XI International Conference on Textile Composites and Inflatable Structures
STRUCTURAL MEMBRANES 2023
C. Lázaro, R.Rossi and R. Wüchner (Eds)

INSTRUCTIONS TO PREPARE A FULL PAPER FOR THE
XI INTERNATIONAL CONFERENCE ON TEXTILE COMPOSITES AND INFLATABLE STRUCTURES
STRUCTURAL MEMBRANES 2023

Architecture for Pigs

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Abstract

Biogas production has the potential to provide three benefits for green energy, waste management, and bio-fertilizers. The process involves converting organic waste materials, such as agricultural waste and food scraps, into methane-rich biogas through anaerobic digestion. This biogas can then be used to generate electricity and heat, reducing the reliance on fossil fuels. Additionally, the waste materials are broken down, reducing the amount of waste in landfills, and the process produces nutrient-rich fertilizer for crops. In summary, biogas production can play a significant role in creating a sustainable future. In recent decades, membrane materials have been used and improved to become a proven solution for covering the roof of anaerobic digesters. Coated textiles, with advanced technical properties such as good gas barrier properties, flexibility, and durability, are ideal for this application. The aim of this paper is to provide the reader with a clear understanding of biogas production and the focus on the impact of some plasticizers which can be used for the development of a gas membrane in anaerobic digesters.

Keywords: biogas; biomethane, green energy production, gas permeation, flexible roof.

1. Biogas, the power from the dung

Biogas is a type of renewable energy that is formed from biogenic matter in the absence of oxygen, consisting primarily of methane, carbon dioxide, and water vapor. It is produced from various sources, including agricultural and food waste, industrial waste, and wastewater. While the biogas industry has faced obstacles to widespread adoption due to technical, economic, and environmental challenges, it has still experienced rapid growth in recent years. In Europe, the biogas sector currently produces over 19 billion standard cubic meters of biogas, with projections indicating growth to 35 billion standard cubic meters by 2030.[1]

National and international entities have conducted feedstock analyses to evaluate the viability of biogas production. Recent reports have also emphasized the profitability of side products generated by biogas plants, such as CO_2 and digestates, which reduce reliance on fluctuating gas prices.[2]

The EU commission has established a program to support the growth of the biogas industry within the frame of EU energy security and to support the goals of the EU green deal.

2. From organic wastes to biogas

A biogas plant operates on a principle similar to that of a cow's stomach. Microorganisms found in cow dung break down organic waste to produce methane through a series of biological processes. To be suitable for this process, a substrate must have a high level of biodegradable organic matter and should not contain any digestion-disturbing elements.

Animal waste is the primary source of biodegradable material for farm projects, but its methanogenic potential is low compared to other biomass sources. Agricultural plant materials, such as silage, straw, and crop residues, have high carbon content and good degradability, making them ideal for co-use in biogas production.

Anaerobic digestion, a process in which microorganisms called methanogens break down organic matter in the absence of oxygen, is used to produce biogas. This process occurs in a closed system called an anaerobic digester or bioreactor, and it involves four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Figure 1).

During hydrolysis, complex biopolymers are broken down into simpler molecules, and acidogenic bacteria produce volatile fatty acids and alcohols during acidogenesis. Methanogens then use these acids to produce methane during methanogenesis. Balancing the nutritional needs and environmental conditions of acid-forming and methane-forming microorganisms is essential to prevent instability in the reactor. Inhibitory substances can also affect the process, leading to a reduction in production or total failure of the process.

