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Packing materials for biotrickling filters used in biogas upgrading – biomethanation

Z. Kusnere*, K. Spalvins, D. Blumberga and I. Veidenbergs

Riga Technical University, Institute of Energy Systems and Environment Azenes street 12/1, LV 1048 Riga, Latvia
*Correspondence: Zane.Kusnere@rtu.lv

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Abstract. One of the promising methods of biogas upgrading is biological methanation (biomethanation). During biomethanation process hydrogenotrophic microorganisms use carbon dioxide from biogas and added hydrogen to generate biomethane. Application of biotrickling filter reactors is one of the prospective biotechnologies for methanation where hydrogenotrophic methanogens are immobilized over a material that is used in reactor. Packing materials for biomethanation are critical in terms of hydrogenotrophic methanogens immobilization on the surface of packing material. It acts as support for biofilm growth. Therefore, characteristics of filter material are important parameters that influence the growth of microorganisms and methane production. Factors, such as optimal specific surface area and porosity are important to sustain growth and activity of microorganisms. Optimal particle size and capability to mechanically resist compaction ensures avoiding high pressure drop. Optimal particle size also ensures uniform gas flow as gases distribute through the packing material. This review paper summarizes and compare the characteristics of different packing materials important for biomethanation through ex-situ biotrickling filter reactor systems.

Key words: biogas upgrading; biomethanation; biotrickling filter; biofilm; packing materials.

INTRODUCTION

Biogas production is an important process for dealing with different types of waste. It is particularly difficult for farms to live without a biogas station. If there were no biogas plants, the surrounding population would have problems with both smell and local environmental. Biogas production is one of the technological components of agriculture. Waste recycling produces heat and energy, as well as digestates (material remaining after anaerobic digestion), which is a much more valuable fertilizer for soil than fossil fertilizers.

Biogas is a product of anaerobic digestion - a renewable fuel which can be produced from different organic waste materials. In raw biogas methane content is about 50–70%, while carbon dioxide content is 30–50% (Baena-Moreno et al., 2019; Witte et al., 2019). Therefore, upgrading biogas by increasing methane concentration is a way to increase its usefulness. Upgraded biogas with methane content up to 96% can be directly added into the grid of natural gas (Dupnock & Deshusses, 2019; Witte et al., 2019). Unlimited biogas injection into the gas grid can be achieved by removing carbon dioxide to acquire biomethane. The main advantage of biological biogas upgrading technologies is conversion of carbon dioxide into high value products under light operational conditions, which significantly promote to a sustainable bio economy and life cycle economy (Angelidaki et al., 2018). One of the promising methods of biogas upgrading is biological methanation (biomethanation). During biomethanation process hydrogenotrophic microorganisms use carbon dioxide from biogas and added hydrogen to generate biomethane. This method of biogas upgrading is energy intensive as it requires hydrogen as a material input (Mehrpooya et al., 2020). To ensure this method is sustainable, the hydrogen for the required reaction should come from a renewable source. Hydrogen can be produced via electrolysis using electricity from off-peak electricity surplus from solar or wind energy power systems (Akhlaghi & Najafpour-Darzi, 2020; Mehrpooya et al., 2020). Although in this system the cost of biomethane is determined of the cost of hydrogen used for biomethanation (Vo et al., 2018). If there is surplus renewable power, it can be utilized for biogas upgrading and make biomethanation as an energy storage solution (De Vrieze et al., 2020). This kind of system is known as 'Power to Gas' concept (Bensmann et al., 2013).

The biological hydrogen methanation using methanogens is possible to be applied in two different systems. First one is in-situ system (Luo & Angelidaki, 2012) where biomethanation is performed within anaerobic digester system. In this process organic matters are transformed into biogas under specific conditions (Holm-Nielsen et al., 2009). Second is an ex-situ system, where a separate external reactor for biomethanation is used (Lecker et al., 2017). Main reaction for the biomethanaion process is known as Sabatier reaction (Eq. 1),

$$CO_2 + 4\cdot H_2 \leftrightarrow CH_4 + 2\cdot H_2O \tag{1}$$

where methane is converted from molecular hydrogen and carbon dioxide (Leonzio 2016). Carbon dioxide is used as a waste gas in this reaction to produce methane. Therefore, raw biogas which contents 30–50% of carbon dioxide can be upgraded to biometane. Methanogens are able to metabolize hydrogen into methane. These microorganisms are called hydrogenotrophic methanogens and they are often already present in anaerobic cultures that carry on the reaction. (Zabranska & Pokorna, 2018).

Various reactor types can be outfitted for ex-situ biomethanation, such as biotrickling filter reactors (Burkhardt et al., 2015; Rachbauer et al., 2016), continuously stirred tank reactors (Thema et al., 2019), fixed bed reactors (Alitalo et al., 2015), biofilm plug-flow reactors (Savvas et al., 2017) and other bioreactors (Dupnock & Deshusses 2019; Germec et al., 2020). There are several advantages for ex-situ systems. Industrial carbon dioxide can be easily added from external sources, if the biomethanation is carried out in ex-situ reactor by hydrogenotrophic methanogenesis. In this system CO_2 can be used in biogas upgrading by conversion into biomethane (Michailos et al., 2020). But in external bioreactor systems only gases (H_2 and CO_2) can be used as substrates and added to fermentation liquid as energy source (I. Bassani et al., 2016). Therefore, efficient gas diffusion systems and different biofilter configurations are important for increasing gas-liquid contact time and enhancing biofilm growth. By increasing biofilm growth more efficient methane production can be achieved (C.L. Bassani et al., 2017).

Application of biotrickling filter reactors is one of the prospective biotechnology for methanation where hydrogenotrophic methanogens are immobilized over a material that is used in reactor (Ashraf et al., 2020). By immobilizing microorganism cells it is possible to increase efficiency of the substrate conversion, shorten retention times and minimalize microbial contaminations. Microorganisms are more protected from shear stress compared to stirring reactors and can be reused. Therefore, the costs of process can be reduced (Sekoai et al., 2018). If cells are not immobilized, microorganisms are prone to washout which causes instability in process and reduces biomethane yield (Kourkoutas et al., 2004). Packing materials and characteristics of the materials within biotrickling filter reactor system play a large role. (Sekoai et al., 2018). Defined characteristics of materials can facilitate bioreactors setup configurations for biomethanation process.

