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Investigation of the Theoretically Potential for Biogas Production from Mucilage in the Marmara Sea

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ABSTRACT

This research is about the disposal and evaluation of mucilage, which threatens human health, marine ecosystem, social life and economy. For this purpose, the idea of providing benefits by creating an alternative to meet the energy need, which is one of the world's priority problems, has been adopted. It has been determined that mucilage can be used in the production of biogas, which is a popular energy type in recent times, in line with its structural properties and content. Biogas, which has the potential to be an alternative to fossil fuels thanks to its numerous advantages, is a versatile renewable energy source that can be used in many different areas. In this study, the biogas production potential of mucilage was investigated theoretically with two different methods. One of the methods is to calculate the methane yield based on the protein, lipid and carbohydrate content of the organic matter. In the other method, according to the results of elemental analysis, the methane yield was calculated using the stoichiometric equation. According to the analysis and calculations, the theoretical methane yield of the mucilage was found to be 528.68 mL CH4/g VS according to the organic matter content and 526.15 mL CH4/g VS according to the elemental content. Theoretical calculation of the methane yield before the experimental study saves material and time. In this direction, it has been concluded that the biogas production potential of the mucilage is high and suitable for experimental work, since the methane yield values calculated using different methods are high and close to each other. It is believed that this study, which investigates the disposal of mucilage, which is a harmful formation, and its usability in the production of biogas, which is an efficient energy type, makes a multi-faceted contribution to the literature for humanity.

Keywords: Biogas, Bio-fuel, Methane, Mucilage

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1. INTRODUCTION

In our age, energy demand is mostly met by conventional fuels derived from petroleum and electricity produced from fossil fuels. Industrialization and urbanization lead to an increase in the use of fossil fuel resources and thus an increase in toxic and harmful substances released into the environment. Although it takes millions of years for fossil resources to originate, existing supplies are exhausted considerably faster than new fossil fuels are created. The world is in danger of running out of non-renewable energy resources. The rapid decrease in fossil fuel reserves also causes these fuels to become more expensive. In addition, the widespread use of non-renewable fossil energy sources causes an increase in environmental problems that are unacceptable for humanity in the long term, such as global warming, greenhouse gas emissions and climate change. For example, when the carbon footprint is evaluated as a result of the activities of a Waste Recycling Facility located in the province of Kayseri in Turkey; the share of carbon footprint was found to be 76.8% in transportation activities originating from waste collection, 23.1% in natural gas from consumption for heating purposes, and less than 0.1% in electricity use. The total CO2 emission of the facility was found as 132711 tons. For suchreasons, the search for clean, cheap, renewable and sustainable energy has attracted great interest in recent years. Solar energy, wind energy, biomass energy, tidal energy, and geothermal energy are examples of renewable energy that can be recycled in nature. Natural resources for renewable

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energy are plentiful, inexhaustible, and good to the environment. One of the renewable energy types is biogas energy. Biogas has been a considerably more popular research issue in the last ten years as worldwide energy demand and environmental consciousness have increased[1-5].

Biogas is a versatile, renewable energy source that may be used to generate heat and power instead of traditional fossil fuels.This type of energy, which can also be used in electricity generation, also has the potential to be used as a gas fuel in the automotive industry.Biogas is obtained by the degradation of the biomass source with microorganisms under anaerobic conditions[6,7]. It mostly contains two main components, methane (CH4) and carbondioxide (CO2). However, other trace species are also present, such as hydrogen sulfide (H2S), hydrogen (H2), nitrogen (N2), ammonia (NH3), oxygen (O2) and carbon monoxide (CO). Water, dust particles, siloxanes, aromatic and halogenated chemicals are also found in ordinary biogas, although the concentrations of these trace components are quite small compared to methane and carbon dioxide power[8].The anaerobic digestion (AD) process consists of several successive biochemical steps. All of these biochemical steps are carried out by microorganisms in the environment. During the AD process, the waste of some microorganisms becomes a food source for other microorganisms. These biochemical steps consist of hydrolysis, acidification and methanogenic phases, respectively[9]. The methanogenic phase is the phase in which the production of CH4 gas occurs prominently. This phase is the last step of the reactions and stands out as the rate determining phase in some waste types. While the methanogenic phase is the rate-determining step when the raw materials are easily degradable, the hydrolysis phase is the rate-determining step in raw materials with a complex structure [10].

General components of organic substances; can be listed as carbohydrates, protein, lipid and lignin. Hydrolysis is generally characterized as the breakdown of nutrients in water into small building blocks. Carbohydrates are hydrolyzed in a few hours, proteins and lipids in a few days, and lignin and lignocellulose in longer time [11]. Another disadvantage of raw materials with lignin and lignocellulose components is that the degradation process cannot be performed completely. The presence of non-biodegradable raw materials causes low CH4 yields and long processing times. Therefore, it is required to deconstruct the complex structures and slowly biodegradable components in the waste into small building blocks in order to improve the CH4 production. Examples of these slowly degrading components are lignocellulosic biomass. Some processing steps have been proposed to achieve high degradation of such biomass [12]. These steps are called preprocessing.