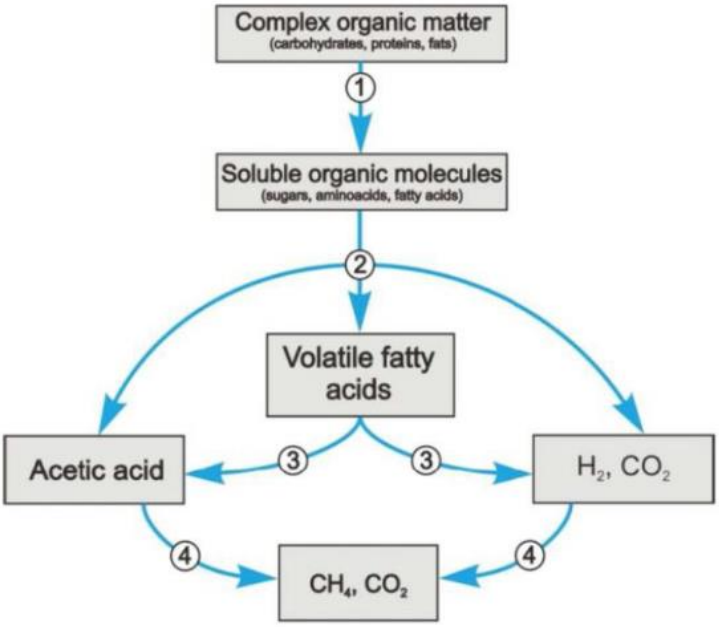


Figure 1 Anaerobic pathway of digestion of organic material.

Approximately 50% of the biogas produced is biomethane (Table 2), biogas has a calorific value of around 6-20 MJ/m^3 whereas biomethane's calorific value is 35-40 MJ/m^3.

Biogas can be used in cogeneration units to generate energy and heat, but the yield of electricity is moderate. Biogas can be purified and the biomethane (CH_4) separated from other gases to be injected directly into the natural gas grid.

The purification path represents today the biggest part of the new anaerobic digester projects, but also the usual upgrade realized on existing biogas installations. Other by-products, such as CO2 and digestate, are being investigated and promoted for their potential to make the biogas industry more circular.

Component of generated biogas	Content (%)
Methane (CH_4)	50-75
Carbon dioxide (CO_2)	25-50
Nitrogen (N_2)	0-10
Hydrogen (H_2)	0-1
Hydrogen sulphide (H_2S)	0-3
Oxygen (O_2)	0-2

Table 2: Biogas composition

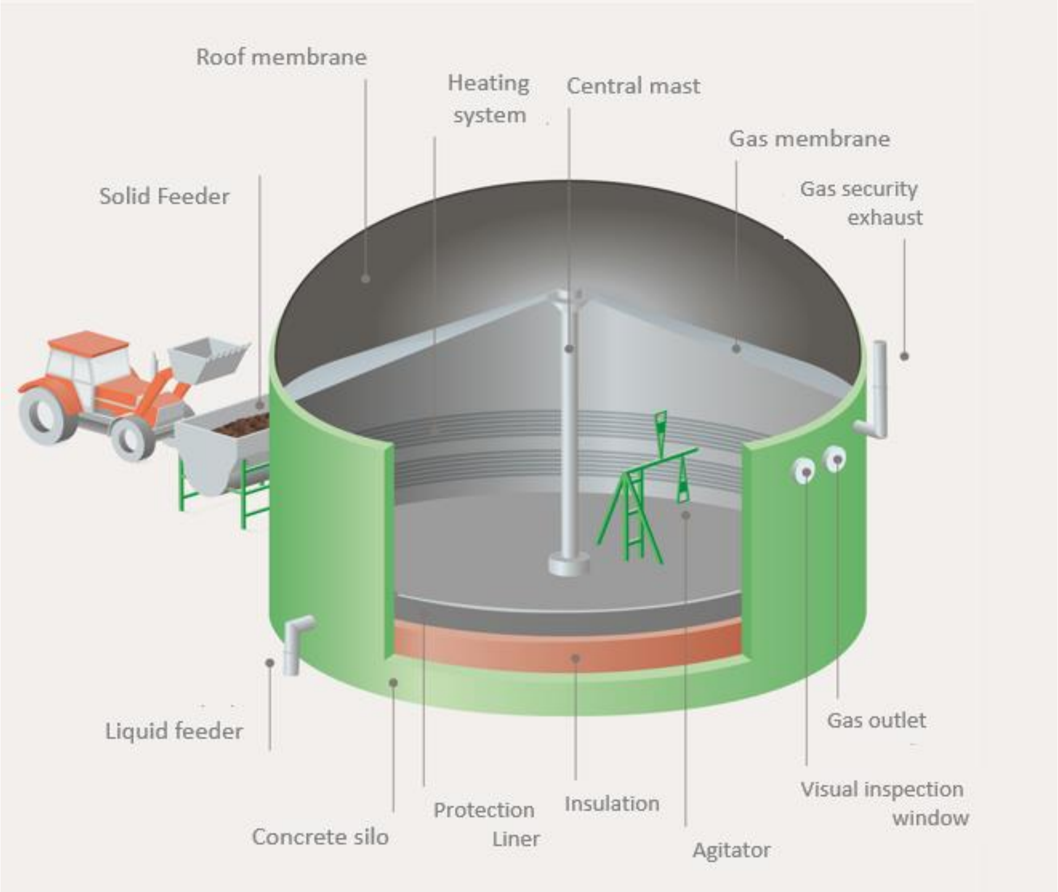
3. The architecture of a biogas installation