Biological trickling filter reactors

Biological trickling filter (BTF) reactor is the most promising technology for biomethanation, based on recent research studies on the ex-situ biomethanation design (Rachbauer et al., 2016; Strübing et al., 2018; Sieborg et al., 2020). The main and most important reason is that biotrickling filter is equipped with large surface area available to form biofilm and this means that methane production per unit volume is higher than in most other reactor types (Ashraf et al., 2020). In the biotrickling filter packing material supports the biofilm and generally offer more valuable gas to liquid mass transfer. Because of larger surface area of biofilter between liquid and gaseous substrates, low gas and liquid flow rates are maintained. Fermentation liquid can be recirculated to maintain efficient CH_4 production. Liquid biofilm on the packaging materials as well as rate of recirculation has been studied by Burkhardt et al., 2015. Results show that biomethanation of hydrogen and carbon dioxide in biotrickling filter was successful and productive using anaerobic sewage sludge as inoculum (Burkhardt et al., 2015).

Biotrickling filter reactors have been studied in different conditions within biometnanation using hydrogen as energy source. By using trickle bed reactor, biomethane concentration successfully reached more than 98% in the output product (Rachbauer et al., 2016). This type of reactor was also used for syngas biomethanation and was successful at being very productive and having efficient conversion rates (Grimalt-Alemany et al., 2018). Tests are made to research appropriate conditions such as flow rate, pH rate, pressure, gas-liquid mass transfer, duration of reaction (Rachbauer et al., 2016; Porté et al., 2019) and also, best reactor setup for biomethanation efficiency. In the last few years many research works have been published where biotrickle filter reactor technology was used for biomethanation (Dupnock & Deshusses 2019; Porté et al., 2019; Dahl Jønson et al., 2020; Germec et al., 2020), making this one of the most promising novel technology for biogas upgrading. Using biotrickling filters, the energy demand is substantially lower as there is no need for stirring and dispersing liquid phase. Energy is used to pump the fermentation liquid to the top of the filter column where it is sprinkled over the packing material (Thema et al., 2019). The filter consists of packing material and microorganisms - hydrogenotrophic methanogens. Packing material act as support for biofilm growth, therefore characteristics of filter material are important parameters that influence the growth of microorganisms and, therefore, methane production. Packing materials could be examined as one of the main factors of the biotrickling filter reactor systems (Wu et al., 2018). Choosing an effective packing material in a biotrickling filter for hydrogenotrophic methanogens to grow biofilm may be major design variable for the biotrickling filter reactor. However, testing the packing in a continuously operating biotrickling filter reactor is costly both in time and resources (Ashraf et al., 2020).

The main function for packing material in biotrickling filter reactor is to ensure contact between microorganisms and substrate to allow production of high concentration methane (Wu et al., 2018; Maegaard et al., 2019). Surface on packing materials of biofilter is larger for microorganisms to attach. Therefore, using biotrickling filter reactors the speed of the methanation process is significantly increased. Immobilizing microorganisms in biomethane production stabilizes the pH of the medium, prevents microorganism washout and extends microbial activity providing continuous methanation process (Sekoai et al., 2018).

CHARACTERISTICS OF PACKING MATERIALS

Packing materials used as biotrickling filters can normally be classified into three categories: organic, inorganic, and mixed materials. Organic materials, such as soil, peat, and wood chips were being used in biotrickling filters at the beginning. Inorganic packing materials normally come directly from natural sources, such as lava and perlite. All these natural packing materials have good surface properties, but their shape may be irregular (Wu et al., 2018). With time a variety or inorganic packing materials were sythethized and used for biotrickling filters (or other systems), such as ceramic, plastic Pall rings, Rasching rings or rubber particles, clear polyvinyl chloride (PVC), polyurethane foam (PUF) and other materials (Park et al., 2011). Synthesized materials as packing materials sometimes have improved porosity and larger surface area. These materials have smoother surface, and specific made shape and strength that ensures good conditions for microorganisms. The escalated area of synthetized materials improves biotrickling filters performance. Most inorganic materials have advantage of uniform size and structure. These characteristics ensure better gas flow and reduce the compaction of materials (Ortiz et al., 2003). Mixed materials are combination of organic and inorganic packing materials.

Packing materials for biomethanation are critical in terms of hydrogenotrophic methanogens immobilization on the surface of a material. Efficient contact time between added gas bubbles and liquid inoculum ensure effective gas retention but also allows sufficient gas flow. In a biotrickling filter the packing filter can be either filled with packing materials randomly or with specifically designed structured packing materials.

Packing material should have following requirements in order to be suitable for immobilization of biomethane producing microorganisms (Freeman, 1984; Sekoai et al., 2018):

- Adequate surface area.
- Optimal particle size.
- Mechanically robust.
- Chemical and thermal stability.
- Non-toxic for biomethane producing microorganisms.
- Able to resist compaction.
- Able to resist plugging.
- Reusable, inexpensive.

These are one of the core factors in BTF reactor systems. Packing materials must comply with some requirements such as optimal specific surface area to sustain growth and activity of microorganisms, optimal environmental conditions for activity of methanogens, optimal particle size and capability to mechanically resist compaction therefore avoiding high pressure drop. Particle size also is important to prevent high pressure drop and ensure uniform gas flow as gases distribute through the packing material (Dorado et al., 2010). Pressure drop is the difference of pressure between the inlet and the outlet of a biotrickling filter and is essential operating parameter as it is connected to the energy demands to drive gases through the reactor. Materials should be able to resist plugging and provide adequate homogeneity within a bioreactor. These requirements are defined by several physicochemical properties of materials, such as high porosity (%), high specific surface area (m^2 m^{-3}), density (kg m^{-3}), water retention capacity, etc. Microorganisms should be evenly distributed on the surface of the carrying packing material, and gas flow should be unrestricted through the packing material. Materials used for microbial adhesion should not be toxic for hydrogenotrophic methanogens but also be chemical and thermal stable to ensure reusability and sustainability. An advantage is low cost of material. Sustainability of packing materials should be considered when biotrickling filter system is set up and when selecting packing materials.

Specific surface area

Specific surface area is one of the main factor of packing material in methanation within biotrickling filters. The larger the surface area of packing material is, the more biofilm can grow on material and increase methane production speed. Microbial populations are adhered to a filter packing material within trickling reactor achieving maximum surface area.