With the pretreatment stages, the waste components become easily biodegradable, thus reducing the most important disadvantage in AD processes [13]. In the literature, pretreatments are grouped into three groups: physical, chemical and biological. In addition, to reduce the effect and expense of biogas production, these pretreatments are administered concurrently or sequentially with two or more pretreatments, referred to as combined pretreatments. In this case,oil extraction has been defined as a combined pretreatment in the literature and has been successfully applied to biomass (microalgae) grown in water [11].In the literature, there are comprehensive studies on biogas and methane production from a wide variety of organic wastes such as tea factory waste, brewed tea waste, orange pulp, grass, pond sludge mixed with apple, vegetable waste, fruit pulp waste, algae, cow dung, cow urine, wheat straw, water hyacinth and banana peels[14-22].

Mucilage can be defined as a slimy, sticky structure formed by the overgrowth of plant organisms called phytoplankton, the rise in sea temperature and the resulting increase in bacterial activities. In the literature review on mucilage, studies in different fields were identified. For example, with the use of remote sensing techniques, a system for detecting mucilage production in the Sea of Marmara has been devised. It has been demonstrated that mucilage production may be detected rapidly and accurately from satellite photos anywhere across the world using this new technology [23].In a study on the formation and structure of mucilage, it was determined that foam accumulation occurs in the North Sea's coastal waters every spring, on the sea surface and on the beaches under windy conditions. For this reason, a single phytoplanktonic species called Phaeocystis multiplied, causing the food chain to deteriorate and mucilage was observed [24]. Öztürk et al., on the other hand, examined the dispersion of mucilage in the Marmara Sea’s water and determined that it reached the lower layer waters[25].

Giuliani et al. researched the effects of mucilage on other organisms in their study on mucilage formed in theTyrrhenian Sea in the Mediterranean[26]. Another study was carried out in the Mediterranean. Viruses in seawater containing mucilage were investigated to examine the mucilage's potential to host new microbial diversity and/or spread marine diseases. The development of mucilage in the Mediterranean has been connected to climate-related sea surface warming, according to the findings[27]. In some of the studies, the importance of bacteria in the mucilage phenomenon in the North Adriatic Sea, temporal dynamics of dissolved and particulate organic carbon, phytoplankton community structure, hypotheses and the relationships between mucilage events and climate variability were investigated [28-32]. Phytoplankton composition, environmental conditions and harmful algae growth production of mucilage in the Marmara Sea are also among the investigations [33,34]. In a study conducted on the shores of Büyükada in the Marmara Sea, the role of unicellular organisms in mucilage formation was investigated [35].

In addition, temporal changes in phytoplankton composition in the Northeast Marmara Sea, as well as changes in zooplankton population abundance and community structure, were explored [29,30]. In another study, temporal changes in picoplanktonic Synechococcus (Cyanobacteria) abundance during a mucilage formation in Bandırma and Erdek Bays were investigated [31]. Additionally, the effects of the mucilage event on a fish species in the shallow waters of the Dardanelles and North Aegean Sea are among the researched subjects [32]. Another study was conducted on Cryptobenthic fish communities affected by the mucilage formation in the northeastern Aegean Sea [33].Aslan et al. reported that in their study investigating the effect of mucilage on peraccharide communities, which have an important place in the marine ecosystem, negative results were revealed [34].In the study of Caronni et al., the ecology of microalgae species that cause mucilage formation in the Western Mediterranean was investigated[35].Furthermore, a study was conducted to research the effects of mucilage on ship operations in maritime and it was aimed to minimize the effects of mucilage [36].In their study, Uflaz et al. investigated the large-scale mucilage event that consisted in the North Aegean Sea and the Dardanelles Strait in 2021 and investigated the effect of some benthic species on mass mortality[37]. As can be seen, studies on mucilage structure have focused on the causes of formation, its structure, and its effects on other living things and nature. No study has been found in the literature regarding the disposal of mucilage or its conversion into high value-added products.

As mentioned in the previous lines, biogas is considered as a clean energy type obtained from organic wastes by anaerobic digestion and can be an alternative to fossil fuels.Biogas is suitable for utilize in many different areas such as electricity production, domestic heating, automotive industry, purification and chemical industry.Carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S) are important elements for biogas production[45,46].In addition, according to the information obtained from the literature, methane yields of biomass (microalgae) grown in water were found at a good level[47-50].Based on these, this study aimed to obtain and dispose of a beneficial product from the environmentally harmful mucilage structure formed in the Marmara Sea in Türkiye. In this study, which aims to provide multi-faceted benefits, the potential of biogas production from the mucilage structure formed by the combination of many biological and chemical conditions in the seas was investigated. The theoretical potential of the mucilage structure for biogas production, which is such a useful energy type, has been investigated. It is thought that converting mucilage into biogas, which is a clean energy type, will make important contributions both in the field of energy production and in the disposal of mucilage, which is harmful to the environment.