The choice of process for digestion depends on factors such as the type of feedstock, the ratio, and the incorporation method. Liquid phase is the most commonly used method, and it works well for mixtures with less than 18-20% dry matter. To ensure proper mixing, digestate recirculation may be used. For projects involving only solid manure, the solid route may be more appropriate.

During incorporation, it is important to carefully consider the type of material being used. Liquid materials are typically stored in tanks and pumped into the digester several times per day using eccentric screw pumps, chopper pumps, or lobe pumps for thicker substances. Solid materials are loaded into a hopper connected to the digester by an endless screw or a piston. This is also the stage where any undesirables such as pebbles, strings, or metals must be removed. It may be necessary to include a crusher and a stone trap depending on the type of manure being used.

The digester itself may be constructed of concrete or stainless steel and may be semi-buried. To ensure the optimal conditions for digestion, the parts of the digester in contact with the gas are protected against corrosion. The size of the digester must be calculated carefully to ensure sufficient residence time for the bacteria to express the methanogenic potential while maintaining a sufficient organic load. To maintain optimal conditions, the digester must be sealed, and temperature and pH levels must be maintained while ensuring there is no oxygen present.

Material flows are quasi-continuous, with one cubic meter of digested material being evacuated for every cubic meter of feedstock incorporated. The digester’s roof consists of a double membrane, with the outer membrane providing structural support and protection from weathering elements, and the inner membrane acting like a lung, inflating or deflating during gas generation and extraction (Scheme 1). The double membrane roof is being over pressured from 5-25 mbar. In Europe, the process is typically run at a constant temperature between 35 and 42°C using the mesophilic temperature regime.



Scheme 1: Overview of anaerobic digestion reactor (adapted from ADEME brochure)

Before the gas membrane has reached is maximum capacity, the biogas is being stored in a gas holder system, or being used to generate heat and electricity in a side CPH unit, or the gas is being purified thanks to a complex gas scrubbing system before being normalized (pressure, odour,…), verified (purity) and injected in the natural gas grid.

The solid and liquid content has generally a residence time in the digester is around 40 days. For 1 m^3 of feedstock entering, 1m^3 of digestate is being evacuated. The digestate is being filtered to separate the liquid and the solid parts. Both of them are used to fertilize the fields depending on the soil and crops need.

Recent studies have highlighted the need to regulate carefully the incoming and outcoming fluxes of matters, pressure and temperature in order to maintain a robust and performing process.[3] Due to the complex pathways of anaerobic digestion together with the side products generated, both biological selection together with numerous additives have been developed to buffer and increase the CH_4 yields.

4. Technical textiles at the service of Biogas plants

There are numerous technical textiles located near the biogas plant, and their main purpose is to create reliable and durable barriers against the dispersion of odors and matter in the environment. This allows for efficient storage and delayed processing. The focus of this discussion, however, is on the peculiarities of gas membranes and outer membranes used in anaerobic digester units, and not on these other applications.

Roof membranes, also known as outer membranes, need to be resistant to weathering conditions while maintaining their structural shape against various factors such as wind, snow, gas production, and degassing. To achieve this, a positive pressure system (including compressors and gas sensors) is used to adjust the overall pressure of the structure to the calibrated values. These overpressures can range from 5 to 50 mbar.