Using packing materials is one of a methods how volumetric gas-liquid mass transfer in methanation process can be increased. The coefficient k_La (volumetric mass transfer coefficient) indicates systems ability to diffuse specific gases into liquid. It can be unique for different reactor types and can be adjusted by changing parameters, such as hydrogen diffusion devices, gas recirculation and mixing. These parameters are being tested in biogas upgrading systems (Díaz et al., 2015; Rusmanis et al., 2019; Voelklein et al., 2019; Díaz et al., 2020). As for packing materials, cost of time and resources would be too large to test different packing materials in constantly operating biotrickling filter reactors.

Gas-liquid contact time mostly is not enough for all added hydrogen to dissolve. One way to deal with this matter is by recirculation of the gaseous substances (Zabranska & Pokorna, 2018). Some reactor configurations can influence the gas-liquid contact time. For example, the type of diffuser in the reactor and size of bubbles can be adjusted by the size of pores, as well as the ascending bubbles velocity (Bassani et al., 2017). Gas liquid contact time also can be increased by larger surface area of the packing material over which the hydrogen gas bubbles flow, thereby they are being separated into smaller bubbles. The gas-liquid mass transfer rate is increasing when surface area is larger. Bassani et al., 2016 performed an experiment, where packing material was replaced with one that had larger surface area. In the experiments within hydrogen injection chamber alumina ceramic sponge with higher surface area was used instead of ceramic rashing rings as a packing material. As a result, 67% of input hydrogen was utilized and the output methane content using ceramic sponge was higher than with ceramic rashing rings. Also, H_2 in output gas was reduced to smaller amount, which means that it was consumed by hydrogenotrophic microorganisms (Bassani et al., 2016).

The surface area may be the most important factor in the biomethanation. Therefore, any aspect of the material surface is important. By applying materials with crumpled surfaces (Germec et al., 2020), the surface area can be expanded, and more bacteria can be attached and applied to the process.

Porosity and particle size

Packing material particles vary in size, which affects important media characteristics, such as the resistance to gas flow and the effective biofilm surface area. If the size of the particles is small, large specific surface areas essential for mass transfer, are provided. However, smaller sizes also create a larger resistance to gas flow and, thus, larger operating costs due to the electrical power consumption of the gas pump. Conversely, large-size particles favours gas flows but reduce the number of potential sites for the microbial activity. (Dorado et al., 2010). Optimal particle size ensures uniform gas flow as gases distribute through the packing material and high pressure drop can be avoided.

Porosity also provides larger surface area for microorganism to attach. Synthesized inorganic materials sometimes have improved porosity and larger surface area as packing materials. Sometimes addition of foaming agent is used to increase porosity of packing materials (Lee et al., 2013). But if pores are too small, then they can be cluttered, and porosity would not be a core factor for methanation.

The porous matrix of the materials enables the microorganisms to be placed in a suitable sheltered place against the hydraulic shear forces (Massol-Deyá et al., 1995; Ho et al., 1997). In porous materials, biofilm is formed not only on the surface but also in the pores. By using materials with large pores, some problems can be eliminated, such as accumulation of metabolites in pores and lack of nutrient diffusion to the cluttered pores (Germec et al., 2020). Some research work shows the importance of the distribution of gases for an efficient utilization of hydrogen by bacteria. The upgrading performances showed that the influence of pore size and porosity of the packing material demonstrates on efficient utilization of hydrogen (Muffler et al., 2014; Yang et al., 2014; Liu et al., 2015; Sekoai et al., 2018). Many materials that can be used as packing materials have high specific area and porosity. Liu et al., 2015 performed an experiment, where ceramic saddles as a random packing material had the largest porosity on the surface between other materials but the specific surface area is comparatively low. On the other hand, upon closer examination of the saddles showed even smaller pores on the surface of the material, which was assumed not to be considered when the particular surface area was provided by supplier (Liu et al., 2015).

Porosity and particle size of material are quite important factors for microbial growth. In comparison with mammalian cells, the bacteria widely show no limitations in regarding growth inhibition by cell-with-cell contact. If pore size is too big, then distribution on the liquid within the reactors filter can be uneven (Grimalt-Alemany et al., 2018). If the particle size of the support material is smaller, then provided surface area will be larger accordingly. However, a crucial point to acknowledge is the variation of particle size of the packing material as support for microorganisms to retention strategy. Therefore, to meet specific requirements of the microbial growth, an adjustment between the surface area and particle size is an important factor (Germec et al., 2020).

Physical and mechanical properties

One of the features a packing material should have is mechanical resistance. In the mechanics of all materials, the physical strength of a packing material is its capability to resist an adjusted load without any plastic damage and failure. Mechanical resistance of any packing material is identified by some physical factors such as density, hydrophobicity, surface charge and roughness. They also influence the adhesion of microbiological cells and following attachment onto them (Cheng et al., 2010; Germec et al., 2020). Density is one of the characteristics of materials that can be easily defined in studies for different kind of packing materials. Density can be known for most typical materials that are used or it is easy to measure using variety of methods, for example with graduated cylinder or analytically calculated (Haoran et al., 2013). Usually organic materials have less density than inorganic materials (Muffler et al., 2014). Biofilm should also be adapted to the specific conditions and have the required high cell density (Fortuny et al., 2008). Packing materials should be robust towards fermentative by-products (Sekoai et al., 2018). Compaction of material and water accumulation in it can be indirectly measured by pressure drop. This parameter is a consequential part of the costs operating bioreactor and also the majority of energy costs in bioreactors (Dorado et al., 2010). Compacted material increases she shear strength of the filter, but if it is too compacted than gas flow is lowered. Therefore, gas-liquid mass transfer decreases and there may be high pressure drop.

Other characteristics of packing materials in bioreactors should be considered os, such as, good environment of the growth of microorganisms. It can depend on water holding capacity, nutrient content that can be inorganic or high organic, and water retentively of materials. All these parameters are involved in keeping the optimal productivity of the microorganisms that are immobilized on the surface of the packing material inside biotrickling filter reactor. It is important to test new materials that could be used for biomethanation and provide better results in methane content of the final product, but testing packing materials in the operating bioreactors costs too much time and money. There have been small scale experiments, where an assay of testing packing materials for ex-situ biomethanation was demonstrated by Ashraf et. al., where small amount of materials were put in laboratory bottles as mini reactors and tested for biomethane production between different configurations. Laboratory methods like this can be used to predict production of methane and overall gas composition in the reactor (Ashraf et al., 2020).

