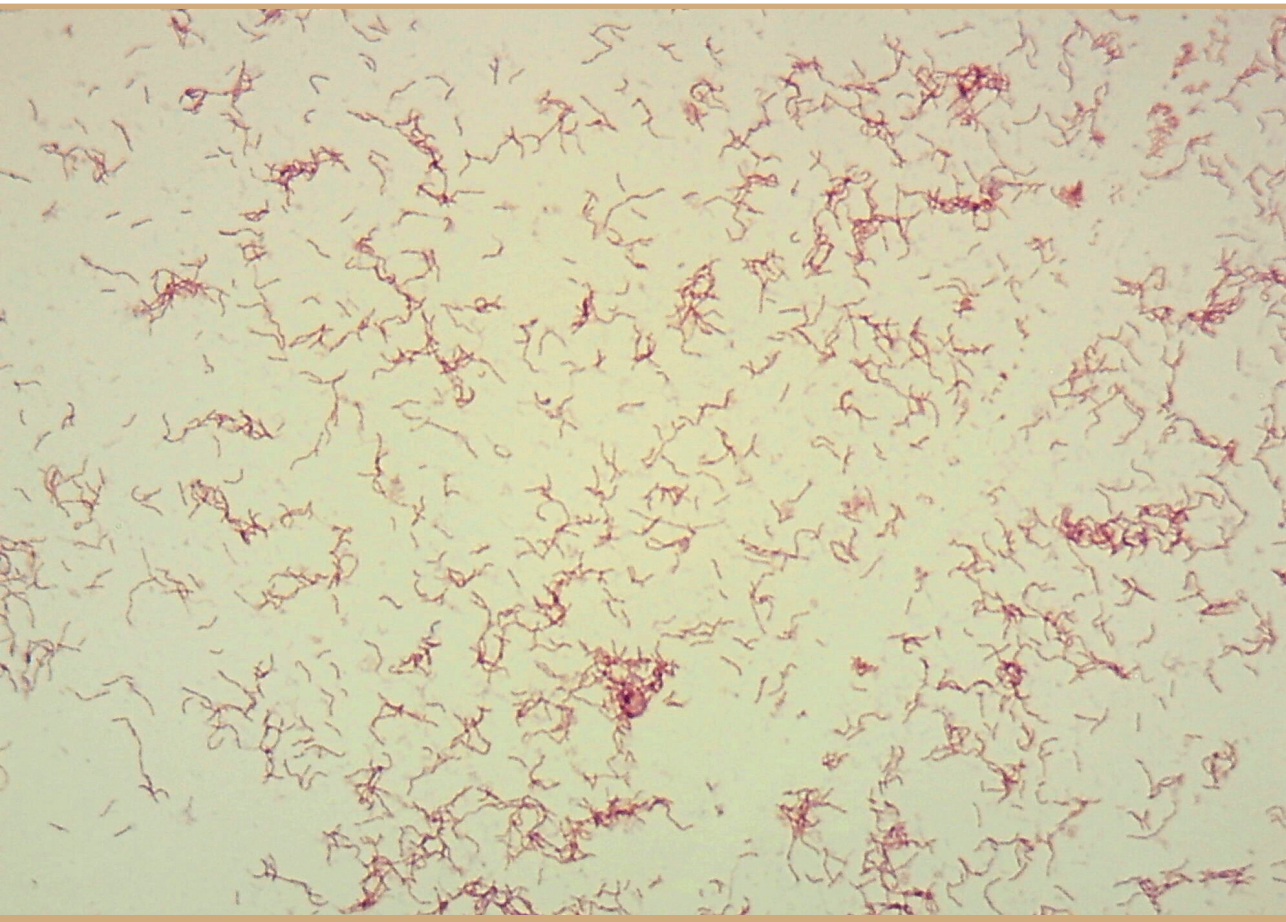
RIGA TECHNICAL UNIVERSITY

Zane Kušnere

BIOMETHANATION THROUGH THE APPLICATION OF WASTE-DERIVED FILTER MATERIALS

Summary of the Doctoral Thesis



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RIGA TECHNICAL UNIVERSITY
Faculty of Natural Sciences and Technology
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DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for defence at the open meeting of RTU Promotion Council on 31 October 2024, at 14.00 at the Faculty of Natural Sciences and Technology of Riga Technical University, 12/1 Āzenes Street, Room 607.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for review to Riga Technical University for promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for promotion to a scientific degree.

Zane Kušnere ……. (signature)
Date: ……

The Doctoral Thesis has been written in Latvian. It consists of an Introduction, 3 chapters, Conclusions, 40 figures, 10 tables, and 4 appendices; the total number of pages is 111, including appendices. The Bibliography contains 145 titles.

Contents

INTRODUCTION

Topicality

Energy autonomy has recently become one of the European Union's key strategic objectives. To achieve climate neutrality by 2050, the European Commission's REPowerEU plan aims to accelerate the deployment of renewables in the EU. This initiative has the potential to have an impact on the biogas sector. It aims to extend the EU Emissions Trading Scheme by setting a minimum carbon price and reducing the number of free allowances. The biogas sector could benefit significantly from this policy change, as it will become a more attractive and competitive option to meet the EU's energy needs in a cleaner and more sustainable way.

Through anaerobic digestion, organic waste and biomass are converted into biogas – a sustainable source of energy. Bioproducts play a crucial role in promoting a circular economy by efficiently converting organic waste into environmentally friendly and renewable energy, thus minimising the amount of waste going to landfills. In addition, the use of biogas can also contribute to job creation and economic development in rural areas where organic waste and biomass resources are abundant. Biogas use can also contribute to diversifying the EU's energy sources and reducing dependence on imported fossil fuels, thereby improving the security and stability of the energy supply. The continued growth of the biogas sector in the EU is therefore essential to achieve climate neutrality objectives, promote sustainable development and guarantee a greener future for future generations. The amendments to the emissions trading scheme proposed in the RePowerEU plan, such as the introduction of a minimum carbon price, can significantly boost the growth of the biogas sector, making improved biogas a much more attractive and economically viable alternative to traditional fossil energy sources.

An effective way to improve the economic viability of biogas plants is to improve the quality of the biogas so that it meets the standards required for feeding into the natural gas network. This upgraded biogas can then be used as vehicle fuel or as a feedstock for industrial purposes. Biogas upgrading is the process of removing carbon dioxide and increasing the energy content of the gas.

Historically, biogas upgrading has typically been carried out using physicochemical methods, which require significant amounts of energy and incur high costs. The use of biotechnology-based upgrading methods, therefore, offers the opportunity to significantly reduce both the energy consumption and the costs associated with biogas upgrading. The use of biotrickling filter reactors for biomethanation is widely recognised as a promising method for biogas upgrading. The filter material in these reactors is crucial to creating a suitable environment for the growth and proliferation of microorganisms, thus maximising the efficiency of methanogenesis. Different compositions and generations of materials have been investigated to improve the efficiency of biomethanation, but more cost-effective and efficient solutions are needed. By using sustainable materials for this technology, it is possible to increase the efficiency of methanogenesis while reducing the environmental impact. It is expected that with continued research and development,

more economical and environmentally friendly alternatives to filter materials will soon be available.

One alternative involves using waste to create such filter materials. Given the significant accumulation of solid waste and the depletion of natural resources, recycling of industrial by-products and waste has become an essential element of future waste management. Worldwide, the amount of waste glass produced in 2018 amounted to around 130 million tonnes, 80 % of which ended up in landfills. As well as a significant proportion of wood ash waste being landfilled. In order to increase the potential for the economic re-introduction of these waste materials into the economy, it is important to explore as many recycling and reuse options as possible. Involvement in recycling and reuse contributes to the development of a circular economy characterised by material and resource efficiency and waste minimisation. This is one of the key aspects of the European Green Deal and plays a key role in promoting a sustainable society by reducing environmental impacts and optimising resource use.

Research on filter materials made from ash and glass waste identifies new uses for the waste and helping to determine the exact properties needed to use these materials effectively in biomethanation processes. Researchers can identify the most suitable filter materials for biomethanation by conducting experiments to discover options that have the properties needed for more efficient use. This research not only contributes to waste management but also to the development of sustainable and efficient energy production technologies and encourages the transfer of knowledge and experience, promoting technical progress and the expansion of knowledge.

Aim and objectives

The aim of this work is to test the suitability of materials made from waste glass and waste wood ash for biomethanation in biotrickling filter reactors through experimental investigation and data analysis.

Objectives to be achieved:

1. To investigate and identify the most important parameters determining the suitability of filter material for immobilising biomethane-generating bacteria.
2. Develop, test and characterise a wood ash filter material in combination with a foamed glass material and other industrial filter materials.
3. Experimentally assess the suitability of filter materials for *ex-situ* biomethanation.
4. Perform stoichiometric calculations to estimate the theoretical yield of biomethane.
5. Validate the results of the experiment against the results of the gas analysis.
6. To investigate the role of microorganisms in the efficiency of biomethanation using specific filter materials.
7. Perform a multi-criteria analysis to select the most sustainable filter materials for biomethanation, taking into account both environmental and economic aspects.

Hypothesis

Filter materials made from waste glass and waste wood ash are suitable for biomethanation in biotrickling filter reactors and can provide efficient biomethane production comparable to or better than conventionally used filter materials.

Scientific novelty

Biotrickling filter reactors systems, as promising biogas upgrade technologies, are currently under intensive investigation to determine the optimum parameters for efficient biomethanation. One of the most important parameters influencing system efficiency is the filter material used to support the catalysts. Although various organic and inorganic materials have been investigated, there is no information in the literature on the use of ash aggregates in biotrickling filter reactors. This study is the first to address the potential of using ash filter materials and glass foam material in biotrickling filter reactors.

The results of the study could increase the knowledge of biomethanation processes and stimulate further research in this field, which in turn could lead to new innovations and improvements in biogas production technologies:

- New sustainable filter materials made from glass and wood ash waste are tested and characterised.
- Potential of foamed glass and ash filter material for biotrickling filter reactors.
- Investigating the role of *Methanobacterium alcaliphilum* microorganisms in biomethanation efficiency.
- A methodology for multi-criteria analysis to select the most sustainable filter materials for biomethanation has been developed.

Practical relevance of the research

Practical implications:

- New filter materials from industrial waste are developed and characterised, contributing to resource reuse and waste reduction.
- Advanced biogas with high methane content can be directly connected to the natural gas grid, promoting energy independence and the use of renewable energy sources.
- The technology offers an alternative to traditional biogas upgrading methods using biological methanation.
- The results of the study contribute to new innovations and improvements in biogas production technologies.

The research carried out in this Thesis not only provides data but also new knowledge and experience, contributing to technical progress and the expansion of knowledge.

Structure and description of the research

The Thesis consists of an introduction and four main chapters:

- Literature review
- Methodology
- Results and discussion
- Conclusions

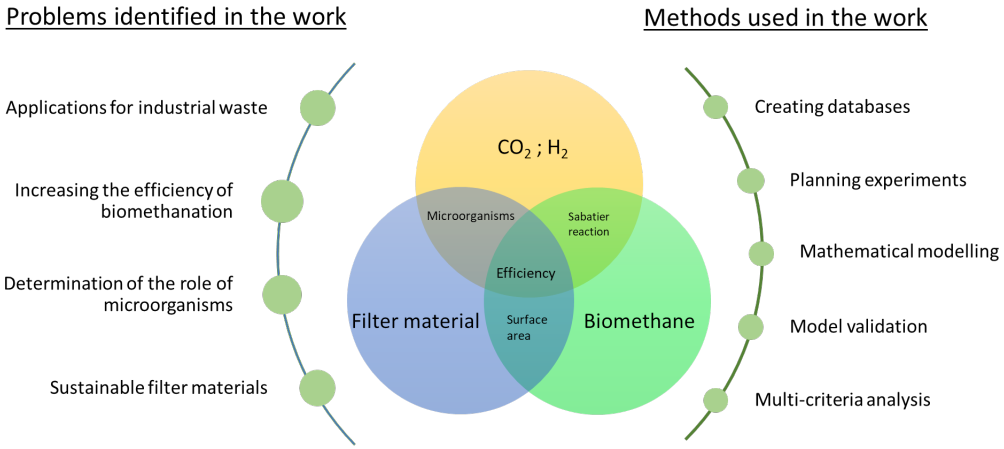
The introduction of the Thesis reflects the topicality and novelty of the Thesis, defines the aim of the research, proposes a hypothesis, as well as provides information on the research structure, methodology and practical application of the Thesis.

