with BMP values of 204.6, 184.1, 305.1, 361.7, 308.3, and 273.1 L CH_4/kg VS, respectively. The case study of Kozani, Greece, demonstrated the methodology's applicability, revealing a potential annual CH_4 production of 15,429,102 m^3 (corresponding to 551 TJ of energy), with SGM, WS, and CM as key substrates. Kozani, aiming for climate neutrality by 2030, currently employs conventional waste management, like composting, while many local business residual streams remain unused. The proposed model facilitates the design and implementation of AD units for a sustainable, climate-neutral future.

Keywords: biowaste; biogas; biomethane; bioeconomy; anaerobic digestion; biochemical methane potential

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1. Introduction

In recent years, efforts to reduce anthropogenic greenhouse gas emissions and transition to clean energy have been intensified globally. Merely having a positive environmental impact is no longer sufficient for green technologies. Both global and European strategies currently focus on the need for socio-economic development alongside climate neutrality. The traditional linear waste management model has proven to have more significant environmental and social repercussions than previously thought [1]. With most of the world's population projected to reside in urban areas by 2050, waste management challenges are escalating [2]. In response, the European Union (EU) is advocating a top-down approach to assist local authorities in achieving their net-zero objectives. Circular economy principles are nowadays integrated into EU's waste management policies and guidelines to municipalities, aiming to achieve climate neutrality by 2030 [3]. Over 84% of participating cities in the EU's NetZeroCities initiative plan to adopt circular economy business models for the waste management [4]. Circular waste management contributes to both air pollutant emissions' reduction and resource conservation while also supporting sustainable energy production.

This necessity has driven the exploration of innovative technologies, particularly in biogas production and smart waste management solutions.

Anaerobic digestion (AD), a well-known biowaste-to-bioenergy technology, has gained significant attention for its ability to convert organic waste into methane-rich biogas [5]. Half of the cities and municipalities involved in the EU's NetZeroCities project are considering AD for future waste utilization policies [4]. AD, as a renewable energy source, not only reduces reliance on fossil fuels but also mitigates greenhouse gas emissions from organic waste decomposition. AD closely aligns with the principles of circular economy, contributing to sustainable resource management [6]. Its socio-economic benefits are significant, since AD plants manage and valorize local waste streams, foster local economic growth, create new jobs, and save electric/thermal energy and raw materials by producing clean bioenergy and nutrient-rich compost fertilizer for agriculture [7]. Overall, AD is the most preferable choice compared to other WtE technologies [8].

This study introduces a systematic review meta-analysis methodological approach for reliably and tractably estimating the biowaste-to-biomethane potential production of different organic waste categories. No similar methodological framework has been synthesized and applied, at least to the authors' knowledge. The central aspect of the study is the systematic review meta-analysis according to the PRISMA 2020 guidelines (PRISMA 2020 Checklist presented in Table S1 in the Supplementary Materials), with the objective of quantifying the characteristics of certain waste substrates, needed for the estimation of biomethane production. This approach can be a practical tool for the stakeholders of the quadruple helix. Local government authorities emerge as key beneficiaries, given their central role in waste management and infrastructure development [9]. Moreover, private companies that aim to develop successful circular AD bioeconomy models could find the developed tool as a useful alternative to estimate the potential produced bioenergy of biowaste. On this basis, the adoption and application of this step-by-step approach as a starting point can lead to effective biowaste management, landfill reliance reduction, and promotion of renewable energy sources like biomethane within local communities. Moreover, collaboration with various stakeholders, such as waste management companies, food industries, and primary production (agricultural and livestock farming) businesses, can be facilitated, with the aim of achieving a certain level of industrial symbiosis and waste valorization. The methodology focuses on categorizing waste streams according to their production sources, ensuring relevance and applicability across diverse contexts.

2. Materials and Methods

The main structure and components of the developed methodological framework are depicted strategically in Figure 1 and analytically presented and discussed in Sections 2.1–2.6.

