RIGA TECHNICAL UNIVERSITY

Faculty of Materials Science and Applied Chemistry
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ANAEROBIC DIGESTION OF DAIRY RESIDUES AND PROCESS ENHANCEMENT USING COMPOSITE MATERIALS FROM INDUSTRIAL WASTES

Summary of Doctoral Thesis

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Riga 2015

Ruģele K. Anaerobic digestion of dairy residues and process enhancement using composite materials from industrial wastes. Summary of Doctoral Thesis.-R.:RTU, 2015.-30 lpp.

Printed in accordance with RTU Institute of General Chemical Engineering resolution from 05.06.2014., protocol Nr. 16-13/14.

EIROPAS SOCIĀLAIS FONDS
EIROPAS SAVIENĪBA

This work has been supported by the European Social Fund within the project «Involvement of Human Resources for Development of Integrated Renewable Energy Resources Energy Production System».
Project No. 2013/0014/1DP/1.1.1.2.0/13/APIA/VIAA/026.

ISBN 978-9934-507-85-4

THE DOCTORAL THESIS IS SUBMITTED FOR AWARD OF DOCTORAL DEGREE IN ENGINEERING SCIENCES AT RIGA TECHNICAL UNIVERSITY

The Thesis for the doctoral degree in engineering sciences is to be publicly defended on the 12th March 2015, at the Riga Technical University, Faculty of Materials Science and Applied Chesmistry, 3 Paula Valdena Street, room No. 272, at 15.00.

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CONFIRMATION

I confirm that I have developed the present Doctoral Thesis, which is submitted for consideration at Riga Technical University for scientific degree of the doctor of engineering sciences. The Doctoral Thesis has not been submitted at any other university for the acquisition of a scientific degree.

Kristīne Ruģele …………………………….

Date: ………………………

The Doctoral Thesis is written in Latvian language, it contains Introduction, 3 chapters - Review of Literature, Methods, Discussion of Experiments, Conclusions, list of References, as well as 60 illustrations, 26 tables, 120 pages. 110 references are used for this Doctoral thesis.

ACKNOWLEDGEMENTS

I would like to kindly thank my scientific supervisor, associate professor Dr.Sc.ing. Juris Vanags and advisors – professor Tālis Juhna and Ph.D. Peep Pitk.

Many thanks to Dr.sc.ing. Līga Bērziņa-Cimdiņa for support and opportunity to work with biotechnologies.

I am thankful to „Materials team" – to Dr.Sc.ing. Diāna Bajāre and Ģirts Būmanis for cooperation.

Many thanks to colleagues of Water Research Laboratory - Linda Mežule, Kristīna Tihomirova, Viktorija Deņisova, Alīna Neščerecka, Brigita Daļecka, Jānis Rubulis and Jānis Neilands.

Many thanks to colleagues of Institute of General Chemical Engineering – Jānis and Dagnija Loči, Daina Vempere, Lāsma Mālniece, Jānis Gintauts, Inga Dušenkova, Kristīne Šalma-Ancāne un Agnese Pūra.

I would like to thank Institute of energy systems and environment for the opportunity to finish my thesis during the ESF Project.

I would like to thank student team – Laura, Madars, Pāvels and Oskars.

I am thankful to SIA Smiltenes piens, SIA Vecsiljāņi, SIA Rīgas Ūdens for the providing of raw materials

Many thanks to Ēriks Skripts for advices.

The greatest thanks to my family for the support and patience.

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OVERVIEW OF THE DOCTORAL THESIS

Introduction

The world has to end growth in greenhouse gas (GHG) emissions within some years and reduce annual carbon emissions from today's 8 billion tons down to about 2 billion tons to balance the assimilation capacity of the world's carbon sinks (such as oceans, forests, etc.). Renewable energy provides one of the leading solutions to the climate change issue. By providing 'carbon-neutral' sources of power, heat, cooling and transport fuels, renewable energy options such as biogas offer a safe transition to a low carbon economy. Biogas can be produced from different substrates, such as animal manure, energy crops and industrial wastes, however, there is limited competition with food if an industrial wastes and wastewater is used to produce biogas.