The literature review analyses the practical applications of industrial waste, the biogas sector and biogas upgrading technologies, in particular the use of biotrickling filter reactors, and explains the concept of power-to-gas. The main filter materials used in industry are also discussed in the context of biomethanation and their properties affecting the efficiency of biomethanation are analysed.

Chapter 2 describes the methods and materials used in the research, ranging from the preparation and characterisation of filter materials to various microbiological methods in laboratory tests with microorganisms. The manometric method is presented for biomethanation experiments, data analysis, mathematical modelling and multi-criteria decision analysis for filter material selection.

Chapter 3 presents and analyses the results of the work, discusses the implications of the studies and experiments, and compares and analyses the data. At the beginning, data on the manufacture of the wood ash filter and the characteristics of the filter materials are presented. The suitability of vulcanised film material and foamed glass material for biomethanation in the context of *ex-situ* biotrickling filter reactors are then discussed by analysing the data obtained from the experiments. This is followed by a review of how different criteria influence the choice of filter material for biomethanation.

Finally, the conclusions reached on the basis of the data and analysis are presented. The results are compared with the hypothesis, and conclusions are drawn from the work carried out.



1. Fig. Thesis research structure.

The Thesis addresses a number of research questions related to the biomethanation technology studied. The main process parameters of the technology investigated in the Thesis are shown in the centre of Fig. 1 and have a significant impact on the efficiency of biomethanation. The biotrickling filter reactor contains a filter material inside, on the surface area of which the methanogenic microorganisms are immobilised. When carbon dioxide and hydrogen gas are fed into the reactor, a *Sabatier* reaction takes place in which the microorganisms act as catalysts. This reaction results in the final product, biomethane.

The Thesis research is focused on a number of research questions related to biomethanation technology:

- industrial waste applications;
- increasing the efficiency of biomethanation;
- determining the role of microorganisms;
- development of sustainable filter materials.

The Thesis uses several methods: the creation of databases, experimental design and research, followed by mathematical modelling, model validation and finally, multi-criteria decision analysis.

1. METHODOLOGY

CHEMICAL ELEMENTAL ANALYSIS OF ASH SAMPLES

The ash from the combustion of straw and wood chips was used to prepare the samples. The straw ash was obtained from the Environmental Monitoring Laboratory of Riga Technical University during straw burning, while the woodchip ash was heavy bottom ash collected from the boiler house of JSC "Jūrmalas siltums". The services of "Virsma", an internationally accredited laboratory specialising in waste and fuel research and testing, were used to analyse the chemical elemental composition of the ash samples. This laboratory is accredited according to ISO/IEC 17025 standard, which ensures high accuracy and reliability of the analyses. Three samples were prepared for analysis: wood chip ash, wheat straw ash and wood chip ash obtained from the thermal energy producer. The analysis determined the moisture content of the ash, the oxide composition and the concentration of various chemical elements in the dry material, including the heavy metal content. All tests were carried out in accordance with internationally recognised methods and standards, including ISO/TS 16996:2015, LVS EN 15309:2007, and ISO/TS 16996:2015, LVS EN ISO 16968:2015.

ASH MELTING POINT TESTS

To investigate the correlation between the chemical composition of ash and its melting point, a series of experiments were carried out under laboratory conditions. These experiments were carried out with the aim of understanding how the chemical properties of ash affect the production process of filter materials that use high temperatures to cure wood or straw. Ash samples, including wood chips and wheat straw ash, were used to determine the melting point using a Carbolite CAF G5 muffle furnace. Testing was carried out using the methodology of EN ISO 21404:2020. The method involved pelletizing the ash samples and placing them in the oven, where the temperature was gradually increased until deformation of the ash pellet was observed. The onset temperature of the deformation was recorded, although the exact moment of deformation is difficult to determine, and the resulting melting point is therefore expressed as a temperature range.

Experiments in the production of wood ash material

Before further processing, the ash was sieved through a 2 mm sieve to remove larger particles and impurities. After sieving, the ash was ground using a laboratory grinder to ensure a homogeneous particle size. After grinding, the ash was weighed using a KERN 572 laboratory balance to ensure the appropriate mass proportion of the sample. The weighed ash sample was mixed with water in a laboratory container until a homogeneous mass was obtained, from which the beads were manually formed. The formed beads were left at room temperature to dry until baking. The beads were then placed in crucibles of 6–8 units each and baked for 3.5 hours in a Nabertherm LT 5/13 muffle furnace. To ensure an even temperature flow, the crucibles were

arranged evenly over the baking pan, which was placed in the muffle furnace in such a way as to minimise the impact on the thermal insulation material of the furnace. The material samples prepared in this way were used in subsequent experiments. In order to determine the approximate temperature for the tests, a number of preliminary tests were carried out, including melting point determination and moisture and chemical composition analysis of the samples. Samples of wood chips and straw ash were prepared in different proportions – 100:0, 80:20 and 50:50. Different maximum baking temperatures were tested to assess the ash melting properties, and an accurate temperature programme was used for all baking steps.

SELECTION OF FILTER MATERIALS FOR BIOMETHANATION EXPERIMENTS

In the Thesis, two filter materials made from industrial waste were chosen for the tests of the biomethanation experiment: a filter material made from wood chip ash and a filter material made from waste glass. The aim of the experiment was to test the suitability of these filter materials for biomethanation, in which this material would play the role of immobilisation of methanogenic microorganism biofilms. The sub-ash remaining after the combustion of wood chips in boiler houses is often considered as waste material if it does not have a wide range of applications, so this type of research may provide an opportunity to valorise such waste materials. Given that filter materials need to provide gas-liquid transfer between substances in a bioreactor, the material requires a large surface area to provide this. The processing of ash into aggregates increases the surface area of the material.

Glass foam is a substance made from recycled glass, and its production process is similar to that of woodchip ash filter material. This material has proven to be very versatile and adaptable, making it a valuable asset in a variety of industries. In addition, its sustainable production process is in line with current environmental trends, making it an attractive solution for companies wishing to reduce their carbon footprint.

Expanded clay is an inorganic material composed of clay minerals. Its main use is in horticulture, where it is used as a drainage and thermal insulation material. Expanded clay is commercially widely available and economically viable. Similar to expanded clay, glass foam is produced from recycled glass material, and interest in its production and use has increased in recent years. Glass foam is particularly sought after due to its properties such as high surface area, high permeability (when pores are interconnected), low density, low specific thermal conductivity, high thermal and acoustic insulation and high chemical resistance. In addition, glass foam is fire resistant and resistant to water and water vapour. Expanded clay, such as Leca®, is a cost-effective and readily available natural material that has a wide range of horticultural applications and is increasingly used in construction.

Polyurethane foams were selected for comparison with materials of different origin and quality. Polyurethane foam, which is an organic material, is used in a variety of applications including insulation, packaging, cushioning and others. It is a durable and multifunctional material.

PUF is a man-made substance derived from fossil fuels, and it is both cost-effective and characterised by high porosity, which provides a significant surface area. The advantage of using PUF and expanded clay, both of which have been extensively studied and used in similar applications, is that a larger dataset is available for comparative analysis in this research. Their origins are different – one is a natural material, the other is a synthetic material with fossil raw materials. The availability of data on polyurethane foams and expanded clay allows a more comprehensive assessment of their performance in different applications. This comparative analysis can provide valuable insights into the strengths and weaknesses of each material, helping in the decision-making process for future research.

Fig. 1.1. Filter materials used in the research:
PUF – polyurethane foam; EC – expanded clay, vulcanised ash material (FA – fine ash material and CA – coarse ash material); GF – glass foam.

Figure 1.1 shows the material aggregates tested and used in the biomethanation experiments: polyurethane foam (PUF), expanded clay (EC), two different types of vulcanised ash materials (VAM) – sieved and homogenised ash beads (FA), sieved ash beads (CA), and glass foam (GF).

DETERMINATION OF MATERIAL PROPERTIES

A number of key physical and chemical parameters were determined for all filter material samples, including density, water retention capacity, external porosity and pH, as well as specific surface area. The dry density (Equation (1.1)) of the EC and VAM material was calculated as the

ratio of the mass (weight) of the dry material to the total volume of the wet material. A 2 L beaker was filled to the brim with the filter material, and then the material was weighed.

$$\rho_b = \frac{M_s}{V_t}, \tag{1.1}$$

where M_s is dry particle mass (kg) and V_t is the total volume of particles (m^3).

A method based on the measurement of three perpendicular diameters of 30 particles of filter material was used to determine the specific surface area (m^2/m^3) of the material. The diameters were measured using a shear gauge $d_{1,i}, d_{2,i}, d_{3,i}$ of balls, each containing three different granules of filter material. The measured data were then used to calculate the specific surface area (Equation (1.2)) and the average particle density (Equation (1.3)), assuming an ellipsoidal particle shape.

$$a = \rho_b \cdot \frac{\sum_1^{30}\left(\frac{4\cdot\pi\cdot\left(\left(d_{1,i}^{1,6}\cdot d_{2,i}^{1,6}\right)+\left(d_{1,i}^{1,6}\cdot d_{3,i}^{1,6}\right)+\left(d_{2,i}^{1,6}\cdot d_{3,i}^{1,6}\right)\right)}{3}\right)^{\frac{1}{1,6}}}{M_{tot}}, \tag{1.2}$$

$$\rho_p = \frac{\sum_1^{10}\left(\frac{1}{6}\pi d_{1,i}\, d_{2,1} d_{3,i}\right)}{M_{tot}}, \tag{1.3}$$

where

a – specific surface area, m^2–m^{-3};

ρ_b – bulk density, kg/m^3;

$d_{1,i}, d_{2,i}, d_{3,i}$ – perpendicular diameter of the i-th particle, m;

M_{tot} – the mass of 30 particles of filter material, kg.

The water holding capacity (%) of the filter material was determined using 100 mL serum bottles adapted for biomethanation experiments. The measurement of this parameter is essential as it indicates whether the reactor is able to maintain sufficient moisture levels for the growth and development of microorganisms, thus ensuring the efficiency of the methanogenesis process. Serum bottles were filled with filter material and water so that the material was completely covered with liquid. After an hour of exposure, during which the filter material became uniformly moist, the water was discarded. The amount of water released was measured after 1 minute, 10 minutes and 30 minutes, and the average water holding capacity was calculated based on these measurements.

The pH of the material was determined by measuring the pH of the water in which the filter material was soaked for one hour. This measurement is essential to assess the effect of the filter material on the viability of microorganisms and the methanogenesis process, as an optimum pH level is essential for successful biomethanation.

The external porosity (%) of the filter material is another important parameter indicating how much of the filter material will be actively involved in the biomethanation process. Biofilm formed on the pore surfaces of the material can clog the pores and thus reduce the efficiency of the

material. Pre-wetted filter materials were used to determine the external porosity. The material was first soaked in water, and then the amount of air expelled from a 500 mL beaker previously containing the water-absorbing filter material was measured. The material was placed in the beaker and soaked in water for 10 minutes. After soaking, a sieve was attached to the beaker, and it was inverted for 10 minutes to allow the water to drain completely from the material. The external porosity was calculated by dividing the volume of water that could be added to the wetted filter material by the total volume of the container using Equation (1.4).

$$\varepsilon_{ex} = \frac{V_w}{V_v}, \quad (1.4)$$

where

ε_{ex} – external porosity, %;

V_w – the volume of water, L

V_v – a volume of the container, L

Biomethanation experiments

Different filter materials were used in the experiments: polyurethane foam (PUF), expanded clay (EC), two different types of vulcanised ash materials (VAM) – sieved and homogenised ash beads (FA), sieved ash beads (CA), and Glass foam (GF). 100 mL and 250 mL laboratory glass bottles were used as bioreactors in separate experiments. For each sample type, three replicate bioreactors were prepared in the tests for later statistical data analysis. In addition, control bioreactors without materials were also set up to observe whether the use of filter materials increases the biomethanation efficiency compared to a reactor without material.