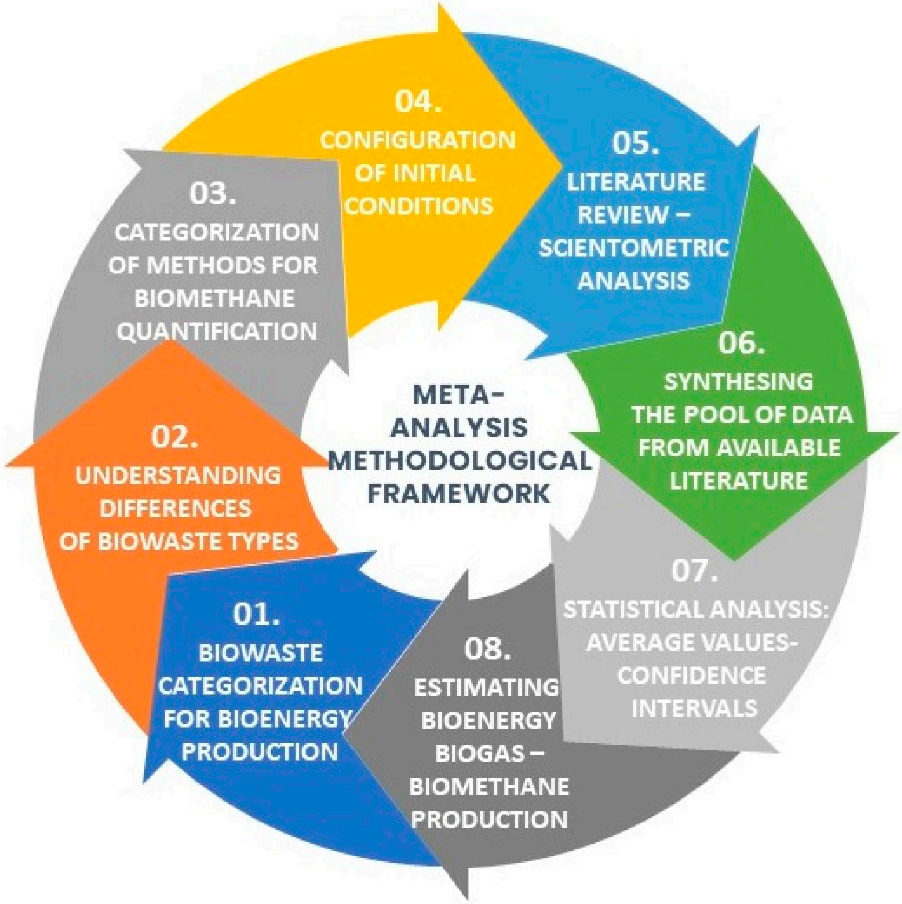

Figure 1. Basic structure and components of the proposed "meta-analysis" methodological approach.

2.1. Categorization of Organic Waste

The initial step of the methodology is the identification of waste categories available for AD. The categorization of organic waste into agricultural, municipal, and industrial sectors (Figure 2) serves as an efficient strategic framework for waste management practices, each with its unique significance [10]. Agricultural organic waste, consisting of crop residues and livestock waste (manure), can contribute to circular soil enrichment and sustainable farming practices [11]. More than 5 billion tons of crop residues are produced annually worldwide, with Asia contributing the largest share (47%), followed by the Americas (29%) and Europe (16%). The leading crops generating these residues are wheat, maize, rice, sugarcane, soybean, and barley, collectively accounting for 85% of global production [12]. Implementing a decision support system for the optimization of crop biowaste valorization for bioenergy production is recommended [13]. Regarding animal manure, animal farming in the EU27 generated more than 1.4 billion tons of manure annually between 2016 and 2019, with cattle contributing over 75% of the total production [14].

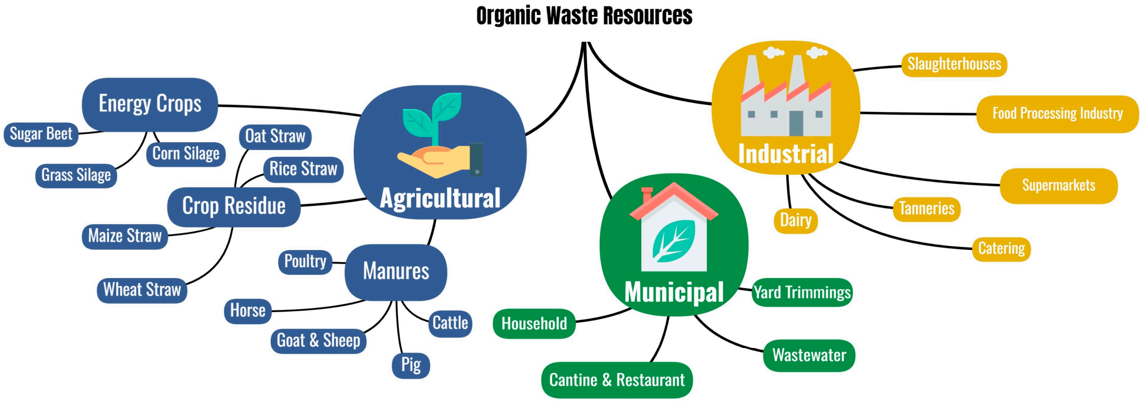

Figure 2. Organic waste stream strategic categorization.

Municipal organic waste, as a subdivision of municipal solid waste (MSW), is generated mainly by households, and includes mostly food waste and yard debris. Food waste has a high methane yield potential [15] and often constitutes a notable percentage (>40%) of MSW [16]. The EU27 produced 96 million tons of organic MSW in 2020. This figure is expected to rise to 2.2 billion tons by 2025 [17]. Industrial organic waste, originating especially from the food processing industry and agro-industry, demands specialized handling to minimize environmental impact [18]. Approximately 380 million tons of industrial food processing waste are produced annually. The beverage industry contributes 26%, followed by the ice cream industry (21.3%), fruit and vegetable processing (14.8%), processed grain products (12.9%), and meat production (8%) [19]. The importance of categorization of organic waste becomes particularly pronounced when considering AD, as properly identified organic waste provides a consistent efficiency of methane production, whereas unidentified waste results in unpredictable biogas production [20]. The indicative values of macro-molecule analysis (carbohydrates, proteins, lipids, and lignin content) of the different waste sectors are presented in Table 1. By understanding the differences between agricultural, municipal, and industrial organic wastes, targeted strategies can be implemented, such as the estimation of the optimal mix and ratio of different substrates in a co-digestion setup. In many cases, co-digestion has shown to notably improve the total methane production, due to synergistic effects of the co-digested substrates, as noted by Alatriste-Mondragon et al. [21].

Table 1. Indicative macro-molecule analysis of organic wastes.