With the help of an elemental analyser (Leco/TruSpec Micro model, USA), the C, H, O, N, and S contents of each substrate were determined. Theoretical biological methane potential (mL CH_4/g VS) was then estimated from elemental analysis findings ($C_nH_aO_bN_c$) offeedstocks using the stoichiometric equation (Eq. (2)) (BMP_{thAtC})[51].

Elemental analysis is the process of measuring certain elements in a sample. Elemental analysers work with a combustion reaction-based logic. With combustion at high temperatures (950-1300^{o}C), organic matter containing C, H, N and S decomposes in pure oxygen environment and turns into gaseous compounds. As a result of combustion, carbon turns into CO_2 gas; hydrogen to H_2O; nitrogen turns into N_2 gas and finally sulfur into SO_2 gas and the device reports the C, H, N, S amounts in the sample as percentages over these gases. The percentage of O other than these was calculated by subtracting the C, H, N, S percentages and the percentages of trace metals from the percentage. Experiments were carried out at Recep Tayyip Erdoğan University Central Research Laboratory Application and Research Center (Merlab) in Türkiye, using a TruSpec Micro brand device. The experiments were repeated three times, and the averages of the results were taken.

2. MATERIALS AND METHODS

2.1 Determination of Protein, Lipid and Carbohydrate Percentages

The amounts of organic waste components such as protein, lipid and carbohydrates affect the biogas and methane yield. Theoretically, 1014, 740 and 370 mL CH_4/g VS methane can be produced from lipids, proteins and carbohydrates in the AD process, respectively [52].In order to determine the theoretical biogas and methane yield of wastes, carbohydrate, protein and lipid ratios should be measured. Protein determination was determined by Kjeldahl protein method, lipid percentages were determined by Soxhlet method and ash determination was determined according to the method applied in VS calculation. Carbohydrates were obtained by adding other percentages and subtracting from 100.

2.2 Determination of Theoretical Methane Yield

It is possible to compute the theoretical methane yield by two different methods. In the first method, methane yield is calculated using protein, carbohydrate and lipid percentages and is shown in Equation (1) (BMP_{thOFC}).In the second method, the methane yield is calculated from the stoichiometric equation (Equation (2)) (BMP_{thAtC}). The n, a, b, c values in the stoichiometric equation were calculated according to the elemental analysis results of the samples ($C_nH_aO_bN_c$)[51].

$$BMP_{thOFC} = 415 \times Carbohydrate\% + 496 \times Protein\% + 1014 \times Lipid\% \qquad (1)$$

$$BMP_{thAtC} = 22.4\,\frac{\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}}{12n+a+16b+14c} \qquad (2)$$

3. RESULT AND DISCUSSION

3.1 Determination of Protein, Lipid and Carbohydrate Percentages and Theoretical Methane Yield

Table 2 shows the organic fraction composition analysis of mucilage and the theoretical methane yield computed with Equation 1 based on this. The protein, lipid, ash and carbohydrate percentages of the mucilage were measured as 2.7, 28, 18 and 51.3%, respectively. Accordingly, the methane yield was calculated as 528.68mL CH_4/g VS. This result is significant.

Nielfa et al.[53]investigated the experimental and theoretical methane yield of samples obtained by mixing organic fraction municipal solid waste and biological sludge at different ratios. Theoretical methane yield of Co-digestion 1 sample prepared at the ratio of 80/20 (organic fraction municipal solid/biological sludge % weight) was calculated as 506.3 ml CH_4/g VS, according to the organic fraction composition. The experimental methane yield of the same sample was found as 220.6 ± 6 ml CH_4/g VS. In another study, Maya-Altamira et al.[54] investigated the methane potential of food processing industry wastewater. The theoretical methane yield of the wastewater used in the production of peas was 0.49 STPl-CH_4/gCOD and the experimental methane yield was 0.36 ± 0.05 STPl-CH_4/gCOD, according to the organic fraction.

Table 2 Protein, Lipid and Carbohydrate Content and Theoretical Methane Yield of Mucilage

	Protein (%)	Lipid(%)	Ash (%)	Carbohydrate (%)	BMP_{thOFC}(mLCH_4/gVS)
Mucilage	2.7	28	18	51.3	528.68

3.2 Determination of Theoretical Methane Yield by Elemental Analysis

The elemental analysis consequencesbelong to the mucilage are shown in Table 3. In the structure of mucilage, the C ratio is 51.40%, the H ratio is 7%, the O ratio is 40.08%, the N ratio is 1.44% and the S ratio is 0.08%. Considering these data, the methane yield was calculated as 526.15mL CH_4/g VS by means of Equation 2.It is believed that the fact that the theoretical methane yields calculated by the organic fraction composition analysis and calculated with the stoichiometric equation according to the elemental analysis results are so close to each other increases the accuracy.