MICROORGANISMS USED

Digestate contains many methanogenic microorganisms that are essential for the biomethanation process. These microorganisms play a key role in the conversion of organic material into methane, which is the main component of biogas. Digestate provides a stable microbial community that is adapted to anaerobic conditions and is capable of efficient methanogenesis. Digestate is also a by-product of existing biogas plants, making it a readily available and cost-effective source of inoculum. It also reflects the actual conditions under which the biomethanation process takes place in commercial installations. The inoculum used in the experiments was obtained from the digestate of the biogas plant of "Agro Iecava" Ltd. After collection, the digestate was incubated at 37 °C for seven days, each day removing the excess gas produced. This gas removal was necessary to free the digestate of the biodegradable organic residues that were still present. After degassing, the digestate was passed through a sieve to remove fractions larger than 2 mm. The dry matter content of the digestate was determined by drying at 105 °C in an Ecocell oven for 24 hours, and the change in mass before and after drying was determined.

To increase the biomethane concentration in the final product, two strains of *Methanobacterium alcaliphilum* were evaluated along with the biogas digestate as inoculum. The strains, alkalophilic methanogens, are isolated from lake sediments in the Wadi el Natrun region of Egypt and were ordered from the Leibniz Institute DSMZ-German collection. They were H_2 oxidizing, CO_2 reducing methanogens obtained from lakes with low concentrations of dissolved salts and pH levels between 8 and 10. The *Methanobacterium alcaliphilum* strains are monocultures selected for their ability to thrive in alkaline environments. Methanogens are diverse obligate anaerobic microorganisms that are widely found in various oxygen-deficient environments such as waterlogged soils, sediments, sewage sludge digesters and the digestive tracts of some animals.

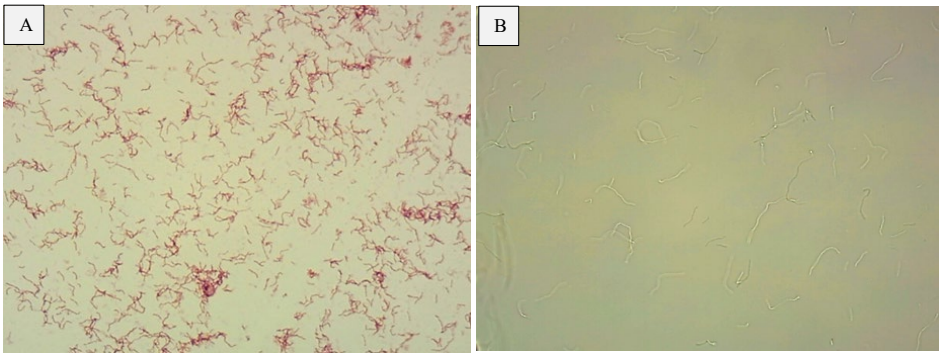


Fig. 1.2. Methanogenic bacteria:
A – 200× magnification, stained bacterial cells; B – 400× magnification, unstained bacterial cells.

Methanogenic bacteria are small and transparent as shown in Fig. 1.2 B, so staining is necessary to see them clearly and to distinguish their structures. Samples treated in this way are easier to monitor during the experiment when it is necessary to assess the growth of the bacterial culture after cultivation.

ANAEROBIC MEDIA FOR MICROORGANISMS

Methanogens that can only grow with H_2/CO_2 as substrate are grown in media prepared with a mixture of H_2/CO_2 gases in an oxygen-free environment. The vials in which these strains are grown are pressurised between 0.5 bar and 1 bar with a mixture of 80 % H_2 and 20 % CO_2 gases. In order to ensure optimum growth conditions, a fresh gas mixture is supplied to these strains at regular intervals, which prevents a pressure drop due to H_2/CO_2 consumption and facilitates the removal of CH_4 produced by the microorganisms.

The bacteria were anaerobically propagated, which means that a few important aspects of the medium preparation process also need to be taken into account in order to provide suitable growth

conditions for the methanogenic microorganisms. One is a low redox potential (0.33 V), and the other is a low oxygen partial pressure. To achieve this, the medium must be reduced during preparation, which can be done in three ways. The first way is boiling, which helps to get rid of the dissolved oxygen in the medium. The next is to keep the medium in an anaerobic gas environment, which prevents the medium from becoming re-saturated with oxygen. Finally, the addition of a reducing agent and an oxidation-reduction indicator to the medium makes it possible to reduce the medium and, at the same time, monitor the oxidative state of the medium. The oxidation-reduction indicator resazurin was added to the media used in the study, which gives the medium a pink colour in oxidised media, but when the medium is reduced, the pink colour disappears and the medium takes on a yellowish tint, which is due to the minerals, salts and vitamins dissolved in the medium. Resazurin is the most commonly used indicator of oxidation-reduction because it is generally non-toxic to microorganisms and is effective at very low concentrations of 05 mg/l to 1 mg/l.

To prepare Methanobacterium alcaliphilum microorganisms for the experiment, it is necessary to follow the manufacturer's instructions. The medium for the methanogenic monocultures was prepared from pre-prepared solutions A, B and C. On completion of the medium preparation, the pH of the complete medium was adjusted to 8.3–8.4. After the media had been prepared and poured over the reactors, they were rinsed with a sterile H_2/CO_2 gas mixture until the media were reduced before adding the microorganisms. After the media were reduced, the micro-organisms and sterile H_2/CO_2 gas mixture were added to a pressure of 1.5 bar.

In the experiments with biogas digestate, however, a basic anaerobic medium was used as an inoculum and contained the macronutrients, trace elements and vitamins required by the microorganisms. To the medium was added 0.5 g cysteine hydrochloride and 2.6 g $NaHCO_3$ dissolved in 10 mL water to stabilise the pH. The medium was then rinsed with nitrogen and sterilised in an autoclave. After autoclaving, the H_2/CO_2 oxidation-reduction indicator turned pink, indicating successful oxygen reduction of the medium, after which the medium was rinsed with a mixture of H_2/CO_2 gases before the addition of the micro-organisms.

BMP TESTS

One of the main ways to determine the suitability of filter materials for biofilm development by hydrogenatrophic microorganisms is to test them under laboratory conditions. Biofilm development is characterised by how fast the microorganisms can produce methane, or the efficiency with which the bioreactor can carry out the conversion of carbon dioxide and hydrogen, and the time the gas is allowed to stay in the reactor. When testing filter materials, one of the main objectives is to determine whether or not the material is suitable for biofilm and hydrogenotrophic methanogen development.

The biochemical methane potential (BMP) of a sample is the maximum amount of CH_4 that can be extracted from a given substrate. The method used to calculate the amount of CH_4 produced is based on substrate suitability and quality tests, which indicate the BMP of the sample. BMP

studies are one of the most common applications, also used in the design and management of biogas production facilities, the evaluation of the efficiency of bioreactor plants, the assessment of the quality of different substrates and the maintenance of the equilibrium of anaerobic digestion processes. In this context, BMP tests can also be used to assess the efficiency of biogas production and treatment procedures.

For the BMP test, 100 mL reactors (serum bottles) were filled with equal volumes of filter media – 50 mL, 1 mL of $NaHCO_3$ buffer solution, 0.386 g of substrate (winery yeast residue), and 30 mL of water. The inoculum from biogas digestate (20 mL) was then added to the reactors. Nitrogen was injected into the reactors for 5 min by flushing them from oxygen. The reactors were then hermetically sealed with rubber glands and secured with aluminium caps. The incubator in which the reactors were placed was kept at a stable temperature of 37 °C.

Using 20 mL syringes, silicone tubing, needles and forceps, the biogas was collected from the reactors. For the dissolution of CO_2, 3M NaOH solution was added to 5 mL of each syringe. The syringe was connected to the needle at the other end by a silicone tube fitted with a knapsack. The needle was introduced into the reactors through a rubber stopper, and the stopper was then opened, allowing the gas in the reactor to enter the syringe and raise its plunger. When the piston stopped moving, it was found that all the gas had been completely removed from the reactor. The gas volume was then measured and documented, and the needle was removed from the reactor. The bottles were gently mixed and returned to the incubator.

MANOMETRIC TEST

For the manometric test, the reactors were filled with 100 mL of wet filter material, 1 mL of inoculum and 15 mL of basic anaerobic medium. A gas mixture consisting of CO_2 and H_2 in a ratio of 1:4 was used to ensure the metabolism of microorganisms in the reactors. The serum bottles were hermetically sealed using rubber stoppers secured with aluminium caps.

To ensure the accuracy of the experimental data, three replicates were prepared for each type of filter material, while five control reactors were prepared following the same procedure but without the addition of material. In addition, control reactors without inoculum were used to correct for the pressure drop that could be caused by gas leakage during the puncture of the reactors. After sealing the reactors, needles were inserted through the rubber plugs to inject the gas mixture to an absolute pressure of approximately 1.5 bar. An Additel 672 pressure gauge was used to measure the pressure and was connected to the reactor via a needle through a rubber plug (see Fig. 1.3).

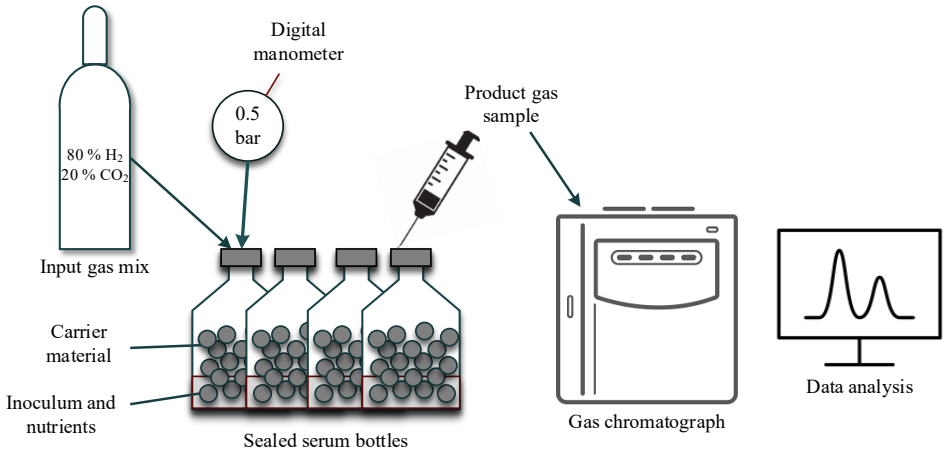


Fig. 1.3. Manometric test: filling serum bottles with a mixture of CO_2 and H_2 gas and analysing the samples.

Needles attached to the measuring instruments with silicone tubing are inserted into the serum bottles through the rubber cap. The silicone tubing connects the needles of the gauges in the serum bottle to the manometer and the CO_2 and H_2 gas mixture. The CO_2 and H_2 gas mixture is injected to an absolute pressure of approximately 1.5 bar. After incubation at 37 °C, periodic pressure measurements are taken with a digital manometer. At the end of the test, samples of the gases are collected by syringe and then used for gas composition analyses with a gas chromatograph, and the data are analysed.

After preparation, the serum bottles were placed in an incubator at a constant temperature of 37 °C and turned upside down. Measurements were taken daily by determining the volume of biomethane produced in the BMP test and recording the pressure drop in the manometric test. Such measurements provide accurate data on the biomethanation process and help to determine the suitability of the filter material for the process. The serum bottles are fitted with instrument needles through rubber caps and connected to the manometer and the source of the CO_2 and H_2 gas mixture via silicone tubing. The gas mixture consisting of CO_2 and H_2 is injected into the bottles until an absolute pressure of approximately 1.5 bar is reached.

The manometric test consists of two steps: Step I – enrichment and Step II – testing. In both the first and the second step, pressure measurements are taken at regular intervals, which show a trend in the rate of pressure decrease, which in turn indicates the rate of production of CH_4 in the reactors. Using the rate of pressure drop as an indication of the hydrogenotrophic methanogenesis reaction, it is possible to compare the CH_4 production potential of different filter materials.

The first stage involves the enrichment of microorganisms and the formation of biofilm on the surface of the filter material. The aim of this step is to build up and enrich the biofilm of methanogenic microorganisms on the filter material or to multiply them as much as possible. During this step, pressure measurements are taken once a day using a digital pressure gauge. The measurements are continued until the pressure readings are constant for two consecutive days. This

pressure value shall be recorded as the minimum pressure. The bottles are then refilled with a mixture of CO_2 and H_2 gases to an absolute pressure of approximately 1.5 bar and returned to the incubator. Measurements shall continue daily, and the bottles shall be refilled with the gas mixture until the pressure drop again reaches the minimum value within 24 hours. At this point, the biofilm on the filter material is considered to have fully formed and stabilised, thus completing the first stage.