Waste Sector	Carbohydrates(db)	Proteins(db)	Lipids(db)	Lignin(db)	References
Agricultural Waste	7.9%	3.48–8.7%	0.7–5.9%	3.1–22.3%	[22]
Livestock Manure Waste	44.06–90.2%	8.3–23%	1.5–4.9%	0.3–56%	[23–25]
Municipal Organic Waste	45–67%	15–17%	11–31%	4.9–5%	[26]
Agro-Industrial Waste	30–80%	0.4–38.2%	2.29–30.4%	1–43.2%	[27]

2.2. Categorization of Methane Yield Quantification Methods

The next methodological step is the definition and categorization of methane production quantification methods. Biomethane yield quantification methods encompass a diverse range of experimental and theoretical approaches (Figure 3) that play a crucial role in assessing the efficiency of biogas production in AD. Experimental methods can be broadly categorized into manometric, volumetric, and other specialized techniques, such as infrared spectroscopy. Volumetric methods are one of the most common experimental methods of biochemical methane potential (BMP) testing, and their operating principle is the measurement of the produced biogas volume under constant pressure and temperature in the reactor [28]. Manometric methods, on the other hand, involve measuring the pressure exerted by the produced biogas in a reactor that maintains constant volume [29]. Infrared spectroscopy offers a non-intrusive method by analyzing the absorption patterns of infrared light and is based only on spectral data without requiring any biological or chemical analysis. Theoretical methods complement experimental techniques by estimating the methane yield potential through theoretical calculations based on the composition of the substrate. Elemental composition determination via the ultimate analysis of the substrate allows for the estimation of the carbon, hydrogen, nitrogen, and oxygen content present in the sample, aiding in predicting methane production potential [30]. Chemical composition analysis, including the quantification of proteins, lipids, and carbohydrates, provides a more detailed understanding of the substrate's microbial degradation potential and subsequent methane generation [31]. Additionally, the theoretical method of chemical oxygen demand (COD) removal is employed to estimate the organic content in the substrate that can be biodegraded and converted into methane during AD [32].

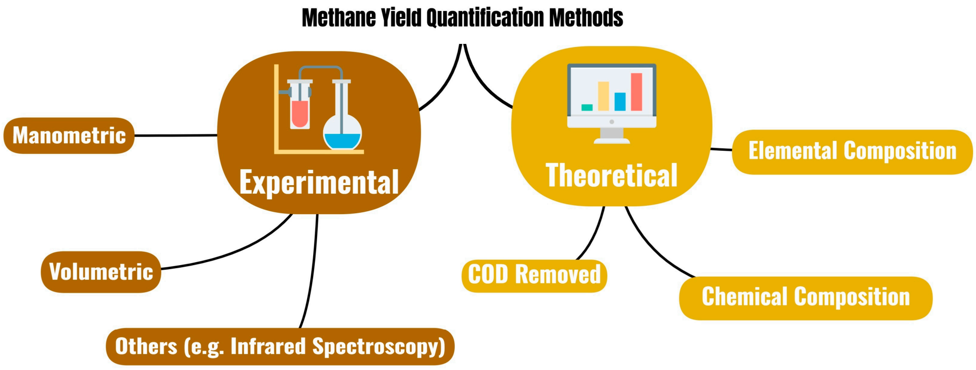

Figure 3. Quantification methods of methane production potential.

It goes without saying that the diversification of methods may have an impact on the estimation of biogas/biomethane production per type of biowaste category if they are considered individually. However, together, these approaches/methods may offer a comprehensive "toolbox" for assessing methane yield and facilitating the optimization of AD processes for enhanced renewable energy generation and waste management [33]. The calculations in this study were based on data from experimental methods, since these provide a more realistic image of the methane yield quantification, contrary to the theoretical methods that usually overestimate the production of methane [34].

2.3. Initial Conditions' Configuration

Establishing a standardized methodology for the assessment of a substrate's methane yield potential remains a challenge due to the multi-variable processes occurring in AD that may have an effect (small, medium, or large) on the final production. The diverse parameters and factors involved exert multifaceted influences on the overall efficiency of methane production [35]. Developing a comprehensive theoretical model and a universally applicable standard for evaluating methane yield potential requires a sophisticated understanding of the intricate interactions within the AD system. The clear recognition of the intricate dynamics and the careful consideration of the diverse influencing factors are essential for advancing efforts towards standardization in this field [28].

Key factors contributing to the efficiency of AD include substrate variables and AD system variables [36]. The substrate's composition and characteristics can vary depending on the type of waste. Moisture content plays an important role in the selection of wet or dry AD [37]. The carbon-to-nitrogen ratio (C:N) must have an optimal value of 20–30 [38]. The volatile solids (VS) content and its reduction are the main indicator of biogas production [39]. Changes in microbial activities, diversity, and composition should be regulated under optimal conditions in the system, as the microbial community activities and structure are in direct correlation with methane production [40]. The presence of toxic substances in the substrate and toxic by-products in the AD metabolic activities can seriously inhibit methane production [41]. AD system variables include reactor temperature ranging from mesophilic to thermophilic, pH levels, organic loading rate (OLR), hydraulic retention time (HRT), reactor design, and the substrate-to-inoculum ratio [42]. The multi-dimensional relationships between these factors pose a complex challenge in developing a theoretical model for the evaluation of BMP [43].

Compiling and extracting normalized methane yield data from various scientific studies and laboratory experiments is a challenging task due to the varying experimental conditions that include several pre-treatment methods and operational parameters. It should be noted that, within the framework of this study, and considering the numerous (hundreds) different approaches in the available literature, the criterion for differentiation was the waste category to produce an average estimation and relevant confidence intervals. Thus, data collection did not include criteria such as various substrate pretreatments or different operational conditions, providing a more general methodological approach without focusing on the large spectrum of diversification across the bibliography.

2.4. Synthesizing the Pool of Knowledge Data

The type of literature review recommended in this study is known as meta-analysis, wherein occurs an exhaustive and comprehensive search for a plethora of quantitative experimental studies, the results of which are combined and undergo statistical and numerical analyses to obtain an overall estimate [44]. In this study, the quantitative data collected play the role of a knowledge pool of input data for the developed methodological scheme from which the user will derive value estimations for the BMP and the VS content of the substrates selected, which are necessary for the computation of methane production in an AD setup. The identification and selection of the available waste categories, the election of quantification methods for BMP, and the determination of the initial conditions of the AD setup can assist in narrowing down the pool of the scientific literature by specifying the conditions that suit the user's scenario. The search engines Scopus Elsevier and Google Scholar are recommended for the collection of the data needed for the statistical analysis and the following calculations.