Table 3 Theoretical Methane Yield of Mucilage based on Elemental Analysis

				$C_nH_aO_bN_c$		$C_nH_aO_bN_cS_d$		BMP_{thAtC} (mL CH_4/g VS)	
				calculation	integer number	calculation	integer number	$C_nH_aO_bN_c$	$C_nH_aO_bN_cS_d$
Mucilage	**C (%)**	51.40	n	4.28	42	4.28	1715	526.15	525.59
	H (%)	7.00	a	6.95	68	6.95	2784		
	O (%)	40.08	b	2.51	24	2.51	1004		
	N (%)	1.44	c	0.10	1	0.10	41		
	S (%)	0.08	d	0	0	0	1		

Aragón-Briceño et al.[55] carried out a study to determine the effects of process conditions on the properties of hydrocoals and process waters during hydrothermal treatment of a wastewater digester, and the effects of the fate of nutrients such as nitrogen and phosphorus on methane yield.Boyle and Buswell equations were used to determine the theoretical methane yields of the hydrothermal products they used in their studies. When they compared the theoretical methane yields with the experimental data, they found that Boyle's equation was closer to the BMP values.For example, the methane yield obtained in one of the experimental studies was 260.0 (mL of CH_4/g of COD added), while the calculated theoretical value was 271.6 (mL of CH_4/g COD).Nielfa et al.[53], on the other hand, tried different methods, including elemental and organic fraction composition analyses, to calculate the theoretical methane production efficiency produced by digesting municipal solid waste and biological sludge together, and compared them with the experimental conclusions. For one of the models they created, the error percentage was 5 for the elemental composition and -3 for the organic fraction composition.

Table 4 Comparison of theoretical methane yields of studies in the literature

Sample	BMP_{thAtC} (mL CH_4/g VS)	BMP_{thOFC} (mL CH_4/gVS)	Reference
Wastewater (Vegetable production: leek and fried onion)	340 (at STP conditions)	300	[54]
Wastewater (Vegetable fats and oils)	350	140	[54]
Biological sludge	333.9	338.2	[53]
Chlorella sp. algae	550	-	[56]
Nannochloropsis sp. algae	630	-	[56]
Mucilage	526.15	528.68	This study

Maya-Altamira et al.[54], in their study to evaluate the methane potential of food industry wastewater, suggested that estimating the theoretical methane yield based on atomic fractions is more precise than estimating based on organic composition. The reason for this, they claimed, was that the VS analytical results were less representative than the COD values. Bohutskyi et al.[56] conducted a study on methane production from different algae strains. For example, in the experimental study in which T. weissflogii algae was used as the substrate, the methane yield was determined to be 0.38 ± 0.01 L CH_4 (g VS)$^{-1}$. The theoretically calculated yield is very close to this value (0.48 L CH_4 (g VS)$^{-1}$).In another study by Bird et al.[57] using marine algae, the theoretical methane yield was given together with the experimental yield. For example, the difference between the theoretical and actual biochemical methane potential obtained from one of the Gracilaria spp. samples was determined as only 0.02 (m^3 kg^{-1} V.S. added).

As can be seen from the examples, the theoretically calculated methane yield can be quite close to the actual yield. Calculating the methane yield with different methods using different data allows the prediction of possible scenarios and the verification of the result.In addition, the theoretical calculations made before the experimental studies save time and material. In this study, the methane yield of the mucilage material was calculated theoretically by two different methods. The fact that the results are very close to each other increases the probability of the experimental study to be successful. The high results also give a hint that experiments to produce methane from the mucilage structure will be successful as well as worth trying.

4. CONCLUSION

In this study, theoretical methane yield of mucilage was investigated by using two different methods.In the first of these methods, the methane yield was calculated according to the protein, lipid and carbohydrate content of the mucilage. The protein percentage of the mucilage was 2.7, the lipid percentage was 28 and the carbohydrate percentage was 51.3.The methane yield calculated accordingly is 528.68 mL CH_4/g VS. The second method used to calculate the theoretical methane yield is the method using elemental analysis results. According to the results of the elemental analysis of the mucilage, the percentages of C, H, O, and N are 51.4, 7, 40.08 and 1.44, respectively. The methane yield calculated from these results is 526.15 mL CH_4/g VS. When the theoretical methane yield calculated by the organic fraction composition analysis and the theoretical methane yield calculated with the stoichiometric equation according to the elemental analysis results are examined, it is seen that the use of mucilage for biogas production is quite promising in terms of energy production.

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