The beneficial use of different industrial wastes to produce energy and reduce environmental pollution is a very attractive topic. Quantity of milk processing wastes is rising every year. 458 368 tons of milk was processed and 90 000 tons of whey was generated in Latvia during 2010. Whey is mostly used for animal feeding or poured out on agricultural lands or as additive to substrate in agricultural biogas plants. Despite the high potential for waste reduction and energy production, anaerobic digestion is not widespread in the dairy industry. This is largely due to the problem of slow reaction rates which require long hydraulic retention time (HRT) and poor process stability.

The amount of industrial wastes is growing, which makes recycling possibility a very significant challenge nowadays. More than 3760 T of glass fibre wastes and 100 T of metal manufacturing wastes were disposal in landfills in Latvia in 2012. It is important to note that diverting non-hazardous industrial and manufacturing by-products for recycling saves disposal costs and preserves natural resources by decreasing the demand for virgin materials.

The PhD project was started due to the needs for both energy production and waste treatment. Whey is a problematic waste for the most of dairies in Latvia. The increase of interest in treatment of whey by anaerobic digestion is a solution to minimise the environmental impact and, at the same time, converted into energy, which could be used for the recovery of energy consumption in factories. Apart from automated online pH control, the pH instability in the anaerobic digestion system of dairy wastes can be controlled via addition of alkaline materials produced from industrial wastes.

The aim of the Doctoral Thesis

Development of anaerobic treatment technology for whey using alkali-releasing composite materials and investigation of the influence of technological parameters on the biogas production rate and yield to justify the sufficient solution of an alternative pH controlling system.

Tasks set to realize the aim of the Doctoral Thesis:

- To investigate anaerobic treatment process of acid whey with automatic pH control system and to evaluate optimal process parameters;
- To evaluate effectiveness of alkaline composite materials in anaerobic treatment of whey;
- To estimate the influence of different material modifications and compositions to the biogas production process;
- To offer the technological scheme for a continuous reactor with an adapted system for pH regulation with alkaline materials.

Scientific significance of the Doctoral Thesis:

- The possibility of use of alkali-releasing composite materials from industrial wastes for pH control has been proved within the anaerobic treatment process of whey;
- The influence of alkali composite materials composition and different modifications on the biogas production yield and rate has been evaluated.

Practical significance of the Doctoral Thesis:

The technology for possible practical applications is developed for anaerobic treatment of whey in continuous stirrer tank reactor with an adapted system for pH control using alkali-releasing composite materials.

Approbation of the Doctoral Thesis:

The scientific achievements and main results of the scientific research of this Thesis have been presented in 8 international conferences, summarized in 9 full text scientific manuscripts and 2 peer-reviewed conference proceeding abstracts.

REVIEW OF THE LITERATURE

During the last quarter a century there has been a growing interest in alternative sources of energy. This is the result of increased demands for energy and the rise in the cost of the available fuels.

Biogas from anaerobic digestion has been identified as an important source of clean energy since it provides an excellent opportunity to reduce greenhouse gas emissions by displacing fossil fuels in domestic and industrial applications [1], [2]. The anaerobic digestion process includes degradation and stabilization of organic matters by microorganisms under anaerobic conditions and leads to biogas (a mixture of carbon dioxide and methane) and biomass formation [3]. Biogas formation process is a complex microbiological process requiring combined activity of several groups of microorganisms with different metabolic capacities. Three stages often are used to illustrate the sequence of microbial events that occur during the digestion process and the production of methane, which are hydrolysis, acid forming, and methanogenesis (Fig. 1). The anaerobic digestion process proceeds efficiently if the degradation rates of all three stages are equal [4].