2.5. Statistical Analysis

Statistical and data analyses for the aggregated data are necessary for the proposed methodology. The analysis includes the computation of mean value, the standard deviation, the statistical sample, and the confidence interval of each category. During the application of the theoretical calculation model, uncertainty margins are crucial since there is always some error probability, which can be approximated with the upper and lower limits of the confidence interval.

Given that the data collected in the present study constituted a sample representing only a subset of all the existing quantification studies, it was postulated that the distribution of this data approximated a normal distribution [45]. The equations used, considering a normal distribution for the sample taken, are displayed and discussed below (Equations (1)–(6)). Equations (1) and (2) represent the calculation of the mean value $\overline{m_{VS}}$ and $\overline{m_{BMP}}$, where $\sum \mathrm{VS_i}$ and $\sum \mathrm{BMP_i}$ are the sum of values, while $\mathrm{n_{VS}}$ and $\mathrm{n_{BMP}}$ are the total number of studies collected for the statistical sample of VS and BMP, respectively. The standard deviations σ_{VS} and σ_{BMP} are computed using Equations (3) and (4), respectively, and the upper and lower limits of the confidence intervals $\mathrm{CI_{VS}}$ and $\mathrm{CI_{BMP}}$ using Equations (5) and (6), respectively. The z-value in Equations (5) and (6) represents a statistically predetermined value derived from the chosen confidence level for a sample following a normal distribution. By incorporating this aspect into the methodology, researchers can obtain a robust estimation for the range of VS content and BMP values based on the aggregated data from relevant studies.

$$\overline{m_{VS}} = \frac{\sum \mathrm{VS_i}}{\mathrm{n_{VS}}} \tag{1}$$

$$\overline{m_{BMP}} = \frac{\sum \mathrm{BMP_i}}{\mathrm{n_{BMP}}} \tag{2}$$

$$\sigma_{VS} = \sqrt{\frac{\sum(\mathrm{VS_i} - \overline{m_{VS}})^2}{\mathrm{n_{VS}} - 1}} \tag{3}$$

$$\sigma_{BMP} = \sqrt{\frac{\sum(\mathrm{BMP_i} - \overline{m_{BMP}})^2}{\mathrm{n_{BMP}} - 1}} \tag{4}$$

$$\mathrm{CI_{VS}} = \overline{m_{VS}} \pm \mathrm{z}\cdot\frac{\sigma_{VS}}{\sqrt{\mathrm{n_{VS}}}} \tag{5}$$

$$\mathrm{CI_{BMP}} = \overline{m_{BMP}} \pm \mathrm{z}\cdot\frac{\sigma_{BMP}}{\sqrt{\mathrm{n_{BMP}}}} \tag{6}$$

2.6. Methane Production Equation

The methane production in an AD setup is calculated by Equation (7), using the BMP and VS content values resulting from the meta-analysis conducted.

$$\mathrm{MP} = \mathrm{m}\cdot\overline{m_{VS}}\cdot\overline{m_{BMP}}\cdot 10^{-3} \tag{7}$$

MP represents the methane production (in m^3 CH_4) from the specific organic substrate selected for AD, m represents the total wet mass (in kg) of the organic substrate, $\overline{m_{VS}}$ is the mean value of VS content (expressed as % wb) of the selected organic substrate, while $\overline{m_{BMP}}$ is the mean value of BMP (in L CH_4/kg VS) of the specific organic substrate experimentally measured in the quantitative studies.

It is crucial to highlight that, for accurate calculations, the BMP index must be consistently expressed in the same units of measurement as it is presented in the equation, and the appropriate conversion of units is needed since there is a great variability in the units of methane yield index. The most common BMP measuring units in the scientific literature is L CH_4/kg VS, but m^3 CH_4/kg VS and mL CH_4/g VS are also common. Additionally, VS must be expressed as a percentage of the total wet mass of the substrate and not as a percentage of the total solids (TS). Many experimental quantitative studies in the scientific literature also express the VS content as g/L or g/kg, and some authors do not mention whether the VS content is expressed as percentage of the total wet mass (wet basis) or as a percentage of the TS content (dry basis). It is important to specify the exact basis of measurement when reporting TS and VS content measurements. To ensure accurate results in the calculations, the careful examination of the measurement units and the appropriate units' conversion is recommended.

3. Meta-Analysis and Case Study Results

In the following sections, the developed methodology is used for a real Greek municipality (Kozani) to demonstrate its applicability and validate the model estimations for the biomethane potential in the area under study.

3.1. The Case Study of Kozani, Greece

The Western Macedonia region of Greece (Figure 4) has historically played a crucial role in the country's energy production due to its lignite mines. The lignite-fired power plants in total contributed up to 58% of the nation's electricity in 2009, while a decade later, the contribution dropped down to 10% [46]. In line with global decarbonization efforts, Greece has set an ambitious target to finally phase out all lignite plants by 2028 [47]. The European Union's NetZeroCities project, through its Neutron initiative, is supporting Kozani's transition. Neutron aims to develop a methodology for accelerating a "just transition" towards clean energy, focusing on sectors like renewable energy production, Waste-to-Energy (WtE), and the digitalization of energy systems [48].

Figure 4. Map of Western Macedonia and the municipality of Kozani [49].