PACKAGING MATERIALS FOR BIOMETHANATION

Mostly experimental biotrickling filter reactor setups are made with inorganic packing materials that have been used in industry before and are easily available. Those materials are silica, ceramic, and plastic, polypropylene materials in different shapes. Materials that are mentioned in literature as applicable for use in bioreactors as packing materials are shown in Table 1. In some cases, there are data on many characteristics of materials that are used in bioreactors, in other cases materials are just mentioned, but no additional information about them is given. Therefore, data is collected from various sources about materials in general to display average values of product specifications that are available. Also, some organic materials are included, though these are not commonly used in biotrickling filters nowadays.

Table 1. Packing materials for biomethanation

Packaging material	Specific surface area (m^2 m^{-3})	Porosity/ Pore size (%)/(μm)	Density (kg m^{-3})	Particle size (mm)	Estimated durability (years)	Cost (€)	References
Ceramic (Rashing rings), ceramic saddles	338	75/-	94	-	10	€€€	(Liu et al., 2015) (Bassani et al., 2016) (Ashraf et al., 2020) (Kougias et al., 2020) (Jiangxi Kelley, n.d.) (Wu et al., 2018)
Ceramic balls	504	-	-	80–110	10	€€€	(Daglioglu et al., 2020)
Silica ceramic sponge	-	79.9/100	-	-	-		(Jee et al. 1987) (Bassani et al., 2016)
Glass tubes	111	-	-	-	10	€€€	(Daglioglu et al., 2020)
Polypropylene packing rings, saddles	313	91/-	-		15	€€	(Liu et al., 2015) (Rachbauer et al., 2016) (Jiangxi Kelley, n.d.)
Polyfoam – plastic matrix material	600	-	-	-	15	€€	(Baransi-Karkaby et al., 2020)
Polyurethane foam	600	97/20–30	35	-	15	€€	(Sakuma et al., 2006) (Fortuny et al., 2008) (Ashraf et al., 2020) (Sieborg et al., 2020)
Polypropylene HD Q-PACO	430	88/4	-	-	-	€€	(Fortuny et al., 2008)
Lantec HD Q-PAC®	650	87.8/-	120	-	15	-	(Daglioglu et al., 2019)
Lava Rock	458	57/80–160	96	8–16	15	€€	(Liu et al., 2015)
Leca, clay pelets	372	91/-	25	80–100	5	€	(Jee et al.1988) (Liu et al., 2015) (Ashraf et al., 2020) (Jiangxi Kelley, n.d.)
Perlite	3.2	40	30–150	4	-	€	(Sakuma et al., 2006) (Alitalo et al., 2015)
Porcelite		35	85	4	15	€€	(Sakuma et al., 2006)
Vermiculite	30	70	172	0.1–4	15	€	(Séguin et al., 2005) (Alitalo et al., 2015)
Cellulose	383	98	2	-	1–2	€	(Liu et al., 2015)
Woodchips	532	58	21	-	1–2	€	(Hernández et al., 2013) (Liu et al., 2015)
Cattle bone porcelite	300	35	81		1–2	€	(Sakuma et al., 2006)
Fish bone		33	78		1–2	€	(Dorado et al., 2010) (Voelklein et al., 2019)

Ceramic random materials

Ceramic random shape materials are often mentioned within biogas industry. Ceramic packing material are with acid resistance and heat resistance (Jiangxi Kelley, n.d.), which is great for reactor configurations that include thermophilic microorganisms. They can resist corrosion of different organic solvents. These characteristics ensure longer biomethane production without change of packing material. Ceramic packing materials come in various shapes and sizes. Ceramic materials have quite large surface area ranging from 300 to 500 m^2 m^{-3}. Also porosity or void fraction is considerably high - up to 79.7%.

Many researchers have used ceramic packing materials in biomethanation tests, for example, back in 1988 experiments in thermophilic reactor with ceramic material particles size of 2–3 mm. The achieved conversation efficiency was 80% and volumetric content of biomethane was 5.2 L/L/h (Jee et al., 1988). In recent biomethanation experiments slightly larger ceramic pellets (4–5 mm) were used in in biotrickling filter reactor as packing material (Zhang et al., 2020). Though, biomethane production rate is not comparable, because other reactor configurations and fermentation parameters are not similar.

Ceramic material is also used as a diffuser for biotrickling filter reactor. Small holes in diffuser provide good gas flow and breaks bubbles (Daglioglu et al., 2020) to enhance gas-liquid contact time on biofilm.

Plastic random materials

Plastic packing materials are the most often used materials in biomethanation experiments in recent years. Most plastic packing materials, such as plastic saddles, rings, or other shape polypropylene materials are heat and chemical resistant, therefore the durability is much longer than organic materials (Dorado et al., 2010; Jiangxi Kelley, n.d.). These can be made in different sizes and shapes as it is commercially available material and also price is affordable (Dorado et al., 2010). These materials are cheaper than other materials except when compared to some organic packing materials. But durability of plastic materials compared to organic materials outstands the costs, because plastic materials can be used in biotrickling filters for 10 to 15 years (Dorado et al., 2010). Various forms of plastic (polyurethane) packing materials have very large specific surface area reaching up to 650 m^2 m^{-3} (Daglioglu et al., 2019). Porosity is also very high from 85 to 97%.

There have been many research studies with these plastic materials in context of biomethanation (Cheng et al., 2010; Hernández et al., 2013; Lee et al., 2013; Sieborg et al., 2020). Biomethane production in biotrickling filter with polyurethane foam (PUF) as packing material was mentioned in several studies (Sakuma et al., 2006; Fortuny et al., 2008; Zabranska & Pokorna, 2018; Sieborg et al., 2020). Although, results of methane conversion rate are quite high, they are not comparable between the studies, as different fermentation setups were used. There is one experiment, where identical lab batch reactors were set up and used to compare how packing materials perform in context of biomethanation. Between three materials (PUF, cley pellets and plastic rasching rings) the measured CH_4 production potential was the largest using polyurethane foam (Ashraf et al., 2020). Porosity is the highest (97%) with such type of foam and surface area is very large, up to 600 m^2 m^{-3}. Daglioglu et al., 2020 used polyurethane foam in biotrickling reactor system and similar fed gas H_2/CO_2 ratio (ratio of 4:1) as

Ashraf et al., 2020 in his experiments (Ashraf et al., 2020; Daglioglu et al., 2020). The results showed high methane content in the product (80–89%) (Baransi-Karkaby et al., 2020; Daglioglu et al., 2020). Hydrogen consumption was increased by increasing circulation speed, therefore increasing methane production. With high circulation speed the biomass was not washout from reactor and immobilized polyurethane foam material provided stability. In another experiment plastic material was cubic form with grid openings 4 cm × 4 cm. With such packing material void fraction was 87.8% (Puhulwella et al., 2014). Main disadvantage of plastic materials is they are not sustainable.