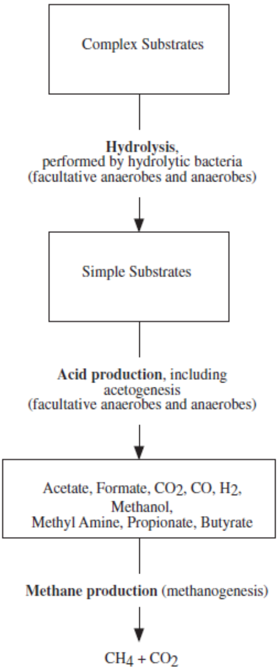


Fig. 1. Stages include in anaerobic digestion [4]

There are a large number of factors which affect biogas production efficiency such as environmental conditions like pH, temperature, inhibitory parameters like high organic loading, etc. Volatile solids input, digester temperature and retention time are operational parameter that have a strong effect on digester performance [5].

Various wastes from food industry such as organic matter rich substrates could be used to produce biogas. In comparison to aerobic processes, anaerobic treatment processes are more favourable to treat waste effluents, particularly those from agricultural or food industries with a high organic content [6]. In milk industry one of such substrates is whey, which is produced during cheese or cottage cheese production[7]. It makes up about 80% of the original fermentation medium, and it retains most of the milk fat, trace minerals, salts and vitamins [8].

Whey is considered the most important pollutant in dairy industry, not only because of the high organic load, but also for the volume generated [9]. Disposal of whey makes up a significant part of environmental problem and contributes substantially to the pollution of surface waters and soil. With increasing cheese and cottage cheese production alternative treatment possibilities besides using it as feed for animals are required.

Whey can be utilized in many ways. Lactose and whey protein can be recovered separately and be used further for other applications. However, it is usually unprofitable due to the high energy cost and the complexity of the process. As whey represents a potential energy source, the anaerobic digestion offers an excellent approach in terms of both energy conservation and pollution control [10]. According to Audic et al. [11], about 90% of hydrolyzed organic matter is converted into biogas in the methanogenesis process. It is estimated that one litter of whey can produce 45 litters of biogas containing 55% methane and the expected COD removal is 80%. For each litter of whey 20 L of CH_4 can be produced, which are equivalent to 200 Wh of energy production [12].

However, anaerobic treatment of whey has frequently encountered difficulties in maintaining stable operation [13]. It is characterized by a very high organic load and low buffer capacity; consequently, the direct anaerobic treatment of raw whey can lead to rapid acidification which results in low biogas productivity [13–15], therefore supplemental alkalinity is required to avoid anaerobic process failure.

Due to the high protein and lactose content, it is highly biodegradable (~99%). Free availability of the lactose in the whey still encompass problems with low pH. Overall whey has acidic characteristics with pH values within the range 3–6 that is not suitable for the growth of methanogenic bacteria [9].

Although biogas production through anaerobic digestion has been established for some decades, there is still a need for optimization of this process in terms of process stability, higher methane yields and inhibition problems [16], [17].

EXPERIMENTAL METHODS

The experimental scheme of Doctoral thesis and determined parameters are shown in Figure 2.