Kozani's plan for tackling the danger of a possible energy deficiency during the transition phase of the post-lignite era towards climate neutrality is the production of green electricity from multiple renewable energy sources (RESs) (Figure 5) to cover its electricity demands and convert the surplus electric energy into "green" heat, which can then be stored for later use in district heating or industrial processes. Heat storage can be achieved with the use of innovative power-to-heat (PtH) and high-temperature energy storage (HTES) technologies [50]. Kozani is examining the combination of these two into a technology called green heat module, wherein low-cost green power is used to produce process heat [51]. In addition, Kozani is exploring WtE as a valorization solution to the region's organic waste. Primary focus is afforded to the AD of organic waste to produce methane-rich biogas that can be used as a fuel in a combined heat and power (CHP) setup, thus covering a percentage of the electricity and heat demand. The produced biogas can also be upgraded into biomethane, as a supplementary alternative fuel to natural gas (NG), which can be either inserted into the NG network of the municipality or used as a fuel for gas-fueled vehicles. This way AD offers a two-fold benefit: the decongestion of landfills along with the reduction in the associated greenhouse gas emissions, as well as the production of bioenergy by valorizing the city's organic waste streams. Currently, in the EU27, 56% of the produced biogas is used for gross electricity generation; 12% is for gross heat generation; 30% is directly used and consumed in the agricultural, industrial, and residential sectors; while only 2% is used for transport as biomethane [52].

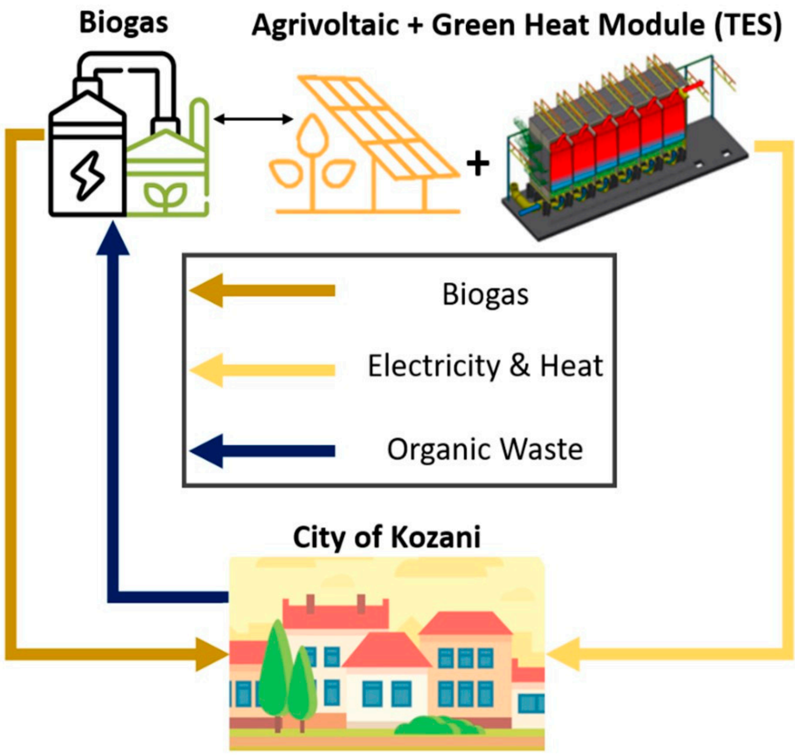

Figure 5. Climate neutrality energy plans of Kozani.

The case study of Kozani serves as a demonstration of the applicability of the presented methodological approach for estimating biomethane potential from organic waste streams. This theoretical calculation provides a preliminary valorization assessment, quantifying the potential methane production from the AD of the available waste. This constitutes the crucial first phase of the feasibility analysis that local authorities and the municipality of Kozani should conduct, informing the design and economic viability of a future WtE unit. By implementing AD, Kozani can not only manage organic waste sustainably but also generate valuable bioenergy, contributing to its renewable energy goals.

3.2. Selection of Case Study's Waste Streams and Collection of Data from the Literature

In the case study, waste streams connected to the municipal and agricultural sectors of Kozani were selected. These included the organic fraction of municipal waste (OFMSW), household waste (HW) that is source-selected, and sewage sludge (SS) from the municipality. Additionally, other biowaste types in the area included cow manure (CM), sheep/goat manure (SGM), and wheat straw (WS).

The eligibility criteria for including scientific articles in the systematic review meta-analysis were: (i) studies containing quantified values of volatile solids (VS) in physico-chemical characteristics tables for the specified organic waste substrates; and (ii) studies providing quantified values from biochemical methane potential (BMP) tests for the specified organic waste substrates.

Data collection was carried out using the Scopus Elsevier and Google Scholar search engines. The search keywords are presented in Table 2, along with the number of studies (sample) collected for each data category. The selection process involved manually picking relevant studies to aggregate a representative number. The data collection also included manually reading each paper to extract the useful data values for the systematic review. No other variables were sought.

Table 2. Categories of data found, keyword combinations, and number of studies collected.

Data Name	Search Keywords	Sample
VS Content for CM	("Volatile Solids" OR "VS") AND ("Cow Manure" OR "Cattle Manure")	74
VS Content for SGM	("Volatile Solids" OR "VS") AND ("Sheep/Goat Manure" OR "Sheep Manure" OR "Goat Manure")	46
VS Content for WS	("Volatile Solids" OR "VS") AND "Wheat Straw"	36
VS Content for SS	("Volatile Solids" OR "VS") AND "Sewage Sludge"	26
VS Content for OFMSW	("Volatile Solids" OR "VS") AND ("Organic Fraction of Municipal Waste" OR "OFMSW")	35
VS Content for HW	("Volatile Solids" OR "VS") AND ("Household Waste" OR "Household Food Waste")	60
BMP for CM	("Biochemical Methane Potential" OR "BMP") AND ("Cow Manure" OR "Cattle Manure")	27
BMP for SGM	("Biochemical Methane Potential" OR "BMP") AND ("Sheep/Goat Manure" OR "Sheep Manure" OR "Goat Manure")	28
BMP for WS	("Biochemical Methane Potential" OR "BMP") AND "Wheat Straw"	6
BMP for SS	("Biochemical Methane Potential" OR "BMP") AND "Sewage Sludge"	2
BMP for OFMSW	("Biochemical Methane Potential" OR "BMP") AND ("Organic Fraction of Municipal Waste" OR "OFMSW")	11
BMP for HW	("Biochemical Methane Potential" OR "BMP") AND ("Household Waste" OR "Household Food Waste")	20