Therefore, the detailing of the membrane and the overall project must be executed meticulously to ensure the smooth operation for a minimum of 10 years. Overall, the structural approach of the roof membrane is not significantly different from the air positive structures commonly encountered in tensile architecture business. Currently, the most commonly used materials for roof membranes include PVC-coated polyester fabrics, EPDM membranes, and PE foils.

Gas membranes, on the other hand, face different challenges. They are not directly exposed to environmental conditions but are instead subjected to a hot, humid, and chemically rich environment due to the anaerobic digestion process. In these harsh conditions, gas membranes need to maintain their gas holding capacity and flexibility. Therefore, several measures are implemented in anaerobic digesters to ensure a minimum lifespan of 5 years for the gas membranes. For instance, the use of a center mast and connected belts prevents physical contact between the gas membrane and slurry, which could otherwise cause degradation and loss of function.

Additionally, the production of side products such as ammonia, hydrogen sulfide, volatile organic acids, and terpenes during anaerobic digestion can rapidly degrade the gas membrane if proper chemistry is not implemented. In most cases, this degradation leads to a loss of flexibility and gas barrier performance, ultimately resulting in the cessation of biogas production and costly operations to clean and repair the structure before resuming routine operations. The presence and composition of these side products are frequently monitored and depend on the biological processes and feedstock composition.

As a company with over 20 years of experience in biogas applications, we have installed our membrane products in more than 80 countries, encountering various conditions and uses. This extensive expertise has led to the development of three ranges of gas membrane products. In the next part of this discussion we will focus on PVC coated polyester fabrics as gas membranes.

5. Gas membranes, performance requirements and evaluations

To assess the performance and suitability of biogas membranes, we conducted a series of tests that consider the application conditions mentioned above. Firstly, we performed characterizations of the mechanical and physical properties of the membranes, such as tensile strength and adhesion, following our standard internal quality control procedures. These procedures are based on the guidelines outlined in the "Prospect for European Guidance for the Structural Design of Tensile Membrane Structures" [4].

Secondly, certain regions, like Germany, have published advanced guidelines for biogas plant safety. For example, the TRAS120 specifies rules for membranes, including requirements such as flame retardancy for the roof, surface resistance within a specific range to ensure conductivity and prevent electrostatic charge, outer membrane tensile strength and tear strength thresholds, reflection of thermal radiation to counteract heating from the sun and unnecessary overpressure in the storage tank, and inner membrane methane permeability limits at a specific pressure difference [5]. When necessary, our biogas membrane products for anaerobic digester roofs are developed and tested in accordance with these guidelines.

Thirdly, due to the variety of feedstocks and side products generated during the biological reactions, we have developed advanced specialty products to enhance the durability of the flexible roof. Although these tests are not officially covered by any guidelines, they are crucial for creating a reliable installation. In addition to locally monitored projects, we have developed two sets of tests to provide innovative and purpose-fit roof membrane products to the market.

The first type of test is typically conducted at specific biogas production sites, and it provides valuable information about the membrane's general behavior and performance degradation (Figure 2).

The second type of test is performed in laboratory conditions to further investigate and characterize the causes of performance loss observed in the field. The materials exposed during these tests undergo advanced surface and atomic analyses conducted internally and with the assistance of competent laboratories.

We have observed rapid performance loss, including degradation and loss of flexibility, in certain applications involving feedstocks derived from specific branches of the food industry and waste processing of fats and flavor derivatives.

Figure 2: Field test exposing the gas membrane to raw biogases before conducting material analyses.

One critical degradation mechanism of the gas membrane is the "loss of plasticizers," which refers to the membrane material becoming more rigid over time, resulting in the loss of gas barrier properties.

This de-plasticization is, to our knowledge, caused by two main factors: 1) hydrolysis of ester plasticizers in the presence of water, alcohols, and temperature, catalyzed by acidic or basic conditions, and 2) displacement of plasticizers through concentration exchange in the presence of organic aliphatic derivatives, catalyzed by heat.

To test and prevent such degradation, we developed various membrane specimens and subjected them to representative and simplified biogas atmospheres. We evaluated the degradation and oxidation of PVC plasticized coatings using FT-IR and SEM EDX analyses, and the comparative results are summarized in Table 2.