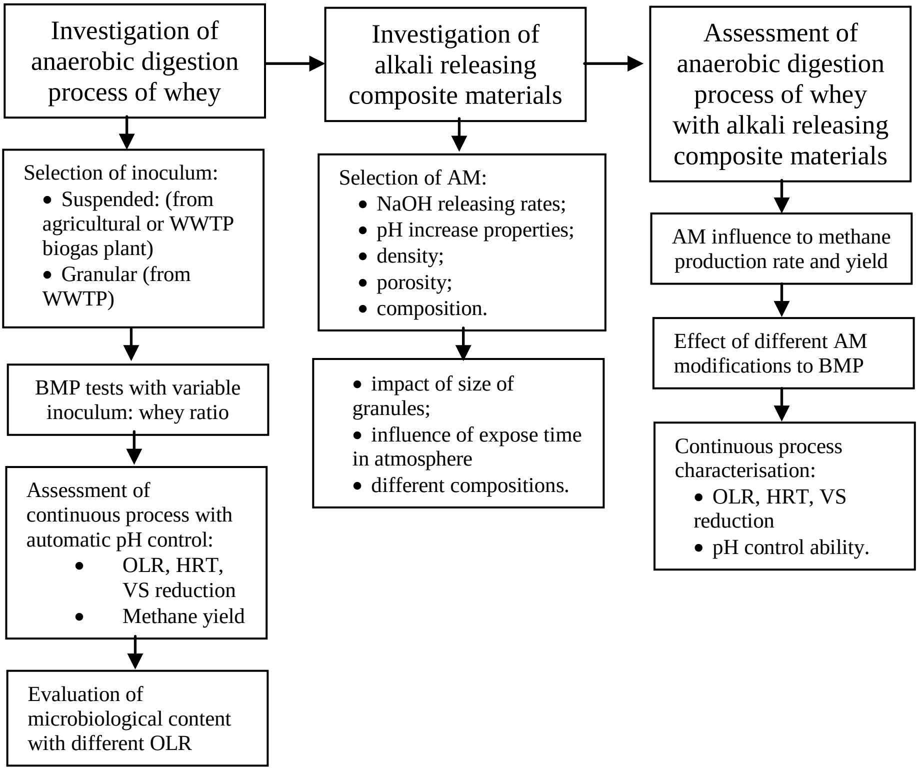


Fig. 2. The experimental scheme

Batch experiments

The cultivation experiments was carried out under mesophilic conditions at 37 °C in 100 ml serum bottles with a maximum loading volume of 70 ml wherein 10% and 15% whey (v/v) was introduced.
Alkaline composite material (AM) was added at the start of experiment without any previous pH correction. The ratio (g/g) between AM granules and VS of substrate added were between 0.2-2.0. Substrate to inoculum ratio was between 0.2–0.4. Dilution process or any other pre-treatment of whey

was not used. During experiments the methane production and gas content was controlled after each 12 hours with syringes filled with 3M NaOH. The results were obtained from the average of triplicate samples collected daily over a total fermentation period of average 20-30 days where upon methane production was measured cumulatively.

Continuous reactor experiments

Anaerobic digestion studies were performed in 6.2 L glass bioreactor (EDF-5.3_1, Latvia) with a working volume of 4 L and a height to diameter ratio of 3:1. The bioreactor was equipped with novel magnetic drive placed in the upper lid. Temperature (Pt-100) and pH (Ingold, Toledo 405-DPAS SC K8S/325) in the reactor, CH_4 and CO_2 concentrations in the exhaust gases (Bluesens, Germany) were measured online. Automatic control of pH at 7.2 ± 0.2 using 12 % sodium hydroxide solution was applied. NaOH solution was added to the bioreactor with peristaltic pump working in on-off pumping rate mode. Temperature set point was 37.0 ± 0.2 ˚C. The anaerobic environment at the start was ensured by flushing with N_2 until the dissolved oxygen was zero. Substrate feeding was performed continuously with various OLR. Biogas production in reactor was continuously measured by water displasing method. Effluent characteristics (VS, TS, FOS/TAC) were analysed twice a day.
Continuous stirrer reactor system was improved with additional loop for pH control with AM.

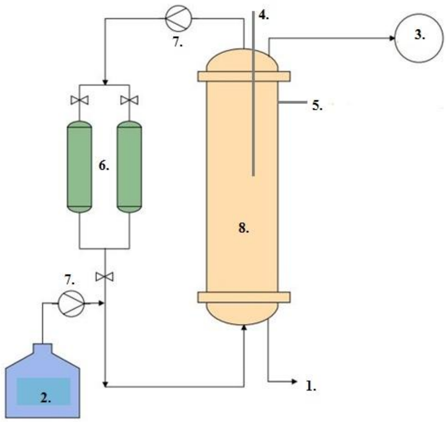


Fig. 3. Scheme of continuous CSTR reactor with additional loop for pH controlling with AM. 1. Sludge; 2. Container for fresh whey; 3. Infra-red analyzers for CO_2 and CH_4 and after water displacement system for quantification of biogas; 4. pH-meter and temperature sensors; 5. Outlet; 6. Filters with AM (volume – 400 ml each); 7. Peristaltic pumps; 8. Reactor with stirrer (volume 4.5L).