The collected data values were manually converted into SI units to ensure compatibility. All studies were within the experimental scientific quantification framework for organic substrates, and no risk of bias was implicated; therefore, no risk of bias assessment was conducted nor were effect measures used. The references for VS and BMP data are presented in Table 3. The flow diagram of the systematic review process is presented in Figure S1 in the Supplementary Materials. The most used keywords of the reviewed scientific studies were analyzed in a correlation-interconnected network map using the VOSviewer software 1.6.20, as shown in Figure 6.

Table 3. Pool of references collected for VS and BMP values.

Type	VS Content	BMP
CM	[53–126]	[57,68,75,78,80,90,91,98,103,111,112,114,122,127–140]
SGM	[56,57,63,68,76,80,82,87,89,91,92,100,103,111,112,114,115,119,122,136,141–167]	[57,68,80,91,103,111,112,114,122,138,142,145,147,150–152,154–156,159,161–165,167–170]
WS	[63,83,88,94,105,106,109–121,124,148,149,161,171–192]	[129,137,161,182,193,194]
HW	[61,64,68,71,74,75,83,87,90,102,112,113,117,124,144,146,192,195–241]	[68,75,112,128,129,137,194,200,210,224,226,241–249]
OFMSW	[66,67,97,110,124,200,220,221,250–275]	[193,194,244,246–248,257,259,268,276,277]
SS	[67,97,199,207,217,221,228,234,261,263,265,278–292]	[246,293]

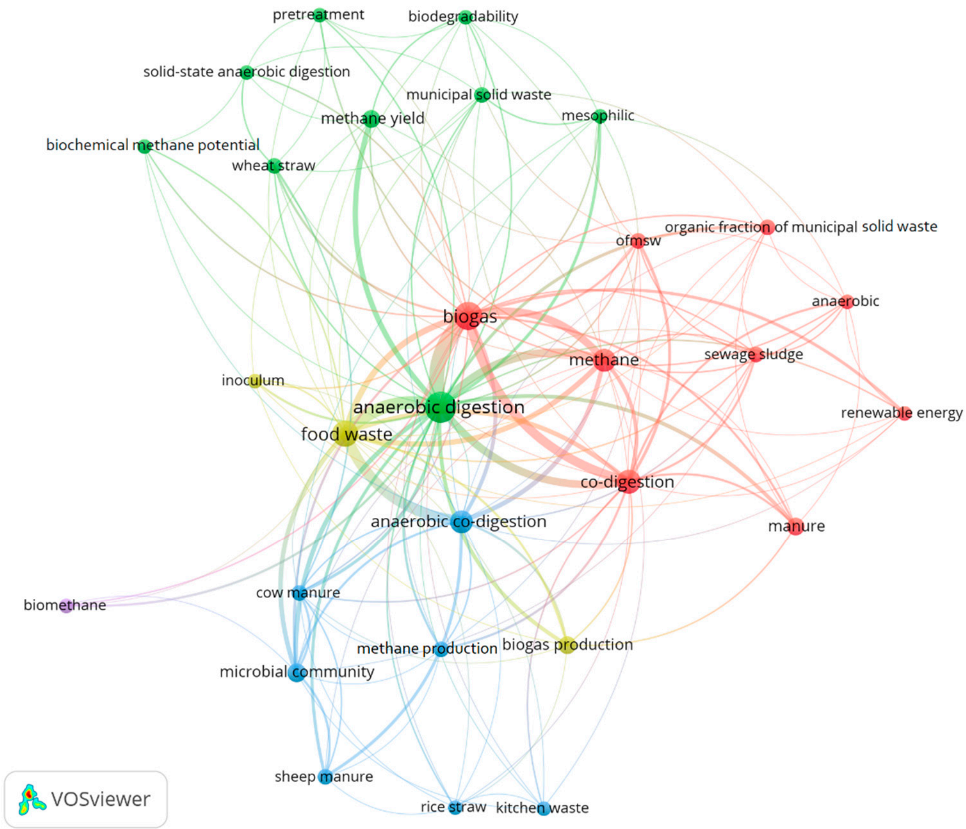

Figure 6. Network analysis of keywords from the pool of references in the VOSviewer software.

3.3. Statistical Analysis Results of BMP and VS

The data collected from all the studies were eligible for the statistical synthesis, as it was selected with careful manual inspection. Each group of data of every category of waste substrate, for VS and BMP separately, underwent separate statistical analysis, and the results were sorted by VS and BMP. The statistical analysis was conducted using Microsoft Excel, including the visual display. The statistical analysis numerical results of each substrate regarding the VS content and BMP index are presented in Tables 4 and 5, respectively. These include the mean values $\overline{m_{VS}}$ and $\overline{m_{BMP}}$, the sample count n_{VS} and n_{BMP}, the standard deviations σ_{VS} and σ_{BMP}, as well as confidence intervals CI_{VS} and CI_{BMP}. In Section 2.5, the steps of the statistical analysis are thoroughly presented, showcasing how the confidence interval was calculated. In this study, the z value was selected for a confidence level of 95%, which corresponded to z = 1.96. As showcased in Section 2.6, the mean values of VS content and BMP were utilized to calculate the produced biomethane. WS presents the highest VS content, while CM and SS have similar values with a low VS content. HW and OFMSW also have similar values, due to the similar waste composition that emerges from the same municipal sources, generally the households [294]. HW and OFMSW present the highest BMP values, along with WS. Even though CM and SGM have a $\overline{m_{VS}}$ difference >20, their BMP values are similar. Hence, regarding BMP, a similarity between the animal manure categories (CM and SGM) can be observed, as well as between the organic municipal waste categories (HW and OFMSW). The VS content and BMP values of OFMSW depend heavily on the mixture composition of the OFMSW, as already noted. If a greater percentage of yard waste is present in the mix, BMP decreases due to the high lignin content, while a greater percentage of food waste results in higher BMP values [295].