In the second stage, the serum bottles are refilled with a mixture of CO_2 and H_2 gases to an absolute pressure of approximately 1.5 bar and placed back in the incubator. At this stage, measurements are taken more frequently, e.g. every one or two hours, in order to accurately observe the dynamics of the methanogenesis process over a shorter period of time. Measurements are taken at different time intervals, e.g. 1 hour, 2 hours, 3 hours, 5 hours, 7 hours, 10 hours and 24 hours after the introduction of the gas mixture, to study the biomethane production process in detail.

MATHEMATICAL MODELLING – THEORETICAL METHANE DETERMINATION

The manometric method is designed for comparing different filter materials under laboratory conditions and is both simple to use and affordable. In addition, the method is capable of using similar consumables to those used in the BMP experiments. The simplicity and cost-effectiveness of the method make it ideal for comparing the performance of filter materials in *ex-situ* biomethanation. A manometric estimate of the hydrogenotrophic methanogenesis rate can be obtained using this method. A stoichiometric calculation is performed according to the already-known metabolic reaction to determine the amount of methane produced. The degree of enrichment of hydrogenotrophic methanogens in bioreactors determines the amount of methane produced. According to the Sabotier reaction equation, enriched methanogenic microorganisms are known to produce 0.2445 moles of methane per mole of hydrogen (Equation (1.5)).

$$4.082H_2 + 1.031CO_2 + 0.008HCO_3^- + 0.008NH_4^+ \rightarrow \\ \rightarrow CH_4 + 0.039CH_{1,8}O_{0,5}N_{0,2(s)} + 2.066H_2O \quad (1.5)$$

The amount of methane produced can be determined using this stoichiometric equation together with the ideal gas law. Assuming that the water produced remains as a liquid in the biofilm, the reaction results in a reduction of 4.113 moles of total gas in the reactor (1.031 mol CO_2 + 4.082 mol H_2 – 1 mol CH_4). A clear correlation is expected between this reduction and a simultaneous reduction of the total pressure in the bioreactor. It is, therefore, possible to calculate the dynamics of hydrogenotrophic methanogenesis by periodically monitoring the rate of pressure drop in the reactor. The pressure measurements are used to determine the theoretical methane yield.

Prior to data standardisation and processing, a thorough data cleaning process was carried out to identify and eliminate missing data, outliers and redundancies, as well as to perform the

necessary unit and data format conversions. After data organization and cleaning, they were standardised to ensure accurate comparability of results: measured gas pressures were adjusted for temperature, gas volume and water vapour pressure using Equation (1.6) given in the guidelines:

$$V_{std} = V_{meas} \cdot \frac{(p_{meas} - p_{H_2O})}{101.325\ \text{kPa}} \cdot \frac{273.15\ \text{K}}{(T_{meas} + 273.15\ \text{K})}, \quad (1.6)$$

where

p_{meas} – measured gas pressure, kPa;

T_{meas} – gas temperature at the time of volumetric determination, °C;

p_{H_2O} – water vapour partial pressure, kPa;

273.15 K – temperature (0 °C);

101.325 kPa – standard pressure (1 atm);

V_{std} – standardised gas volume, NmL.

Pressure measurements were made starting with the gauge pressure, which was then converted to absolute pressure values by adding the ambient pressure reading at each measurement point to the measured pressure. In order to correctly estimate the gas losses that may occur due to the puncture of the reactors, the pressure drop across the control reactors was measured, and this pressure correction was included in the calculated absolute pressure values. The amount of methane produced was calculated using the ideal gas law and the stoichiometric Equation (1.5), which describes the metabolism of hydrogenotrophic methanogen and is based on experimental data. This equation refines the methane yield with respect to the hydrogen mole fraction unit used. The total moles of gas produced were then calculated using Equation (1.7):

$$n_j = \frac{P_j V}{RT}, \quad (1.7)$$

where

n_j – production of gas moles, mol;

P_j – measured pressure, bar;

V – reactor volume, L;

R – ideal gas constant, L·bar·K^{-1} ·mol^{-1};

T – temperature, K.

The calculated moles were standardised to normal conditions (1 atm pressure and 0 °C temperature), and the number of moles of methane produced (Equation (1.8)) and the volume of methane produced (Equation (1.9)) were determined:

$$n_{CH_4} = \frac{n_{j,std} - n_{j-1,std}}{4.113} \quad (1.8)$$

$$V_{CH_4} = n_{CH_4} \cdot V_M, \quad (1.9)$$

where

n_{CH_4} – methane gas content, mol;

n_{std} – quantity of standardised gas, mol;

V_M – ideal gas molar volume, L·mol^{-1};

V_{CH_4} – methane mole volume, L·mol^{-1}.

CH_4 MEASUREMENT BY GAS CHROMATOGRAPHY

During the last measurement of the manometric tests, gas samples from the bioreactors were collected using syringes and then hermetically sealed with stoppers to prevent any leakage of gases before analysis. The gas samples obtained were analysed using a Shimadzu Nexis GC-2030 gas chromatograph equipped with two parallel analysis lines as well as a flame ionisation detector (FID) and a thermal conductivity detector (TCD). A Restek Rt-Q-Bond column (30 m, 0.53 mm inner diameter, 20 µm film thickness) with an FID detector was used for the analysis of hydrocarbon compounds, providing high sensitivity and accuracy in the detection of hydrocarbons. A TCD detector coupled to a three-column system was used to analyse H_2, N_2, CO, CH_4 and CO_2. This system included a size exclusion pre-column (Restek Porapak Q 80/100), a size exclusion column (Restek Porapak Q 80/100) and a molecular sieve column (Restek Molsieve 5A 60/80). This sophisticated column system ensures efficient and accurate separation and quantification of the different gas components, allowing detailed data on the composition of the gases to be obtained.

Multi-criteria decision analysis

After the experiments and the data, a multi-criteria decision analysis was carried out. The multi-criteria decision analysis is based on a literature review, covering both historical and current aspects and newly obtained filter material parameters, as well as data from biomethanation experiments. The algorithm used in the analysis is illustrated in Fig. 1.4, where it can be seen that the subsequent steps involve the selection of materials (alternatives), which include vulcanised wood ash material, foamed glass material from waste glass and other alternatives based on the criteria identified in the literature. The definition of the evaluation criteria has been carried out following a systematic literature analysis. The method used in this study is the ranking of preferences by similarity to ideal solution (TOPSIS). In addition, a sensitivity analysis is performed to strengthen the reliability of the results.

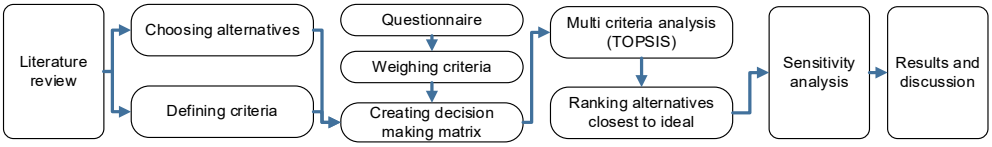


Fig. 1.4. Algorithm for a multi-criteria decision analysis workflow.

The criteria selected were divided into four categories: environmental aspects, economic aspects, technological aspects and performance aspects. All criteria are quantitative, and the relevant data were obtained from literature sources and studies. The criteria used for the multi-criteria analysis of the application of biomethanation materials are listed in Table 1.1.

Table 1.1

Multi-Criteria Analysis Criteria for the Use of Materials in Biomethanation

Criteria category	Criteria
Environmental aspects	The energy required to produce the material, °C Origin of material (fossil or not), 0–1 points
Economic aspects	Raw material costs, EUR m^{-3} Material availability, Mt/year
Technical aspects	pH of the material External porosity, % Bulk density, kg/m^3 Specific surface area, m^2/m^3
Performance aspects	Average biomethane yield, $NmL/L_{Material}$ Water retention, %

CRITERIA WEIGHTS

The weights of the materials in the multi-criteria matrix were determined using expert judgement. For this purpose, experts with a broad knowledge of biology, environmental engineering, biotechnology, chemistry, as well as civil, industrial and mechanical engineering were selected. A total of thirty experts took part in the survey, 11 of whom had a PhD, 15 a Master's degree and four a Bachelor's degree. The survey was conducted using the Google Form platform. The weights for each criterion were determined using a questionnaire method in which participants were asked to rate each criterion on a scale from 1 to 5. The sum of the ratings given to each criterion was then divided by the sum of the total ratings for all criteria, ensuring that the sum of the weights for all criteria was equal to 1. This approach provided a normalised basis for comparisons and decision-making, guaranteeing an objective assessment of the criteria.

TOPSIS

The Preference Similarity to Ideal Situation (TOPSIS) method is a technique that can be used to find the optimal solution that is most closely related to the preferred choice. In this method, the approach uses numerical values of predefined criteria. The TOPSIS analysis consists of a sequence of five processes carried out one after the other. The algorithm can be used to identify the solution that is most similar to the ideal solution (Fig. 1.5).

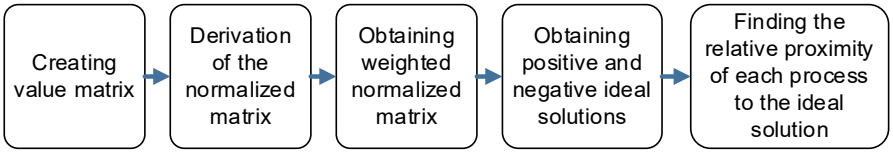


Fig. 1.5. Workflow of the TOPSIS method.

Initial steps include creating a matrix of values. A set of criteria is selected for it. Once the matrix of values has been created, a normalised matrix is created by dividing each value by the sum of all square roots associated with that criterion. This is done using Equation (1.10):

$$r_{ai} = \frac{x_{ai}}{\sqrt{\sum_{a=1}^{n} x_{ai}^2}}, \tag{1.10}$$

where

r_{ai} – normalised value;

x_{ai} – indicator value;

i – criterion;

a – alternative.

The normalised matrix values are then used to construct the weighted normalised matrix. To obtain the weighted normalised matrix values, each normalised value is multiplied by a weight value to obtain the desired results. It is imperative that the overall weighting value is consistent across all criteria. In the TOPSIS multi-criteria analysis normalisation approach, each criterion is assigned a weight. Once the normalised weighted matrix is obtained, the solutions that are considered ideal and ideal in the opposite direction are identified. To do this, the maximum and minimum values are extracted from the previously obtained normalised weighted values. The largest numerical value from the weighted normalised matrix was considered as the positive ideal value. The minimum numerical value was considered as the negative ideal value.

The distance between the numerical value of each alternative and the ideal solution, which is positive, and the ideal solution, which is negative, is then calculated. Equation (1.11) was used to determine the distance to the ideal solution, which is positive, and Equation (1.12) was used to determine the distance to the ideal solution, which is negative.

$$d_a^+ = \sqrt{\sum (v_i^+ - v_{ai})^2} \tag{1.11}$$

$$d_a^- = \sqrt{\sum (v_i^- - v_{ai})^2}\,, \tag{1.12}$$

where

d_a^+ – distance to the positive ideal solution;

d_a^- – distance to the negative ideal solution;

v_i^+ – positive ideal value;

v_i^- – negative ideal value;

v_{ai} – weighted value.

To calculate the relative proximity coefficient based on the distances obtained from the positive and negative values, Equation (1.13) is used:

$$C_a = \frac{d_a^-}{d_a^+ + d_a^-}, \tag{1.13}$$

where C_a is the relative proximity coefficient.

The value of the relative proximity coefficient can range from zero to one, with a higher value indicating a more favourable alternative that could be considered more sustainable. The resulting values are then used to determine both positive and negative ideal values, which are then applied

to derive the relative proximity coefficient. This process is repeated until the values are fully characterised. An illustration of the relative closeness coefficient is provided in the form of a graph to simplify the verification of the results. The results are then compared to decide which alternative is more environmentally friendly.