Volcanic materials

Volcanic packing materials, such as perlite, vermiculite, zeolite. They are valid for biomethanation, because of mechanical and thermal stability, non-toxicity and resistance against organic solvents and fermentation by-products. These materials are used for different purposes and one of them is within filter materials. Such material as perlite is commonly used in biotechnological applications. It provides very good support for immobilization microorganisms and enzymes (Torabi et al., 2007). In a research within fixed bed reactor a vermiculite and perlite were used as packing materials for thermophilic methanogens to produce biomethane. In result hydrogen was completely converted, but only when liquid nutrition was recirculated. Only 3% liquid nutrition of reactor total volume was recirculated (Zabranska & Pokorna, 2018). Perlite, zeolite, vermiculite, and other packing materials were used for hydrogenotrophic biomethanation in different reactor types, such as fixed bed reactors and biotrickling filter reactors (Daglioglu et al., 2020). Costs of volcanic materials vary, but are similar to ceramic packing materials.

Soil materials

Soil materials are also considered as packing materials for biomethanation. These are typically Leca or clay pellets. Clay pellets are a lightweight and expand, when soaked in liquids. Some research work was made for testing clay pellets as packing material for ex-situ biomethanation (Ashraf et al., 2020, Liu et al., 2015). The surface area and porosity of material was not known. The amount of produced methane using clay pellets was almost half on an amount compared to polyurethane foam and 40% less then with plastic rings as packing materials. Clay pellets are very light, and they do not compact. Soil materials cost less than ceramic or plastic materials but are not so durable as volcanic, plastic, or ceramic materials.

Organic materials

Least popular materials for packing bioreactors are organic materials, such as cellulose, woodchips, cattle and fish bones or other materials. These materials are rich with nutrition that can cause an early degradation within fermentation reactors. Different organic materials vary in specific surface area and porosity. The use of organic materials would be most sustainable option for biogas upgrading if choosing amongst other materials. Moreover, if agricultural farm has its own biogas production system, and also some of these organic materials to use as packing materials, biogas upgrading can be efficiently done in one system. These also are the cheapest of all materials mentioned above (Dorado et al., 2010).

CONCLUSIONS

Biomethanation is a prospective method to integrate renewable solar or wind power grid with biogas grid, where excess energy can be used to produce hydrogen for biomethanation of the biogas and produce biomethane. Application of biotrickling filter reactors with suitable packing materials for biomethanation are critical in terms of hydrogenotrophic methanogens immobilization on the surface of packing material. It acts as support for biofilm growth. Therefore, characteristics of filter material are important parameters that influence the growth of microorganisms and methane production. Moreover, the combination of surface area of material, porosity, pore size and mechanical resistance together is important in context of biomethane production and testing their correlation would be great input for further development of biogas upgrading.

Testing of packing materials in constantly operating biotrickling filter reactors would be costing time and resources, considering different characteristics of materials and configurations. Therefore, smaller experiments, data reviews, modelling and simulations options for testing suitability of different packing materials in context of ex-situ biomethanation should be done. Testing packing materials in smaller laboratory setups is one step closer to adjust existing technologies as biotrickling filter reactor systems for more efficient biogas upgrading.

Non-traditional and new - more sustainable packing materials can be tested in laboratory scale tests and then new biotrickling filter reactor systems can be configured to increase biomethane production.

REFERENCES

Akhlaghi, N. & Najafpour-Darzi, G. 2020. A Comprehensive Review on Biological Hydrogen Production. *International Journal of Hydrogen Energy* **45**(43), Elsevier Ltd, pp. 22492–512. doi: 10.1016/j.ijhydene.2020.06.182

Alitalo, A., Niskanen, M. & Aura, E. 2015.Biocatalytic Methanation of Hydrogen and Carbon Dioxide in a Fixed Bed Bioreactor. *Bioresource Technology* **196**, Elsevier Ltd, pp. 600–05. doi: 10.1016/j.biortech.2015.08.021

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H. & Kougias, P.G. 2018. Biogas Upgrading and Utilization: Current Status and Perspectives. *Biotechnology Advances* **36**(2), Elsevier, pp. 452–66. doi: 10.1016/j.biotechadv.2018.01.011

Ashraf, M.T., Triolo, J.M. & Yde, L. 2020. Assay for Testingpacking Materials for Ex-Situ Biomethanation. *28th European Biomass Conference and Exhibition, 6-9 July 2020, Virtual* **3**, pp. 6–9.

Baena-Moreno, F.M., Rodríguez-Galán, M., Vega, F., Vilches, L.F. & Navarrete, B. 2019. Review: Recent Advances in Biogas Purifying Technologies. *International Journal of Green Energy* **16**(5), Taylor & Francis, Apr., pp. 401–12. doi: 10.1080/15435075.2019.1572610

Baransi-Karkaby, K., Hassanin, M., Muhsein, S., Massalha, N. & Sabbah, I. 2020. Innovative Ex-Situ Biological Biogas Upgrading Using Immobilized Biomethanation Bioreactor (IBBR). *Water Science and Technology : A Journal of the International Association on Water Pollution Research* **81**(6), 1319–28. doi: 10.2166/wst.2020.234

Bassani, C.L., Barbuto, F.A.A., Sum, A.K. & Morales, R.E.M. 2017. Modeling the Effects of Hydrate Wall Deposition on Slug Flow Hydrodynamics and Heat Transfer. *Applied Thermal Engineering* **114**, pp. 245–54. doi: https://doi.org/10.1016/j.applthermaleng.2016.11.175