The boxplot diagrams of Figures 7 and 8 reveal that the manure, crop, and municipal waste category datasets exhibit a certain level of consistency in the data, with most observations falling within a reasonable range around an average value. Additionally, it is noteworthy that, in most cases, the mean value closely aligns with the median value, implying a symmetric distribution for these datasets and highlighting a balanced central tendency. Regarding the VS content, CM, WS, HW, OFMSW, and SS have a smaller IQR width in comparison to SGM, with SS having the lowest. It should be noted that, regarding BMP, HW, SGM, and CM exhibit narrower IQRs than HW, OFMSW, and SS. A narrow IQR suggests a minimal fluctuation between values in these cases, denoting a stable and concentrated distribution.

Table 4. VS statistical analysis results.

Substrate	$\overline{m}_{VS}$	σ_{VS}	n_{VS}	CI_{VS}	UCI_{VS}	LCI_{VS}
CM	11.9	5.0	91	1.1	12.9	10.8
SGM	37.3	14.0	53	3.9	41.2	33.5
WS	83.1	5.7	42	1.8	84.9	81.3
HW	20.8	4.2	82	0.9	21.8	19.9
OFMSW	19.4	6.3	46	1.9	21.3	17.6
SS	10.6	2.4	30	0.9	11.5	9.7

Table 5. BMP statistical analysis results.

Substrate	$\overline{m}_{BMP}$	σ_{BMP}	n_{BMP}	CI_{BMP}	UCI_{BMP}	LCI_{BMP}
CM	204.6	74.9	68	18.1	222.7	186.4
SGM	184.1	61.9	32	22.3	206.4	161.8
WS	305.1	77.4	26	31.2	336.3	273.8
HW	361.7	138.5	49	39.8	401.5	322.0
OFMSW	308.3	119.3	61	30.5	338.9	277.8
SS	273.1	160.1	25	66.1	339.2	207.0

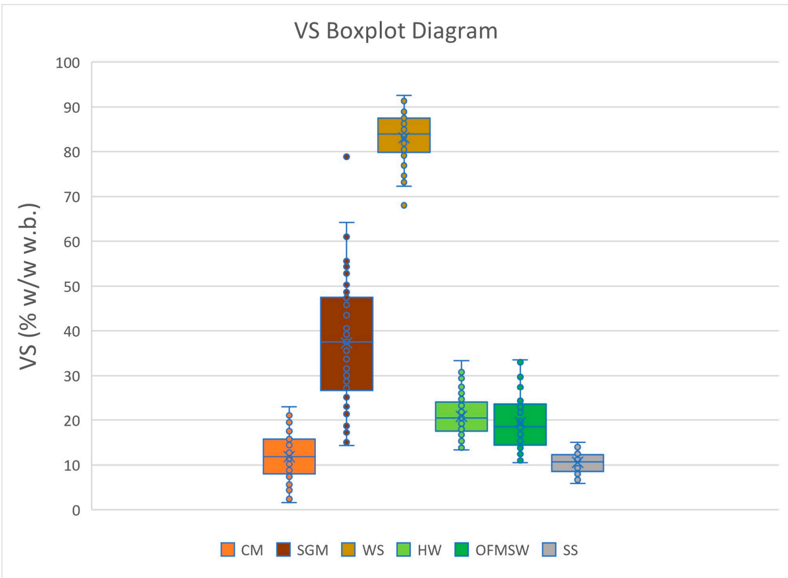

Figure 7. VS content boxplot diagram.

This stability can be valuable for the final methane yield potential especially in agricultural and livestock farming scenarios, where consistent and predictable measurements offer reliable decision-making processes. Only one data point in CM, two in WS, and two in SS were outside the whisker limits. This shows that each data sample had a limited number of outlier deviations, indicating a relative absence of extreme values that could significantly impact the overall distribution. The statistical analysis thus reveals a general homogeneity among study results, and the exploration of possible causes of heterogeneity was not needed. Since no initial conditions' parameters were taken into consideration during the collection of the data, no sensitivity analysis was conducted. Overall, the VS content and BMP mean values can be considered as objective indicators expressing the average of the various experimental quantitative studies and can thus be implemented into the methodology application in the case study, providing biomethane production results that approximate reality.