Active base release test in dynamic system, to determine base release rates, is shown Fig. 4.

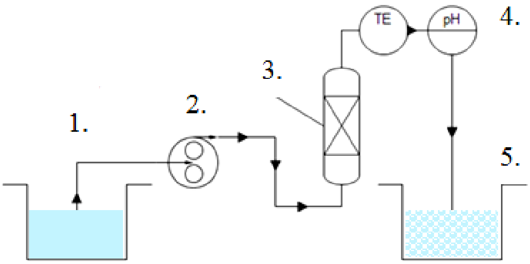


Fig. 4. Active alkaline material base release test scheme: 1. Destilled water; 2. Peristaltic pump; 3. Filter with AM; 4. Temperature and pH sensors; 5. Alkaline water for analyse.

Methods and analyzes

Total solids (TS) were determined by drying a sample at 105 °C for 24 hours. Volatile solids (VS) and ash were analyzed at 550° C in muffle furnace for 150 minutes. Chemical oxygen demand (COD) was analyzed with Hach Lange cuvettes test. Produced methane was measured with syringes contained 3M NaOH. The pH was measured using Lutron pH-208. Capacity of AM to neutralise acid was measured. Titration method with 0.1 M HCl was applied to determine released NaOH in distilled water from alkaline granules for the daily replaced water.
BET method (QuadraSorb, USA) was used to determine surface area of AM. The material was characterized using X-ray diffraction (XRD) (with CuK radiation, Rigaku Ultima, Japan) and scanning electron microscope (SEM) (Tescan Mira/Lmu, Czech Republic). Elemental analysis was performed using energy dispersive spectroscopy (EDS).
Microbiological community structures in reactors were analyzed by fluorescent *in situ* hybridization (FISH) and DAPI technique. The main steps of fluorescence in situ hybridization of whole cells using 16S rRNA-targeted oligonucleotide probes are cell fixation, consequent permeabilization, and hybridization with two probes for quantification of Eubacteria and Archaea. DAPI (4',6-diamidino-2-phenylindole) is a fluorescent stain that binds strongly to A-T rich regions in DNA. Fluorescence microscopy is used for the cells counting.

Materials

Acid cheese whey was supplied by a dairy product manufacturer „Smiltenes Piens Ltd”. The whey samples were provided by the manufacturing company, collected in five litter containers and stored at 4 °C for maximum

two weeks to avoid changes of the chemical composition. Average composition for whey: TS – 5.8-6.2%, VS – 5.2-5.8%, pH – 4.5-5.2, COD - 65.8-85.9 g O_2/L.
As inoculum, anaerobic granular biomass from a pulp and paper industry wastewater treatment plant anaerobic digester was chosen. The inoculum was kept at 37 ^oC in the incubator for 5 days prior to the experiments in order to minimize the possible influence on the experimental results. The anaerobic granules average composition was: 22.3% TS, 13.7% VS and 8.6% ash.

Modifications of alkaline material

The composition of the material consisted of aluminium scrap recycling waste, silicate glass from glass fibre factory and kaolin clay (metakaolin). The alkali – activation of raw material composition was done by modifying water glass (Na_2SiO_3+nH_2O) with an addition of sodium hydroxide (NaOH purity 97%) to increase alkali solution concentration (M_s – 1.675). The porous structure of AM develops from gasses which are emitted from aluminium scrap recycling wastes mixed with activator solution. Material was moulded in 40x40x160mm moulds and cured at temperature 80^oC for 24 h. The density of obtained material was 570kg/m^3, open porosity 35-38%, total porosity 81-84%. Compressive strength was 1.4-2.0 MPa and flexural strength was 0.6-0.7 MPa. AM granules with fraction 2-4mm and 4-5.6mm were prepared for investigation.
Two AM modifications with (AMS1) and without (AMS0) glass were tested with a fraction size of 2-4 mm. AMS1 contained sodium silicate glass waste from fiberglass production with total mixture content of SiO_2/Al_2O_3 ratio 1.7, SiO_2/Na_2O ratio 3.3 and Na_2O/Al_2O_3 ratio 0.5. AMS0 without silica glass waste contained SiO_2/Al_2O_3 ratio 0.9, SiO_2/Na_2O ratio 3.5 and Na_2O/Al_2O_3 ratio 0.2 respectively. The bulk density for granules was 313±4 kg/m^3 for AMS0 347±3 kg/m^3. Increased SiO_2 and Na_2O content (AMS1) provides higher initial leaching properties.