Bassani, I., Kougias, P.G. & Angelidaki, I. 2016. In-Situ Biogas Upgrading in Thermophilic Granular UASB Reactor: Key Factors Affecting the Hydrogen Mass Transfer Rate. *Bioresource Technology* **221**, Elsevier Ltd, pp. 485–91. doi: 10.1016/j.biortech.2016.09.083

Bensmann, B., Hanke-Rauschenbach, R., Peña Arias, I.K. & Sundmacher, K. 2013. Energetic Evaluation of High Pressure PEM Electrolyzer Systems for Intermediate Storage of Renewable Energies. *Electrochimica Acta* **110**, 570–80. doi: https://doi.org/10.1016/j.electacta.2013.05.102

Burkhardt, M., Koschack, T. & Busch, G. 2015. Biocatalytic Methanation of Hydrogen and Carbon Dioxide in an Anaerobic Three-Phase System. *Bioresource Technology* **178**, Elsevier Ltd, pp. 330–33. doi: 10.1016/j.biortech.2014.08.023

Cheng, K.C., Demirci, A. & Catchmark, J.M. 2010. Advances in Biofilm Reactors for Production of Value-Added Products. *Applied Microbiology and Biotechnology* **87**(2), 445–56. doi: 10.1007/s00253-010-2622-3

Daglioglu, S.T., Karabey, B., Ozdemir, G. & Azbar, N. 2019. ch4 Utilization via a Novel Anaerobic Bioprocess Configuration with Simulated Gas Mixture and Real Stack Gas Samples. *Environmental Technology (United Kingdom)* **40**(6), 742–48. doi: 10.1080/09593330.2017.1406537

Daglioglu, S.T., Ogut, T.C., Ozdemir, G. & Azbar, N. 2020. Comparative Evaluation of Two Packing Materials (Glass Pipe and Ceramic Ball) for Hydrogenothrophic Biomethanation (BHM) of CO2. *Waste and Biomass Valorization*. doi: 10.1007/s12649-020-01242-8

De Vrieze, J., Verbeeck, K., Pikaar, I., Boere, J., Van Wijk, A., Rabaey, K. & Verstraete, W. 2020. The Hydrogen Gas Bio-Based Economy and the Production of Renewable Building Block Chemicals, Food and Energy. *New Biotechnology* **55**, Elsevier B.V., pp. 12–18. doi: 10.1016/j.nbt.2019.09.004

Díaz, I., Pérez, C., Alfaro, N. & Fdz-Polanco, F. 2015. A Feasibility Study on the Bioconversion of CO2 and H2 to Biomethane by Gas Sparging through Polymeric Membranes. *Bioresource Technology* **185**, 246–53. doi: 10.1016/j.biortech.2015.02.114

Díaz, I., Fdz-Polanco, F., Mutsvene, B. & Fdz-Polanco, M. 2020. Effect of Operating Pressure on Direct Biomethane Production from Carbon Dioxide and Exogenous Hydrogen in the Anaerobic Digestion of Sewage Sludge. *Applied Energy* **280**(May), Elsevier Ltd, p. 115915. doi: 10.1016/j.apenergy.2020.115915

Dorado, A.D., Lafuente, F.J., Gabriel, D. & Gamisans, X. 2010. A Comparative Study Based on Physical Characteristics of Suitable Packing Materials in Biofiltration. *Environmental Technology* **31**(2), 193–204. doi: 10.1080/09593330903426687

Dupnock, T.L. & Deshusses, M.A. 2019. Detailed Investigations of Dissolved Hydrogen and Hydrogen Mass Transfer in a Biotrickling Filter for Upgrading Biogas. *Bioresource Technology* **290**(July), Elsevier, p. 121780. doi: 10.1016/j.biortech.2019.121780

Dupnock, T.L. & Deshusses, M.A. 2020. Development and Validation of a Comprehensive Model for Biotrickling Filters Upgrading Biogas. *Chemical Engineering Journal* **405**(June), 126614. https://doi.org/10.1016/j.cej.2020.126614

Fortuny, M., Baeza, J.A., Gamisans, X., Casas, C., Lafuente, J., Deshusses, M.A. & Gabriel, D. 2008. Biological Sweetening of Energy Gases Mimics in Biotrickling Filters. *Chemosphere* **71**(1), 10–17. doi: 10.1016/j.chemosphere.2007.10.072

Freeman, A. 1984. Gel Entrapment of Whole Cells and Enzymes in Crosslinked, Prepolymerized Polyacrylamide Hydrazide. *Annals of the New York Academy of Sciences* **434**(1), Dec., pp. 418–26. doi: 10.1111/j.1749-6632.1984.tb29863.x.

Germec, M., Demirci, A. & Turhan, I. 2020. Biofilm Reactors for Value-Added Products Production: An in-Depth Review. *Biocatalysis and Agricultural Biotechnology* **27**(April), Elsevier Ltd, p. 101662. doi: 10.1016/j.bcab.2020.101662

Grimalt-Alemany, A., Skiadas, I.V. & Gavala, H.N. 2018. Syngas Biomethanation: State-of-the-Art Review and Perspectives. *Biofuels, Bioproducts and Biorefining* **12**(1), 139–58. doi: 10.1002/bbb.1826

Haoran, P., Valérie, L., Etienne, P. & Gilles, H. 2013. The Influence of Porous Structure and Biofilm on the Hydrodynamics of Two Types of Trickle Filters. *Chemical Engineering Journal* **231**, Elsevier B.V., pp. 163–71. doi: 10.1016/j.cej.2013.06.115

Hernández, J., Lafuente, J., Prado, Ó.J. & Gabriel, D. 2013. Startup and Long-Term Performance of Biotrickling Filters Packed with Polyurethane Foam and Poplar Wood Chips Treating a Mixture of Ethylmercaptan, H2S, and NH3. *Journal of the Air and Waste Management Association* **63**(4), 462–71. doi: 10.1080/10962247.2013.763305

Ho, K.L., Pometto, A.L. & Hinz, P.N. 1997. Optimization of L-(+)-Lactic Acid Production by Ring and Disc Plastic Composite Supports through Repeated-Batch Biofilm Fermentation. *Applied and Environmental Microbiology* **63**(7), 2533–42. doi: 10.1128/aem.63.7.2533-2542.1997

Holm-Nielsen, J.B., Al Seadi, T. & Oleskowicz-Popiel, P. 2009. The Future of Anaerobic Digestion and Biogas Utilization. *Bioresource Technology* **100**(22), Elsevier Ltd, pp. 5478–84. doi: 10.1016/j.biortech.2008.12.046

Jee, H.S., Nishio, N. & Nagai, S. 1988. Biomethanation of H2 and CO2 by Methanobacterium Thermoautotrophicum in Membrane and Ceramic Bioreactors. *Journal of Fermentation Technology* **65**, 413–18.