SENSITIVITY ANALYSIS

After the TOPSIS multi-criteria analysis, a sensitivity analysis was carried out to check the stability of the criteria. The sensitivity analysis shows to what extent the performance of each alternative in TOPSIS changes in response to variations in the weight of the criterion. A matrix was created for each criterion to show the relative closeness of each alternative as the weight changes. As required, the total weight of all criteria must be equal to one. This means that if the weighting of one criterion is changed, the remaining weighting value will be evenly distributed among the nine criteria that are still valid. The weighted value of each criterion increased progressively from 0.1 to 0.9 by 0.1 units. Equation (1.14) was used to determine the weighting of the remaining criteria. In this equation, the value of each criterion was subtracted from one and then divided by ten, which was the total number of criteria. The remaining weighted value was thus divided equally between all criteria.

$$w = \frac{1-w_0}{10}, \tag{1.14}$$

where w is the weighting of each remaining criterion, and w_0 is the weight of the sensitivity analysis criterion.

Once the sensitivity analysis is complete, graph curves are generated using the updated matrix for each criterion. The purpose of these graphs is to illustrate how the order of alternative outcomes changes as a result of changes in the weights of the criteria. According to the conclusions of the sensitivity analysis, the most appropriate outcome has the highest number of upward-sloping curves and responds positively to changes in the criteria. To obtain the result, the number of downward curves for each option was subtracted from the number of upward curves for each option.

2. RESULTS AND DISCUSSION

Preparation of ash filter material

In the Thesis, two filter materials made from industrial waste were selected for the experimental tests of biomethanation: a filter material made from wood chip ash and a filter material made from waste glass. Filter materials from waste glass – glass foam and materials for comparison – were already proposed, but it was necessary to develop a vulcanised ash material. Ash from the combustion of straw and wood chips was used to prepare the samples. A series of experiments were carried out under laboratory conditions to investigate the correlation between the chemical composition of the ash and its melting point.

Based on the results of the melting test, wood-straw ash samples of different proportions were created and tested at temperatures ranging from 1200 °C to 1250 °C. It was observed that at relatively low temperatures of 1210–1220 °C it is possible to obtain suitable filter material samples from 100 % woodchip combustion ash that do not collapse and retain their shape, therefore aggregates made from woodchip ash without straw ash were used for further tests. This decision was taken because industrially, it may be easier to process the ash from a single feedstock, which is more widely available, into filter media, as this would not require the addition of additional feedstock, and straw ash is less available as waste than woodchip ash. Pre-treatment processes for the preparation of vulcanised ash material were also compared. Based on the results, a material with one or two pre-treatments cooked at 1220 °C was selected for further biomethanation experiments.

Physicochemical characterisation of filter materials

The results of the tests carried out on the physio-chemical properties of the filter material samples are summarised in Table 2.1. Of the calculated edge, expanded clay (EC) shows the highest specific surface area, while the filter material sieved ash beads (CA) shows the lowest.

From the calculated results, EC shows the largest specific surface area, while CA shows the smallest. Although the porosity of the exterior is taken into account when estimating the specific surface area, the porosity or surface roughness of the material in the exterior must be taken into account as it can still have a significant effect on the estimation result. In this case, the contact area of the micro-organisms with the gas available in the bioreactor is increased, and this would ensure a more efficient methane production process. When comparing the specific surface area between materials already used in spray biofilter reactor tests, the two newly developed VAM filter materials in this study are optimal but not competitive enough. However, the surface area of the other filter materials tested is similar, e.g. EC and polyurethane foam (PUF) can range from 250–580 m^2/m^3.

Table 2.1

Physico-Chemical Properties of Filter Materials

Filter material	Specific surface area, m^2/m^3	Bulk density, kg/m^3	Water retention capacity, %	External porosity, %	pH
FA sieved and homogenised ash beads	120.9	607.5	31.3	51	10.7
CA sieved ash beads	107.4	460.8	33.7	52	11.8
EC expanded clay	242.5	292.8	11.8	50	7.6
GF glass foam	200.9	175.2	13.8	55	7.2
PUF polyurethane foam	350.4	12.2	9.6	79	7.0

One way to improve the surface area of filter materials is to increase porosity and pore size. When wood ash samples are vulcanised, the pore formation is enhanced by the release of CO_2 and other gases, increasing the porosity and pore size of the material. When porous materials are formed, it is possible to increase their porosity by adding blowing agents to the material. These may be synthetic or naturally occurring surfactants. Their purpose is to reduce the surface tension of the material or the substances released by chemical reactions. The pore size of the filter material also plays an important role in biomethanation reactors. Sufficiently large pores in the material serve as a refuge for methanogenic microorganisms, thus protecting them from the effects of flow or shear forces during mixing. However, pores that are too small can become clogged with micro-organisms during biofilm growth, while pores that are too large can reduce the density of the filter material, thereby reducing its mechanical strength.

Another way to improve surface area is to design samples of smaller material sizes or diameters. However, it is important to be careful as particles that are too small can create resistance to the gas flow and this can result in a pressure drop in the bioreactor. This results in higher energy consumption, as the gas pump in the reactor needs to be operated more.

The external porosity of a filter material describes the presence of openings, pores on the surface of the material. This characteristic refers to the distribution and quantity of pores localised directly in the surface layer of the material rather than in its internal structure. External porosity is important because it can affect the interaction of the filter material with the environment, including the adsorption of gases or liquids. It is the void fraction of the filter media that allows gas to flow into the reactor. The more space for gas to flow into the reactor, the lower the resistance to this flow and the lower the pressure drop it can cause in the reactor. Porosity also affects the flow of liquids, not only the flow of gases in spray biofilter reactors.

Of the materials tested, the highest bulk density was observed for VAM compared to the other filter materials. The density of a filter material is mainly determined by its composition, as inorganic materials are often denser than organic materials. The density also depends to a large extent on the shape of the particles, which for ash beads is circular. Aggregates of this shape tend to be more evenly distributed in the container than particles of irregularly shaped filter material.

For both ash filter materials, the densities of CA and FA are indicative of smaller pore sizes and lower porosity than for other materials but are also indicative of the higher mechanical strength of the material. This indicates that the filter materials will not compact during operation and will not reduce the surface area required for gas conversion. In this case, filter materials with higher bulk densities do not need to be fixed in the reactors, as the density of the filter material must be high enough to prevent it from floating on top of the liquid in the reactor.

Among the filter materials tested, CA and FA have the highest water retention capacity, followed by GF, EC and PUF. Water retention capacity can have both positive and negative effects on methanation efficiency in a bioreactor. The advantage of a high water holding capacity is that it allows a higher total volume of liquid to be loaded into the reactor, which, in turn, increases the total number of cells present in the biofilm. This, in turn, leads to a higher methane production rate. Materials with a higher liquid retention capacity require less liquid, which reduces the amount of energy needed to run the pump. Disadvantages of higher water retention include the pressure drop caused by flow resistance and the excessive biomass accumulation associated with it.

An important characteristic of filter matrices is their effect on the pH of the environment in the reactor. CA and FA exhibit a significantly higher pH compared to other filter materials, which have a pH close to neutral. The pH of the environment can have a significant effect on the viability and activity of methanogenic microorganisms in the bioreactor. Microorganisms are able to proliferate and maintain their metabolic activity unchanged if they are exposed to specific pH values that are ideal for them. In addition, the pH of the filter material can influence the presence and quantity of unfavourable and or inhibitory compounds in the bioreactor.

Biomethanation test results

BIOMETHANE POTENTIAL

The biochemical methane potential (BMP) of a sample is the maximum amount of CH_4 that can be extracted from a given substrate. The method used to calculate the amount of CH_4 removed is based on substrate suitability and quality tests, which indicate the BMP of the sample. In the BPM experiment carried out in the study, all reactors were supplied with identical amounts of the same substrate and inoculum of biogas digestate so that only the type of filter material placed in the reactor differed. This allows a comparison to be made to see if there is an overall higher amount of methane recovered from the reactors depending on the filter media added. BMP testing is a common and well-developed method that can give an indication of the best biomethanation solutions.

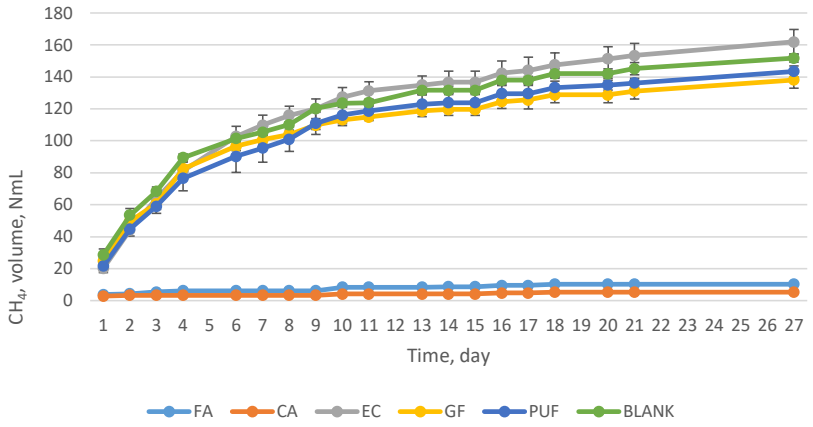


Fig. 2.1. Average methane production and standard deviation for five different material samples and controls:
FA – sieved and homogenised ash beads; CA – sieved ash beads; EC – expanded clay; GF – glass foam; PUF – polyurethane foam; and BLANK – control.

In the BMP experiment, the methane production values were similar for the three filter materials EC, GF and PUF (Fig. 2.1). These values were standardised under normal conditions, at a pressure of 1 atm and a temperature of 273.15 degrees Kelvin. It can be seen that the BLANK control reactors, which did not contain any filter material at all, produce similar results, which are not significantly different from the EC, GF and PUF filter materials. Only the reactors with ash filter materials, CA and FA, show significantly different results, with virtually no methane produced, as shown by the curves in the graph.

The results of the BMP test showed that the reactors with clay as filter material produced the highest amount of methane. Expanded clay had the highest specific surface area of the other filter materials and one of the lowest water retention capacities, but the reactors with clay filter material had the lowest external porosity and the highest methane production. In physicochemical tests, expanded clay showed the highest specific surface area, one of the lowest water retention capacities and the lowest external porosity. These results suggest that the high specific surface area of expanded clay may have contributed to the higher methane formation in this test. For the other filter materials, the maximum amount of CH_4 produced decreases in the following order EC > BLANK > PUF > GF > FA > CA.

No direct correlation with physico-chemical parameters can be observed between the first three materials (excluding control reactors). Due to the fact that the BMP test was developed specifically for quality control of substrates, it can be used to quickly and easily determine whether or not a substrate is acceptable for a given culture of microorganisms and to determine whether or not a substrate is capable of producing CH_4. In these reactors, the substrate is broken down into smaller

organic molecules until methane is produced by the metabolic processes of the microorganisms. The BMP test is a valuable tool for assessing the potential methane production of different substrates in anaerobic digestion processes and can help to optimise biogas production and improve overall process efficiency.

As the control reactors without filter material had higher methane yields than the reactors with glass foam and polyurethane foam, it can be concluded that filter materials do not affect the methane production efficiency of the reactors installed in the BMP test. However, it can be seen that the two materials with the highest pH showed significantly different results compared to the other materials. The alkaline environment could affect the viability and growth of the methanogenic microorganisms present in the digestate, as the optimum pH range for their growth is, on average, between 6.8 and 7.2. Due to the high pH, the micro-organisms could not successfully catalyse methane production under such conditions.

MAXIMUM SPECIFIC VOLUME OF METHANE PRODUCED FOR DIFFERENT FILTER MATERIALS IN A MANOMETRIC TEST

Stage 1. Biofilm development

After the experiment was set up, the first part of the test began when the biofilm started to grow and develop in the reactor. A biofilm is considered mature when the pressure drop or the amount of methane produced reaches a maximum within one day. In the experiment, each filter material initially reached its maximum pressure drop on different days: expanded clay on day four and glass foam and polyurethane foam on day 7. These results are also important as they indicate how quickly the bioreactor should be prepared before it reaches maximum efficiency. Later, when the reactors were refilled with gas, the rate of maximum pressure drop became the same for EC, GF and PUF, and after 18 days it was possible to start the second stage of the test.