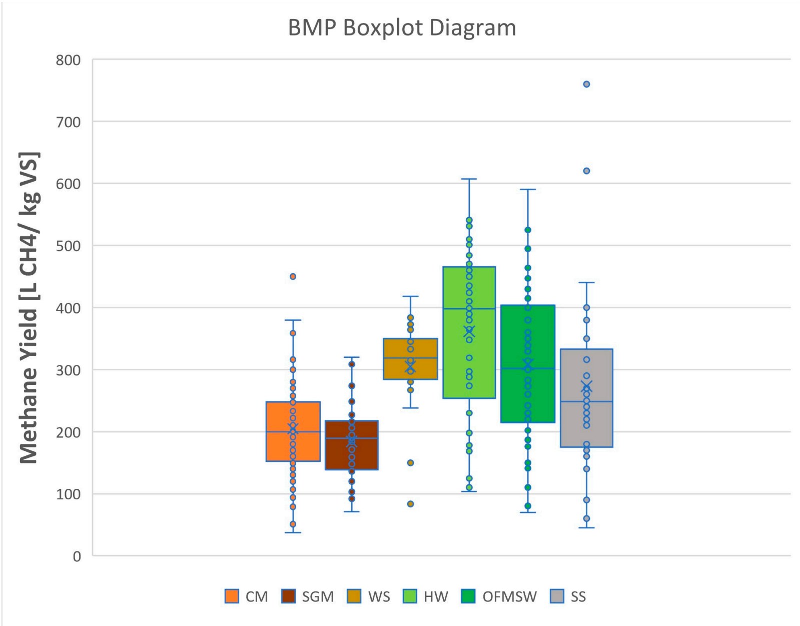

Figure 8. BMP boxplot diagram.

3.4. Case Sudy's Results and Discussion

The results of the methodology applied to the case study are presented in Table 6. For each substrate category, the annual production quantity (Q), the percentage of contribution to the total waste production (PT) in this scenario, the VS content and BMP values, along with the MP, the percentage of contribution to the total MP (MPC), and confidence interval upper/lower limit (UCL/LCL) are presented. A total annual production of 15,429,102 m^3 of CH_4 was estimated from the sum of Kozani's selected waste streams available. SGM, WS, and CM were the main methanogenic substrates and majorly contributed to CH_4 production, while HW and SS cumulatively contribute with an MPC < 1%, due to the minimal quantity of source-collected HS and low production of SS. HW has the highest BMP value; so, in the case that a greater quantity of HW is source-selected, an increased overall biomethane production can be achieved. The total annual CH_4 (volume) production can be converted and expressed as the energy content of the fuel to provide more comparable energy results. By multiplying the CH_4 volume by the CH_4 density (expressed as 0.68 kg/m^3 for surface conditions [296]) and the heat value of CH_4 (expressed as 50–55 MJ/kg [297], with a mean value of 52.5 MJ/kg), the annual energy potential of CH_4 is equal to 550,818,941 MJ or 551 TJ, which will be converted to electricity and thermal energy in the case of CHP.

The results showcase that there is considerable potential of biomethane in the area under consideration, agreeing with a similar case study in Greece [298]. Kozani can include biogas and biomethane in the area's energy mixture towards the production of green and renewable energy. This is crucial considering the need to accelerate the reduction in GHG emissions in multiple economic sectors. It should be underlined that this is feasible considering that the deployment of biomethane requires considerably lower investments of additional resources to develop new infrastructure (the natural gas network is a work in progress in this period in the area). This increases cost-effectiveness, considering the reduction in externalities that are related to fossil fuels. If CHP is selected for the combustion of CH_4, the electrical energy produced can be supplied into the electricity grid of the city, and the thermal energy can be utilized to provide hot tap water to households or cover the thermal needs of nearby industries or greenhouses. In the case that the produced biogas is upgraded to biomethane, the final CH_4 can be inserted into the NG grid of the city, covering a portion of the NG demand, improving the city's energy autonomy.

Table 6. CH_4 production from Kozani's waste streams, 2020 data, expected values, and 95% confidence intervals.

Type	Q (tn/y)	PT (%)	VS (% wb)	BMP (L CH_4/kg VS)	MP (m^3 CH_4/y)	MPC (%)	UCL (m^3 CH_4/y)	LCL (m^3 CH_4/y)
CM	135,300	50.37	11.9	204.6	3,280,516	21.26	3,888,010	2,724,597
SGM	76,418	28.45	37.3	184.1	5,251,185	34.03	6,495,373	4,138,383
WS	18,697	6.96	83.1	305.1	4,739,256	30.72	5,336,136	4,163,091
HW	229	0.09	20.8	361.7	17,256	0.11	20,003	14,678
OFMSW	33,600	12.51	19.4	308.3	2,014,950	13.06	2,426,781	1,641,377
SS	4353	1.62	10.6	273.1	125,938	0.82	169,880	87,242
TOTAL	268,597	100			15,429,102	100	18,336,182	12,769,368

4. Conclusions

Biomethane via AD technology stands as a crucial component for the future of waste management and decarbonization in the energy sector for local authorities, cities, and municipalities. On this basis, the accurate and tractable estimation of this potential based on the available biowaste streams is crucial for the success of circular bioeconomy models.

The proposed methodology can act as a starting point for the standardization of biomethane quantification through the preliminary theoretical estimation of the produced methane during the AD of organic waste. Even though, in the presented case, only specific organic substrates were selected and underwent a comprehensive data analysis through a meta-analysis literature review, this methodology can be applied to all possible organic substrates, depending on the characteristics of the area under consideration.

The case study of Kozani serves as a demonstrational example of the applicability of the current study's methodology, acting as a framework guide that future local authorities can follow to improve their own waste streams' management and utilization. Although the waste included in the analysis can be characterized as a representative organic sample, the compilation of other organic waste substrates that were not included is a future challenge for the authors, as well as the future inclusion of other parameters that have an effect on biomethane production. Also, machine learning algorithms could also be used to optimize the prediction of biomethane yield. Overall, the calculated biomethane values serve as a baseline for potential thermal and electrical energy decarbonization, playing a pivotal role in local authorities striving for net-zero status. Focusing on Kozani, the NetZero European program offers an opportunity for the city to achieve climate neutrality by 2030. Improved waste management, aligned with circular economy principles, is essential for every city trying to achieve its environmental goals.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16156433/s1, Figure S1: PRISMA 2020 flow diagram; Table S1: PRISMA 2020 Checklist.

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