Jee, H.S., Yano, T., Nishio, N. & Nagai, S. 1987. Continuous CH4 Production from H2 and CO2 by Methanobacterium Thermoautotrophicum in a Fixed-Bed Reactor. *Journal of Fermentation Technology* **66**(2), 235–38. doi: 10.1016/0385-6380(88)90054-4

Jiangxi, K. *Chemical Packagin.* http://www.kelley-chempacking.net/2-ceramic-random-packing.html.

Jønson, D.B., Sieborg, U.M., Ashraf, T.M., Yde, L., Shin, J., Shin, S.G. & Mi Triolo, J. 2020. Direct Inoculation of a Biotrickling Filter for Hydrogenotrophic Methanogenesis. *Bioresource Technology* **318**(July), Elsevier, p. 124098. doi: 10.1016/j.biortech.2020.124098

Kougias, P.G., Tsapekos, P., Treu, L., Kostoula, M., Campanaro, S., Lyberatos, G. & Angelidaki, I. 2020. Biological CO2 Fixation in Up-Flow Reactors via Exogenous H2 Addition. *Journal of Biotechnology* **319**(March), pp. 1–7. doi: 10.1016/j.jbiotec.2020.05.012

Kourkoutas, Y., Bekatorou, A., Banat, I., Marchant, R. & Koutinas, A. 2004. Immobilization Technologies and Support Materials Suitable in Alcohol Beverages Production: A Review. *Food Microbiology* **21**, Aug., pp. 377–97. doi: 10.1016/j.fm.2003.10.005

Lecker, B., Illi, L., Lemmer, A. & Oechsner, H. 2017. Biological Hydrogen Methanation – A Review. *Bioresource Technology* **245**(August), Elsevier Ltd, pp. 1220–28. doi: 10.1016/j.biortech.2017.08.176

Lee, S., Li, C., Heber, A.J., Ni, J. & Huang, H. 2013. Biofiltration of a Mixture of Ethylene, Ammonia, n-Butanol, and Acetone Gases. *Bioresource Technology* **127**, 366–77. doi: https://doi.org/10.1016/j.biortech.2012.09.110

Leonzio, G. 2016. Process Analysis of Biological Sabatier Reaction for Bio-Methane Production. *Chemical Engineering Journal* **290**, Elsevier B.V., pp. 490–98. doi: 10.1016/j.cej.2016.01.068

Liu, D., Andreasen, R.R., Poulsen, T.G. & Feilberg, A. 2015. A Comparative Study of Mass Transfer Coefficients of Reduced Volatile Sulfur Compounds for Biotrickling Filter Packing Materials. *Chemical Engineering Journal* **260**, Elsevier B.V., pp. 209–21. doi: 10.1016/j.cej.2014.08.070

Luo, G. & Angelidaki, I. 2012. Integrated Biogas Upgrading and Hydrogen Utilization in an Anaerobic Reactor Containing Enriched Hydrogenotrophic Methanogenic Culture. *Biotechnology and Bioengineering* **109**(11), 2729–36. doi: 10.1002/bit.24557

Maegaard, K., Garcia-Robledo, E., Kofoed, M.V.W., Agneessens, L.M., de Jonge, N., Nielsen, J.L., Ottosen, L.D.M., Nielsen, L.P. & Revsbech, N.P. 2019. Biogas Upgrading with Hydrogenotrophic Methanogenic Biofilms. *Bioresource Technology* **287**(March), Elsevier, p. 121422. doi: 10.1016/j.biortech.2019.121422

Massol-Deyá, A.A., Whallon, J., Hickey, R.F. & Tiedje, J.M. 1995. Channel Structures in Aerobic Biofilms of Fixed-Film Reactors Treating Contaminated Groundwater. *Applied and Environmental Microbiology* **61**(2), Feb. pp. 769–77. doi: 10.1128/AEM.61.2.769-777.1995

Mehrpooya, M., Ghorbani, B. & Manizadeh, A. 2020. Cryogenic Biogas Upgrading Process Using Solar Energy (Process Integration, Development, and Energy Analysis). *Energy* **203**, Elsevier Ltd, p. 117834. doi: 10.1016/j.energy.2020.117834

Michailos, S., Walker, M., Moody, A., Poggio, D. & Pourkashanian, M. 2020. Biomethane Production Using an Integrated Anaerobic Digestion, Gasification and CO2 Biomethanation Process in a Real Waste Water Treatment Plant: A Techno-Economic Assessment. *Energy Conversion and Management* **209**(December), Elsevier, 2020, p. 112663. doi: 10.1016/j.enconman.2020.112663

Muffler, K., Lakatos, M., Schlegel, C., Strieth, D., Kuhne, S. & Ulber, R. 2014. Application of Biofilm Bioreactors in White Biotechnology. *Advances in Biochemical Engineering/Biotechnology* **146**, 123–61. doi: 10.1007/10_2013_267

Ortiz, I., Revah, S. & Auria, R. 2003. Effects of Packing Material on the Biofiltration of Benzene, Toluene and Xylene Vapours. *Environmental Technology* **24**(3), Taylor & Francis, Mar., pp. 265–75. doi: 10.1080/09593330309385559

Park, J., Evans, E.A. & Ellis, T.G. 2011. Development of a Biofilter with Tire-Derived Rubber Particle Media for Hydrogen Sulfide Odor Removal. *Water, Air, & Soil Pollution* **215**(1), 145–53. doi: 10.1007/s11270-010-0466-1

Porté, H., Kougias, P.G., Alfaro, N., Treu, L., Campanaro, S. & Angelidaki, I. 2019. Process Performance and Microbial Community Structure in Thermophilic Trickling Biofilter Reactors for Biogas Upgrading. *Science of the Total Environment* **655**, Elsevier B.V., pp. 529–38. doi: 10.1016/j.scitotenv.2018.11.289