The EC control bottles showed a pressure drop which, among other factors, could be due to the solubility of gases in the liquid or excessive compaction of the material. The solubility of gases in a liquid depends on many different conditions: temperature, pressure, polarity and molecular weight of the gases, salinity of the liquid, pH, effect of mixing and surface area of the liquid available. Of the injected gases, CO_2 has a much higher solubility in water. The incubation temperature, pressure, gases used and stirring were the same in all reactors. No differences could have occurred even if the salinity of the liquid had been affected by the expanded clay pellets since the solubility of CO_2 decreases with increasing salinity. The main influence on solubility in such a case would be pH and surface area. Physio-chemical tests showed that expanded clay has the largest surface area, which means a larger surface area of water available in which to dissolve CO_2, reducing the number of gas moles in the reactor and thus the pressure. At the end of the experiment, the pH of the liquid was measured, which showed that the environment in the clay control reactors was indeed more acidic (5.41) than in the other reactors (8.27), indicating a higher amount of dissolved CO_2. The compaction of the material could also cause a further pressure drop. Compaction of the material reduces the volume of void space through which liquid and gas can

flow, thereby increasing the flow resistance and causing a pressure drop in the reactor. This factor should only be determined in continuous reactors by measuring the inlet and outlet flow pressures. The compaction of the material also affects the amount of energy required to maintain the flow in the reactor.

Stage 2. Testing

After the maximum pressure drop in the reactors was reached within 24 h, Stage 2 of the experiment was started. The pressure drop was measured more frequently every few hours during the day. The last measurement was taken 24 hours after the start of the second phase.

The pressure drop changes obtained in this experimental step are shown in Fig. 2.2, where the pressure drop profile is plotted. From the pressure drop profile it can already be seen in which bioreactors metagenesis is more active. The specific methane production in the reactors was calculated from the Sabotier stoichiometric equation and is shown in Fig. 2.3. By comparing the highest methane production at the end of the second stage or the minimum pressure reached 24 hours after gas injection, it is possible to analyse the total methane production potential of each filter material.

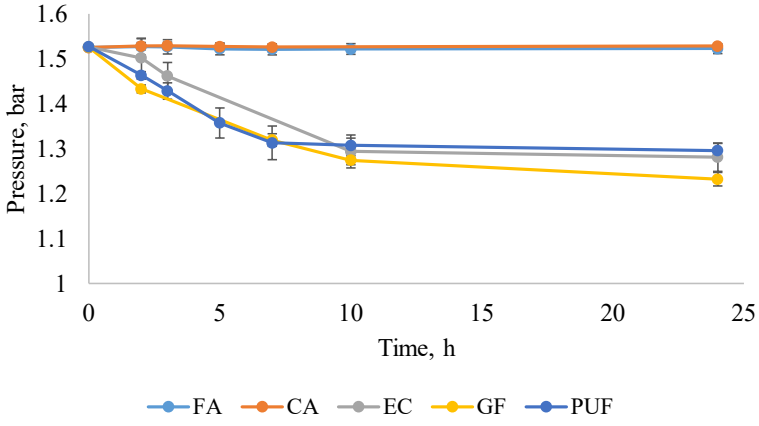


Fig. 2.2. Pressure drop in 100 mL bioreactors during 24 h:
FA – sieved and homogenised ash beads; CA – sieved ash beads; EC – expanded clay; GF – glass foam; PUF – polyurethane foam.

In the manometric test, the bioreactors with glass foam filter media produced the most methane, while the bioreactors with vulcanised ash filter media produced the least. The maximum methane production decreased between filter materials in the following order GF > EC > PUF > FA > CA.

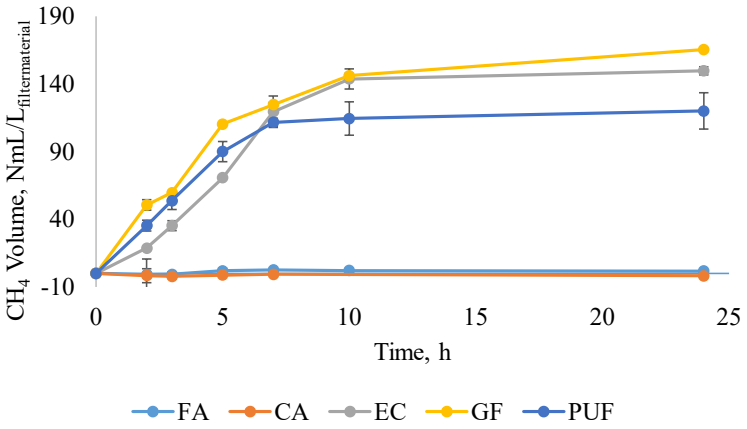


Fig. 2.3. Calculated cumulative biomethane production in 100 mL bioreactors over 24 h: FA – sieved and homogenised ash beads; CA – sieved ash beads; EC – expanded clay; GF – glass foam; PUF – polyurethane foam.

The results of the manometric test are consistent with the water retention capacity of the materials used, with the exception of CA and FA, which were made from wood ash. According to the above conclusion, the reason why the reactors using fly ash materials did not produce methane to the same extent as in the BMP test is the effect of the chemical properties of the material on the population of microorganisms present. The fact that the water holding capacity seems to correlate with the manometric test results provides an explanation for the different results obtained in the BMP test. In contrast, the reactors used in the BMP test contained a solid substrate, whereas the reactors used in the manometric test contained a gas as substrate. The amount of water remaining on the filter material after the flow is stopped is determined by the water retention capacity. This results in a surface that allows mass transfer between the gas and the liquid. In the BMP tests, as the filter material was submerged, the gas-liquid interface surface was formed only by the upper liquid layer, which remained at the top of the reactor. The manometric test resulted in a significantly larger liquid-gas interface surface, which could account for the higher level of methanogenesis activity than in the BMP test. This difference in interface surface is probably the main contributing factor to the different results between the two tests, indicating that the structure of the filter material and the interface conditions have a significant influence on the activity of microorganisms and gas exchange.

In a similar study, a bioreactor with a polyurethane packing had the highest methane yield, while clay-packed bioreactors produced the least methane. However, it is not possible to infer the reasons for the differences as the physicochemical properties of the materials in the other study are unknown. The manometric method is more suitable for testing filter materials in a biotrickling filter reactor in the context of biomethanation, as it uses a gas as a substrate that is compatible with

the technology. Comparatively, the presence of filter material did not significantly affect the methanogen efficiency in the BMP test, as control bioreactors without filter material had similar methane yields.

Biomethanation in elevated pH media with monocultures and biogas digestate

After the initial manometric tests on biomethanation, the decision was taken to re-test the filter materials, this time with a particular focus on the role of microorganisms in biomethanation efficiency and using larger bioreactors to reduce the measurement error when the rubber caps were punctured. The experiment was divided into two parts. In the first part, biogas digestate was used as the inoculum, as it contains different species of microorganisms involved in all four steps of anaerobic digestion and biogas digestate is often used in other research studies. The diversity of microorganisms in the digestate increases their adaptability to different conditions, as they are already adapted to the biogas production process.

The second part of the experiment used monocultures of *Methanobacterium* sp. that had been previously propagated in a strict anaerobic environment using an H_2/CO_2 gas mixture. *Methanobacterium alcaliphilum* strains have not previously been studied in this context. The ability of these microorganisms to grow at high pH offers the potential for their use in biomethanation with VAM materials, which so far in experiments have not shown good results with digestate. The microorganisms in the digestate can provide a wider range of metabolic pathways, which in turn can contribute to more efficient biogas production. At the same time, the use of a monoculture of *Methanobacterium* sp. allows more precise control of the fermentation process, allowing a more detailed evaluation of the effect of specific microorganisms on the efficiency of biomethanation, especially in combination with different filter materials. These results provide a better understanding of the role of microorganisms and filter materials in biomethanation. *Methanobacterium* sp. microorganisms are characterised by their ability to withstand high pH levels and to thrive even under highly alkaline conditions. These bacterial communities are dominated by hydrogenotrophic methanogenesis, which becomes the main form of methanogenesis at pH values above 9. These microorganisms are not only able to adapt to significantly high pH levels but are also able to survive for long periods in such alkaline environments. The use of such monocultures in high pH tolerant research broadens the understanding of their potential applications in the context of biomethanation as well as in various other fields.

BIOGAS DIGESTATE

The pressure drop changes obtained in this experimental step are shown in Fig. 2.4., where the pressure drop profile is plotted. From the pressure drop profile, it can already be seen in which bioreactors methanogenesis is more active. The specific methane production in the reactors was

calculated from the Sabatier stoichiometric equation and is shown in Fig. 2.5. The results with digestate as inoculum showed that in the bioreactors, significantly better results could be observed in the samples where glass foam and edge-expanded clay were used as filter materials. The graph (Fig. 2.4.) shows the pressure variation during the second phase of the manometric test, where it can be seen that the VAM did not show a large pressure drop, similar to previous experiments where ash filters were used.

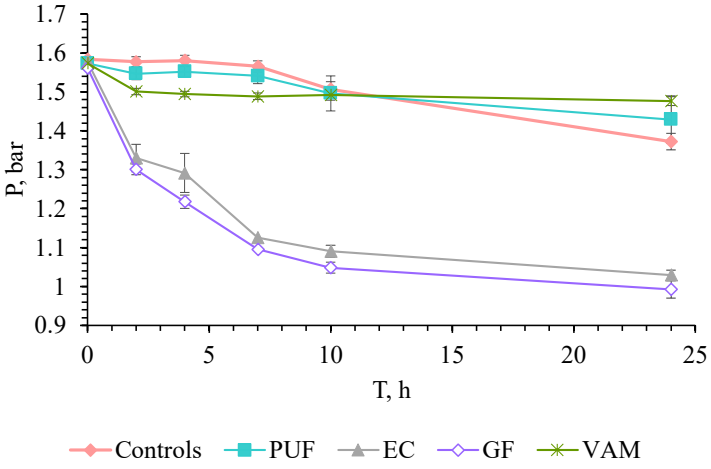


Fig. 2.4. Pressure drop in 250 mL bioreactors with digestate:
Control – no material; PUF – polyurethane foam; EC – expanded clay; GF – glass foam; VAM – vulcanised ash material.

Comparison of the control bioreactors without filter material and with EC and GF materials shows that in their presence the pressure gradients are significantly higher than in the control bioreactors without filter material. This indicates that EC and GF contribute significantly to the efficiency of biomethanation in *ex-situ* sputtered biofilter reactors.

The cumulative amount of CH_4 in the bioreactors was calculated by stoichiometric calculations and showed that the highest volume of methane was obtained in the bioreactors with GF and EC materials. Their results at the end of the experiment were very similar, only the results of the first wells differed, with the EC material undergoing methanogenesis at a slightly slower rate than the GF material reactors (Fig. 2.5). The next highest biomethane content is calculated for reactors without filter material. However, it was three orders of magnitude lower than in the samples with EC and GF.

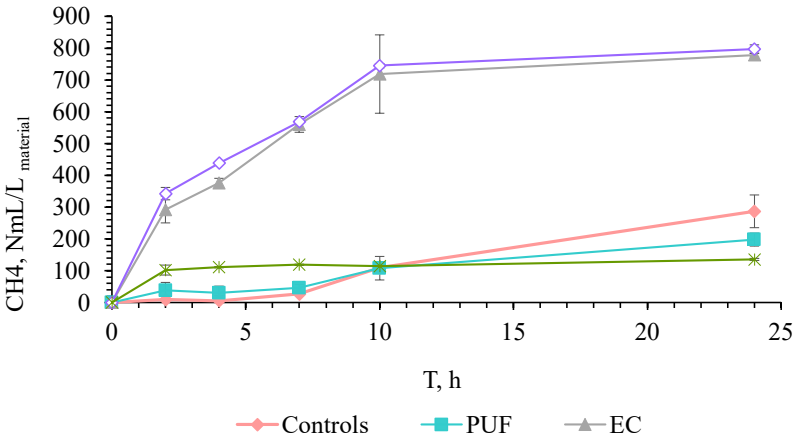


Fig. 2.5. Calculated specific volume of CH_4 produced in 250 mL reactors with digestate: Control – no material; PUF – polyurethane foam; EC – expanded clay; GF – glass foam; VAM – vulcanised ash material. Error bars – standard deviation. Maximum methane production decreased between GF > EC > Control > PUF > VAM filter materials.

The lowest calculated methane results were found in the bioreactors with VAM material, similar to the experiments carried out so far. This is due to the high pH of the medium in the reactors, which hinders the growth of microorganisms in them. The estimated cumulative methane produced in the reactors decreased between the GF > EC > Control > PUF > VAM filter materials.