<table>
<tr><th colspan="2">Specimen</th><th>1</th><th>2</th><th>3</th><th>4</th></tr>
<tr><td colspan="2">Formulated with</td><td>Phtalate derivatives</td><td>Sulfonated phenyl esters</td><td>Adipic esters</td><td>Rubber derivatives</td></tr>
<tr><td colspan="6">Compatibility</td></tr>
<tr><td>Gas</td><td>Water</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Methane</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Ethane</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Propane</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Butane</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Pentane & higher hydrocarbons</td><td colspan="4">–</td></tr>
<tr><td></td><td>Carbon dioxyde</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Nitrogen</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Hydrogen</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Hydrogen sulfide</td><td>+</td><td>++</td><td>+</td><td>+++</td></tr>
<tr><td>Acids</td><td>Sulfuric acid <10% sol.</td><td>++</td><td>+++</td><td>++</td><td>+++</td></tr>
<tr><td></td><td>Acetic acid <10% sol.</td><td></td><td>++</td><td></td><td>+++</td></tr>
<tr><td></td><td>Phosphoric acid <10% sol.</td><td></td><td>++</td><td></td><td>+++</td></tr>
<tr><td>Bases</td><td>Soda <10% sol.</td><td colspan="4">+++</td></tr>
<tr><td></td><td>Ammonia <30% sol.</td><td colspan="4">+++</td></tr>
</table>

Alcohols	Methanol	_			
	Ethanol <30% sol.	+	+	++	+++
	Propanol <30% sol.	+	+	++	+++
	Isobutanol <1% sol.	+	+	++	+++
	Glycol	+++			
	Glycerin	+++			
Oil	Citrus	_	_	_	++
	Organic oils (soja, olives…)	_	_	+++	++
	Orange	_			
Hydrocarbons	Gasoline / Kerozene	_	_	+	++
Solvents	Acetone	_			
	Benzene	_			
	Terpene, limonene <5% sol.	_	_	_	++
	Toluene	_			
UV		++	++	++	_

Table 2: Comparative resistance against different chemicals released during anaerobic digestion

Based on the results obtained, we have reasonable confidence in the following conclusions:

1. Phthalates or sulfonated phenyl esters (specimens 1 & 2) demonstrate stability against hydrolysis conditions. Therefore, it is reasonable to use gas membranes formulated with these substances for crop wastes and manure feedstocks. Moreover, these formulations exhibit good UV resistance, making them suitable for agricultural biogas membranes.

2. The adipic ester formulation shows similar resistance against hydrolysis conditions, albeit with slightly higher hydrolysis rates compared to the previous formulations. Additionally, we observed better performance in terms of resisting plasticizer exchanges when hydrocarbons and oils are present as slurry components in the anaerobic digester.

3. Among the tested specimens, specimen 4 exhibited superior performance, acting as a superhero against the investigated de-plasticization mechanisms. However, it has one clear drawback: poor resistance against UV exposure. As a result, it can only be used as a gas membrane for double-layer anaerobic digesters and is not suitable for low-tech, single-layer digesters. This formulation seems to be the solution for challenging and aggressive feedstocks (such as food, oil, agricultural, and industrial waste) that trigger both de-plasticization mechanisms, scope of this investigation.

6. Conclusions and perspectives

Biogas production plays a crucial role in fostering a sustainable future. Over the past few decades, membrane materials have emerged as a proven solution for covering the roofs of anaerobic digesters, and continuous advancements have been made to enhance their performance. Coated textiles, possessing advanced technical properties such as excellent gas barrier capabilities, flexibility, and durability, are particularly well-suited for this application.

In this study, we conducted an analysis of various plasticizers in relation to the derivatives produced and present in anaerobic digesters. Through our investigation, we were able to identify several key and complementary benefits associated with different formulations. Furthermore, ongoing research is focusing on surface treatments aimed at improving gas barrier properties and resistance. Additionally, significant efforts are being dedicated to developing suitable insulation membranes, aiming to achieve high-performance and reliable technologies for anaerobic digestion processes.

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