Puhulwella, R.G., Beckers, L., Delvigne, F., Grigorescu, A.S., Thonart, P. & Hiligsmann, S. 2014. Mesophilic Biohydrogen Production by Clostridium Butyricum CWBI1009 in Trickling Biofilter Reactor. *International Journal of Hydrogen Energy* **39**(30), Elsevier Ltd, pp. 16902–13. doi: 10.1016/j.ijhydene.2014.08.087

Rachbauer, L., Voitl, G., Bochmann, G. & Fuchs, W. 2016. Biological Biogas Upgrading Capacity of a Hydrogenotrophic Community in a Trickle-Bed Reactor. *Applied Energy* **180**, Elsevier Ltd, pp. 483–90. doi: 10.1016/j.apenergy.2016.07.109

Rusmanis, D., O'Shea, R., Wall, D.M. & Murphy, J.D. 2019. Biological Hydrogen Methanation Systems–an Overview of Design and Efficiency. *Bioengineered* **10**(1), Taylor & Francis, pp. 604–34. doi: 10.1080/21655979.2019.1684607

Sakuma, T., Hattori, T. & Deshusses, M.A. 2006. Comparison of Different Packing Materials for the Biofiltration of Air Toxics. *Journal of the Air and Waste Management Association* **56**(11), 1567–75. doi: 10.1080/10473289.2006.10464564

Savvas, S., Donnelly, J., Patterson, T., Chong, Z.S., Esteves, S.R. 2017. Biological Methanation of CO2 in a Novel Biofilm Plug-Flow Reactor: A High Rate and Low Parasitic Energy Process. *Applied Energy* **202**, Elsevier Ltd, pp. 238–47. doi: 10.1016/j.apenergy.2017.05.134

Séguin, V., Courchesne, F., Gagnon, C., Martin, R.R., Naftel, S.J. & Skinner, W. 2005. *Chapter 2 - Mineral Weathering in the Rhizosphere of Forested Soils*. Edited by P M Huang and G R B T - Biogeochemistry of Trace Elements in the Rhizosphere Gobran, Elsevier, pp. 29–55. doi: https://doi.org/10.1016/B978-044451997-9/50004-0

Sekoai, P.T., Awosusi, A.A., Yoro, K.O., Singo, M., Oloye, O., Ayeni, A.O., Bodunrin, M. & Daramola, M.O. 2018. Microbial Cell Immobilization in Biohydrogen Production: A Short Overview. *Critical Reviews in Biotechnology* **38**(2), Informa Healthcare USA, Inc, pp. 157–71. doi: 10.1080/07388551.2017.1312274

Sieborg, M.U., Jønson, B.D., Ashraf, M.T., Yde, L. & Triolo, J.M. 2020. Biomethanation in a Thermophilic Biotrickling Filter Using Cattle Manure as Nutrient Media. *Bioresource Technology Reports* **9**(January), Elsevier, p. 100391. doi: 10.1016/j.biteb.2020.100391

Strübing, D., Moeller, A.B., Mößnang, B., Lebuhn, M., Drewes, J.E. & Koch, K. 2018. Anaerobic Thermophilic Trickle Bed Reactor as a Promising Technology for Flexible and Demand-Oriented H2/CO2 Biomethanation. *Applied Energy* **232**(July), Elsevier, pp. 543–54. doi: 10.1016/j.apenergy.2018.09.225

Thema, M., Weidlich, T., Hörl, M., Bellack, A., Mörs, F., Hackl, F., Kohlmayer, M., Gleich, J., Stabenau, C., Trabold, T., Neubert, M., Ortlo, F., Brotsack, R., Schmack, D., Huber, H., Hafenbradl, D., Karl, J. & Sterner, M. 2019. Biological CO 2 -Methanation : An Approach. *Energies* **12**(1670), pp. 1–32.

Torabi, S.-F., Khajeh, K., Ghasempur, S., Ghaemi, N. & Siadat, S.-O.R. 2007. Covalent Attachment of Cholesterol Oxidase and Horseradish Peroxidase on Perlite through Silanization: Activity, Stability and Co-Immobilization. *Journal of Biotechnology* **131**(2), 111–20. doi: https://doi.org/10.1016/j.jbiotec.2007.04.015

Trisha, L., Dupnock M.A., Deshusses. 2020. Development and Validation of a Comprehensive Model for Biotrickling Filters Upgrading Biogas. *Chemical Engineering Journal* **405**(June), Elsevier, p. 126614. doi: 10.1016/j.cej.2020.126614

Vo, T.T.Q., Wall, D.M., Ring, D., Rajendran, K. & Murphy, J.D. 2018. Techno-Economic Analysis of Biogas Upgrading via Amine Scrubber, Carbon Capture and Ex-Situ Methanation. *Applied Energy* **212**, 1191–202. doi: https://doi.org/10.1016/j.apenergy.2017.12.099

Voelklein, M.A., Rusmanis, D. & Murphy, J.D. 2019. Biological Methanation: Strategies for in-Situ and Ex-Situ Upgrading in Anaerobic Digestion. *Applied Energy* **235**(October) 2018, Elsevier, pp. 1061–71. doi: 10.1016/j.apenergy.2018.11.006

Witte, J., Calbry-Muzyka, A., Wieseler, T., Hottinger, P., Biollaz, S.M.A. & Schildhauer, T.J. 2019. Demonstrating Direct Methanation of Real Biogas in a Fluidised Bed Reactor. *Applied Energy* **240**, pp. 359–71. doi: https://doi.org/10.1016/j.apenergy.2019.01.230

Wu, H., Yan, H., Quan, Y., Zhao, H., Jiang, N. & Yin, C. 2018. Recent Progress and Perspectives in Biotrickling Filters for VOCs and Odorous Gases Treatment. *Journal of Environmental Management* **222**(May), Elsevier, pp. 409–19. doi: 10.1016/j.jenvman.2018.06.001

Zabranska, J. & Pokorna, D. 2018. Bioconversion of Carbon Dioxide to Methane Using Hydrogen and Hydrogenotrophic Methanogens. *Biotechnology Advances* **36**(3), Elsevier, pp. 707–20. doi: 10.1016/j.biotechadv.2017.12.003

Zhang, Y., Liu, J. & Li, J. 2020. Comparison of Four Methods to Solve Clogging Issues in a Fungi-Based Bio- Trickling Fi Lter. *Biochemical Engineering Journal* **153**(September) 2019, Elsevier, p. 107401. doi: 10.1016/j.bej.2019.107401