METHANOBACTERIUM ALCALIPHILUM STRAINS

In the second part of the experiment, two strains of *Methanobacterium alcaliphilum* were used with the idea that their ability to adapt to alkaline environments would provide insights into the use of VAM filter material in biomethanation. In the first stage of the manometric test, where the biofilm and the microorganism reactor were set up and multiplied to the maximum, it was already concluded that the results would be lower because the feeding stage took 40 days, which was twice as long as using biogas digestate. Even then, the maximum pressure drop was not as great as with digestate. The decision was taken to start the second stage in the manometric test to compare at least the effect of filter materials on methanogenesis using *Methanobacterium alcaliphilum* strains. As there were already large differences between digestate and monocultures in the first phase, it is clear that they do not compete with each other and that the use of digestate is a more efficient solution.

In the second phase of the test, when the measurements started within 24 h, it can be seen that there was a similar pressure drop in all reactors, including the reactors without material, but generally small. After stoichiometric calculations, the cumulative amount of CH_4 in the bioreactors

was calculated and showed that the highest average amount of methane was obtained in all bioreactors with VAM, EC, GF materials and in the control bioreactors (Fig. 2.6).

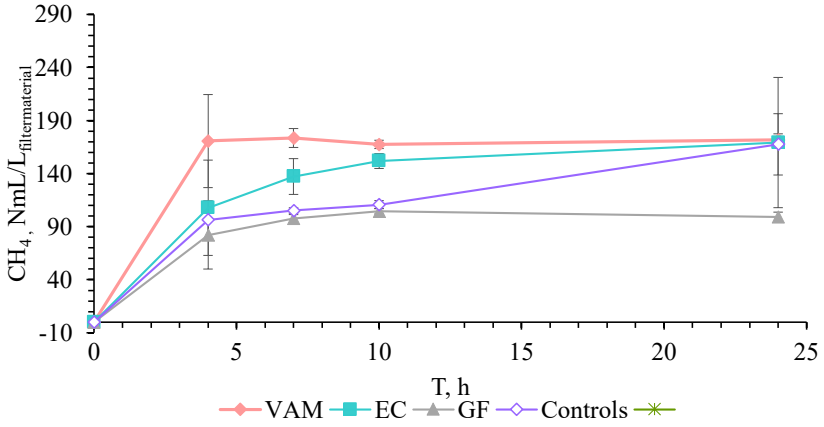


Fig. 2.6. Calculated specific volume of CH_4 produced in 250 mL reactors with digestate: Control – no material; EC – expanded clay; GF – glass foam; VAM – vulcanised ash material.

Note that the smaller the amount of methane produced, the greater the potential measurement error in the manometric test. This is due to the fact that at higher pressures, a higher gas separation is possible at the time of measurement. However, it is already possible to see, indicatively, whether the reaction is actively taking place in the bioreactor or not.

Validation of results

In order to validate the results calculated in the *ex-situ* biomethanation experiment of the manometric test, the final product gas samples obtained were tested by gas chromatography to determine their chemical composition. The gas chromatograph allows the analysis of the composition of H_2, N_2, CO, CH_4 and CO_2 in the samples. The results of the analyses of the samples using biogas digestate as inoculum showed the highest methane yield in the reactors with EC and GF filter materials. In the transition reactors, the methane content was low; in the VAM reactors, no methane was detected in the gas samples. Samples from reactors with glass foam had the highest average CH_4 of 79.7 %, followed by the next highest average CH_4 of 75.4 % in reactors filled with EC. In this experiment, an atypically low yield of CH_4 was found for the PUF material – 5.65 %, which is almost the same as the control reactors without filter material – 5.3 % (Fig. 2.7). The amount of H_2 in the reactors with the highest amount of CH_4 is the lowest, indicating that the microorganisms have used it. In the samples with low CH_4 concentrations, there was a significant amount of unused H_2. If PUF showed the best results in the previous few experiments, this result could be an exception. The viability of the microorganisms could have been influenced by growth

conditions, nutrient levels. As the feeding phase is not the same between different materials, the death of microorganisms during this phase could have occurred between the times of feeding the gas mixture. If microorganisms have proliferated in the bioreactor in large numbers, they need additional nutrients.

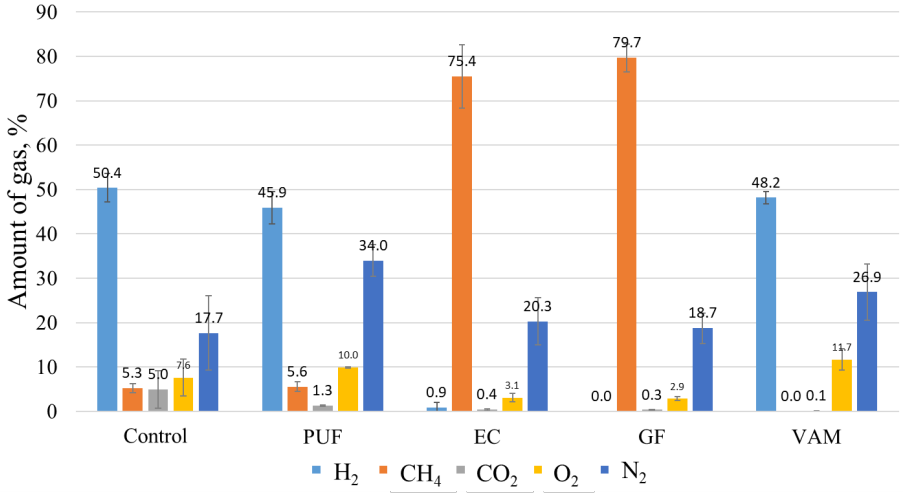


Fig.2.7. Chemical composition of gas samples in which biogas digestate was used:
PUF – polyurethane foam; EC – expanded clay; GF – glass foam; VAM – vulcanised ash material.

Gas analyses of the *Methanobacterium alcaliphilum* monocultures showed a slight presence of methane in the materials (Fig. 2.8).

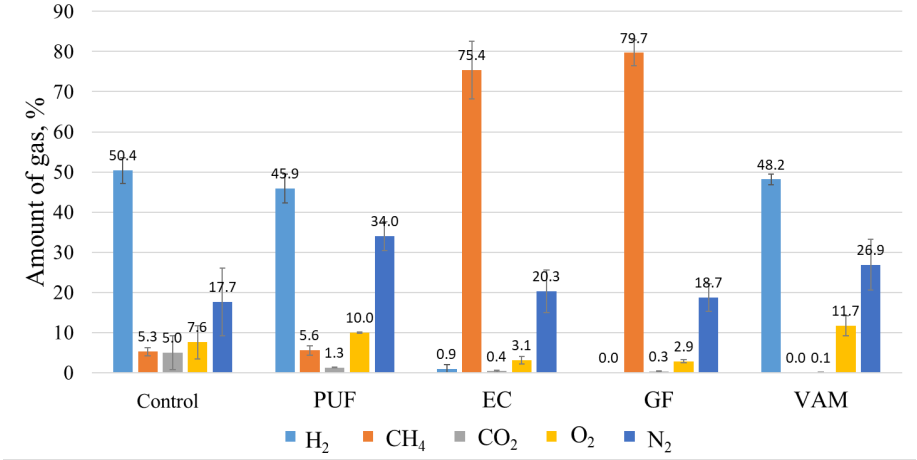


Fig. 2.8. Gas composition of the samples using *Methanobacterium alcaliphilum* monoculture.
PUF – polyurethane foam; EC – expanded clay; GF – glass foam; VAM – vulcanised ash material.

The highest amount of CH_4 was found in the GF material at 18.56 %, the second highest amount of CH_4 was found in the PUF material – 10.43 %, and the lowest amount was found in the reactors with EC material – 0.29 %. No CH_4 was detected in the control reactor. It can be seen from the H_2 in the samples that the gases have not reacted. The amount of CO_2 is low in all samples, indicating that it might have dissolved in the liquid medium.

Comparing the gas composition in this test alone, it can be seen that the reactors inoculated with *Methanobacterium alcaliphilum* monocultures underwent more efficient methanogenesis than the control reactor without material. It can be concluded that the inoculation of *Methanobacterium alcaliphilum* monocultures with filter material contributes to the efficiency of methane production.

In order to determine the relationship between the calculated and the analysed CH_4 fractions in the experiment with digestate as inoculum, a regression analysis of the data was performed after experiments and chromatography. The result of the analysis was a correlation between the estimated and determined amounts of CH_4 in the samples. Based on the regression analysis, which resulted in a coefficient of determination of 0.92, it can be concluded that there is a very strong linear relationship between the estimated and the determined amounts of CH_4 in the analyses. This means that about 92 % of the variation in methane abundance (x) in the samples can be explained by the calculated CH_4 abundance (y). The calculated CH_4 abundances accurately predict the actual methane abundances, indicating high model reliability and fit. The regression model shows a linear relationship, indicating that it fits the observed data points well. The difference between the measured and predicted data is shown in the graph in Fig. 2.9.

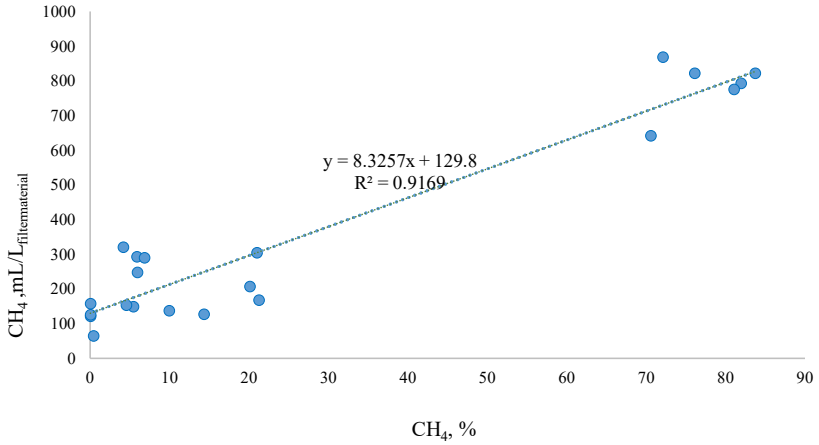


Fig. 2.9. Relationship between the calculated amount of CH_4 (mL/L $_{material}$) and the determined amount of CH_4 (%) for the digestate samples.

In order to determine the relationship between the calculated and analysed CH_4 fractions in the experiment with monocultures as inoculum, a regression analysis was also performed on the data

after experiments and chromatography. As can be seen in Fig. 3.12, a linear relationship was obtained, and the coefficient of determination is 0.64. This is lower than that between the data obtained from the experiment with digestate. These results are due to the fact that the numerical values obtained from the pressure measurements are lower and more imprecise due to the possibility of a higher measurement error.

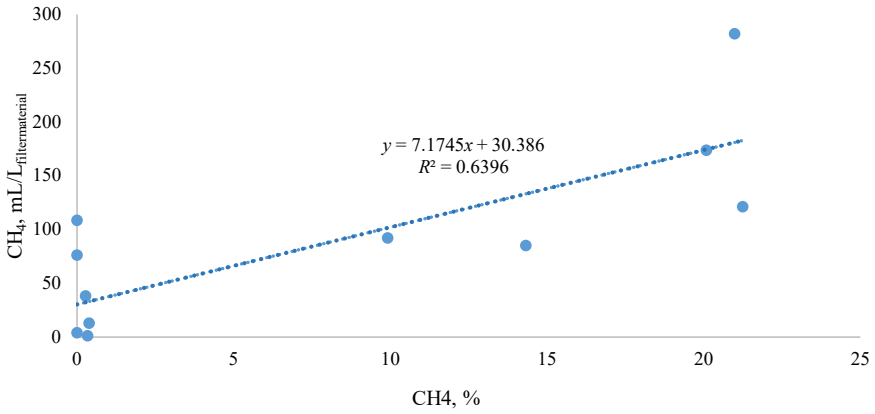


Fig. 3.12. Relationship between the calculated amount of CH_4 (mL/L $_{material}$) and the determined amount of CH_4 (%) for samples using monocultures.

This may be due to the higher measurement uncertainty, especially when the samples contained less methane. To improve the reliability of the model, it would be necessary to extend the data set, improve the accuracy of the measurements and perform additional analyses. However, in both cases, with both digestate and monocultures, the relationship is linear, which confirms the reliability of the model and confirms that the manometric test is suitable to determine methanogenesis activity in this type of reactors set up under laboratory conditions. This opens up a wider range of possibilities for other studies under similar conditions. It is possible to test the suitability of filter materials in small bioreactors without the need to invest heavily in industrial tests in biomethane plants.

Results of the multi-criteria decision analysis

CRITERIA WEIGHTS

The survey results were aggregated and analysed to determine the weights of each criterion, reflecting the relative importance of each selected criterion in the study. The results are summarised and presented in Table 2.2. A questionnaire was used to calculate the weight of each criterion. Participants were asked to rate the importance of a number of criteria, and the results

were used to determine the weight of each criterion. The ratings were then normalised so that the total weight of all criteria was equal to 1.

Table 2.2

Criteria Weights

Criterion number	Criterion	Unit	Weight
C1	Average biomethane yield	$NmL/L_{material}$	0.125
C2	Water retention	%	0.084
C3	Energy required to produce the material	°C	0.102
C4	Raw material costs	EUR m^{-3}	0.112
C5	Availability of material	t/year	0.101
C6	Material origin	Points 0–1	0.091
C7	pH	0-14	0.099
C8	External porosity	%	0.099
C9	Volume density	kg m^{-3}	0.081
C10	Specific surface area	m^2 m^{-3}	0.105

The results of the questionnaire were aggregated and analysed to calculate the weights of each criterion, which represent their relative importance in the research. These results are summarised and presented in Table 2.2. The weight of each criterion was determined using a questionnaire method in which participants were asked to rate the importance of different criteria. The scores were then normalised so that the sum of the weights of all criteria was equal to 1, thus ensuring that each criterion was proportionally represented in the overall score. The average biomethane yield was given the highest weight of 0.125, thus highlighting its importance in determining the overall yield of the material.

TOPSIS RESULTS

The results of the TOPSIS multi-criteria analysis calculations carried out to assess the materials for biomethanation are shown in Fig. 2.10. Based on the values of the relative closeness coefficient shown in Fig. 3.9, it is clear that the expanded clay pallets and the polyurethane foam are closest to the ideal result. Of all the alternatives analysed, a coefficient of 0.57 was calculated for expanded clay pallets, indicating their best suitability as a filter material for the biomethanation process, taking into account the criteria set out in the study. It is important to note that the relative proximity coefficients are also similar for two other materials, polyurethane foam and glass foam. Polyurethane foam differs from expanded clay pallets by only 0.03, while glass foam is in third place, with a coefficient difference of 0.07 compared to expanded clay pellets.

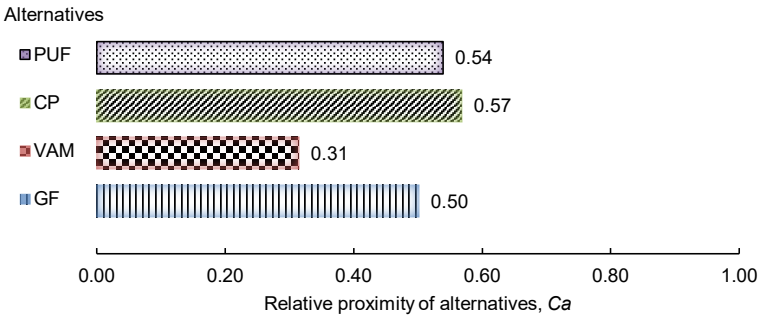


Fig. 2.10. Results of the TOPSIS analysis.
The coefficient of relative closeness ranges from zero to one, with a higher value indicating a more favourable alternative. PUF – polyurethane foam; CP – expanded clay; VAM – vulcanised ash material; GF – glass foam.

These results indicate that all three alternatives – expanded clay pellets, polyurethane foam and glass foam – are close to the ideal solution, which means that these materials can demonstrate good performance as a biomethanation carrier material under *ex-situ* conditions.

However, it should be noted that the values obtained for glass foam and expanded clay granules are very close to those of polyurethane foam, suggesting that the hierarchy of sustainability assessment of materials may change as production methods and technologies for these materials evolve.

CRITERIA SENSITIVITY ANALYSIS

To ensure greater accuracy of the study's conclusions, a comprehensive sensitivity analysis was carried out, covering all criteria in each of the categories of aspects studied. This analysis enabled a precise assessment of the impact of each criterion on the final results of the study. Using different weighting scenarios, the most relevant parameters that had the greatest impact on the outcome were identified. This thorough approach significantly improved the robustness and reliability of the conclusions and deepened the understanding of the results. Figure 2.11 illustrates an example showing the changes that occur as the weight of the criteria changes from 0.1 to 0.9 by 0.1. Figure 2.11 shows the effect on the results of changing the weight of the biomethane extraction criterion. Although the relative changes in the proximity coefficients are different between the different alternatives, in the case of glass foam, the results show an increase in the criterion, suggesting that glass foam may be a suitable choice for biomethanation processes in this case.

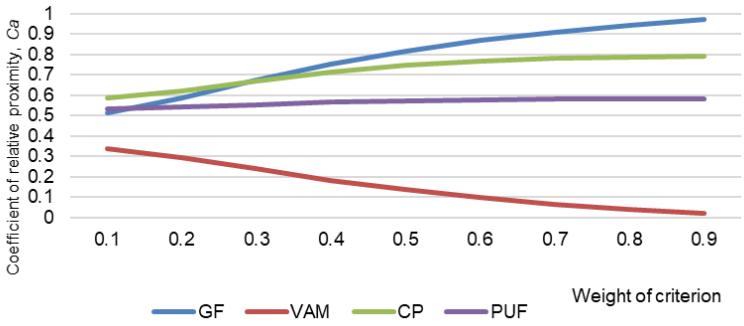


Fig. 2.11. C1 – variation of results with biomethane yield weight from 0.1 to 0.9 by 0.1.

As the weight of the raw material cost criterion increases, the value of the coefficient for expanded clay pellets decreases sharply. However, increasing the weight of the material availability criterion decreases the relative proximity coefficients of all alternatives except expanded clay pellets. Decreasing the weight of the energy required to produce the material decreases the value of the coefficients of all alternatives except polyurethane foam. The opposite results if the weight of the material source criterion is increased. The relative proximity coefficients of all alternatives decrease, except for polyurethane foam.

Increasing the weights for pH, external porosity, bulk density and specific surface area increases the value of the polyurethane foam, while the value of the vulcanised ash material decreases dramatically for all these criteria. These technical parameters could be improved for some of these materials under development.

Based on the sensitivity analysis, the optimal outcome shows the highest number of upward slopes and demonstrates a strong ability to adapt to changes in the criteria. The number of positive curves for each option was subtracted from the number of negative curves in graphs. The optimal choice has the highest numerical score. This numerical result shows that the optimal choice is the most flexible and is able to adapt quickly to changes in the weights assigned to the different criteria.

Table 2.3

Results of the Sensitivity Analysis

	Glass foam	**Vulcanised ash material**	**Expanded clay**	**Polyurethane foam**
Number of upward curves	4	1	4	8
Number of downward curves	6	9	6	2
The Difference	–2	–8	–2	6

The results of the sensitivity analysis in Table 2.3 provide valuable insights into the performance of each alternative material. Based on the number of upward curves, polyurethane foam becomes the best choice. This is followed by glass foam and expanded clay, both of which show promising results. However, the vulcanised ash material performs poorly in comparison, indicating that improvements in technical and performance aspects are needed before it can be considered as a viable solution.

According to the values of the relative closeness coefficient, it is clear that expanded clay and polyurethane foam are the most similar to the ideal solution. The CP ratio is 0.57, which makes it the most suitable filter material for biomethanation based on the criteria indicated. The difference between PUF and CF is 0.03, while GF, which ranks third, differs from CP by 0.07. Of the four options chosen, PUF performs most favourably in the sensitivity analysis, demonstrating its robust ability to adapt to changes in the criteria weights. However, GF, made of recycled glass, also shows excellent performance. A number of undesirable properties and factors hinder the use of vulcanised wood ash as a filter material for biomethanation. However, it is currently being developed and can be improved to better meet the requirements of biomethanation technology. It is possible to select the vulcanised wood ash material for biomethanation by improving the specific values. For example, changing the pH value can improve the growth of microorganisms and biomethane production. The addition of blowing agents can change the porosity, increasing the specific surface area. This improves the efficiency of the material. With further research and material development, vulcanised wood ash material also has the potential to become a highly efficient and sustainable solution for biomethanation processes. The development and improvement of innovative materials such as vulcanised wood ash and glass foam make it possible to reuse waste wood ash and waste glass for biomethanation applications.

3. CONCLUSIONS

1. The original hypothesis that filter materials made from ash and glass waste have potential for use in drip bioreactors for biomethanation has been partially confirmed. Glass foam material is a suitable filter material for biomethanation in *ex-situ* bioreactors, but material made from waste ash did not show good results.
2. Studies on the development of biomethanation technologies have shown that the choice of the right filter material is crucial, as it has a direct impact on the immobilisation of microorganisms and the efficiency of methanogenesis in biotrickling filter reactors. In this study, waste derived materials such as glass foam and vulcanised wood ash material were tested, as well as industrially studied and compared materials such as polyurethane foam and expanded clay pellets to determine their suitability for biomethanation.
3. The results show that glass foam is a particularly effective filter material, providing up to 84 % CH_4 content in the final product, confirming its potential to be suitable for biomethanation technologies.
4. The recycling of ash waste is linked to its specific chemical properties. Although the ash aggregates show good physical characteristics, they are alkaline and contain various heavy metals which can leach out when the pH of the environment is reduced and have a negative impact on living organisms. Therefore, the future technology and use objectives for ash waste recycling are not well established. This study has shown that ash filter materials are not yet suitable for methanogenesis either.
5. Glass foam can be considered an innovative filter material that can be used for biomethanation. In addition, glass foam has excellent properties such as high porosity, good thermal insulation and low density, which make it an ideal choice for biotrickling filter reactors. In addition, the innovative quality of glass foam highlights the possibility of creating value from otherwise discarded resources, in line with circular economy ideas. Glass foam is, therefore, a suitable solution for biotrickling filter reactors due to its advantages and positive environmental impact. The use of waste materials in *ex-situ* biomethanation, where they serve as a filter material, not only improves the overall efficiency of the process but also contributes to sustainable practices.
6. A comparison of biogas digestate inoculum and *Methanobacterium alcaliphilum* strains showed that biogas digestate inoculum produced more biomethane than *Methanobacterium alcaliphilum* strains. These results point to the need for further studies on the composition of microorganism cultures, especially in larger reactors where the microorganism communities can have a significant impact on the methanogenesis process.
7. Regardless of the inoculant used (digestate or microorganism monoculture), VAM do not perform well in methanogenesis. In smaller reactors, the accuracy decreases due to gas leakage, which makes the accurate determination of the gas composition difficult and may affect the experimental results.

8. The manometric method is more suitable for testing filter materials in droplet bioreactors because it uses gas as the substrate. The use of gas as a substrate is an important prerequisite, as one of the most important factors affecting the efficiency of methanogenesis is the gas-liquid mass transfer capacity. A manometric test, tested by regression analysis against gas chromatographic analysis, accurately quantified the rate of CH_4 formation by measuring biomethane production.
9. The numerical results of the experiments are not directly comparable to the potential of commercial biomethane production reactors, but they provide valuable information on the effect of filter materials on the efficiency of biomethanation under certain conditions. It is, therefore, essential to describe in detail all the consumables and experimental set-up used to ensure the reproducibility and scalability of the results in commercial production.
10. As part of a systematic decision-making approach, this study uses a multi-criteria decision analysis and a Preferred Order of Similarity to Ideal method to determine which of the selected materials would be a better solution for biotrickling filter reactors used in *ex-situ* biomethanation. According to the values of the relative closeness coefficient, it is clear that expanded clay and polyurethane foam are the most similar to the ideal solution.
11. Optimisation of biomethanation processes can contribute to more efficient biogas production, in particular through the use of sustainable and affordable filter materials. The results of these studies provide additional information that is relevant not only in the field of biomethanation, but also in other sectors where such materials could be useful. Furthermore, they will help researchers and engineers make informed decisions on the choice of filter materials in bioreactor configurations in order to optimise biomethanation processes and contribute to the development of more sustainable production processes.

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