RESULTS AND DISCUSSION

The experimental results of doctoral thesis demonstrate step-by-step the problem solving possibility aimed at alkali releasing composite material application in anaerobic treatment of whey, ascertainment of sufficient amounts of composite material additive and evaluation of biogas production results depending on different material modifications and whey concentrations.

1. Continuous fermentation with automatic pH control

The aim of this study was to evaluate the process of acid cheese whey anaerobic digestion with respect to changes in microbial population dynamics. To estimate Eubacteria and Archaea concentration dynamics during the fermentation, FISH technique which does not require cell cultivation was applied.

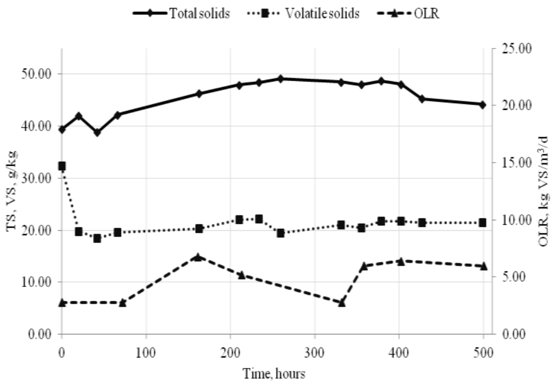


Fig. 5. Daily total solids and volatile solids from lab-scale reactor processing acid whey, and organic loading rate.

To overcome the increase in acid inhibition, ORL concentration was decreased till 2.8 VS m^{-3} day. Only at a final stage a steady state with simultaneous ORL of 6.2 kg VS m^{-3} day was achieved.

In situ hybridization analyses showed that initially in the inoculum *Archaea* constituted almost 45% from all microorganisms and represented more than $5*10^9$ cells per ml of the inoculum. After the addition of the inoculum to the whey substrate, a significant increase ($p < 0.05$) in *Archaea* concentration was observed already after 20 hours of supply and reached more than $1.3*10^{10}$ cells/ml, indicating on active growth. Similarly, an increase in *Eubacteria* counts was observed, however, this did not accounted for a significant increase ($p > 0.05$). The comparison of cell concentration with respect to ORL, did not showed such a rapid increase in cell counts, including *Archaea* (Fig. 5).

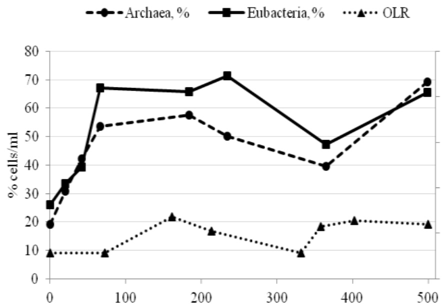


Fig. 7. Amount of *Archaea* (Arch) and *Eubacteria* (EUB) in the reactor during anaerobic treatment with various OLR.

The highest *Archaea* proportion was observed after 45 hours of fermentation when simultaneously one of the highest methane concentrations were recorded (55.9%). Rapid increase in OLR (to 6.8 VS m^{-3} day) after 80 hours of fermentation, decreased cell concentration, but when OLR was decreased to 4.9 VS m^{-3} day *Archaea* amount increased.

The average biogas yield during the study was 348.7 L kg^{-1} VS (0.56 L $L^{-1}_{reactor}$ d^{-1}) where methane yielded around 50% (Fig 3.). The obtained methane yields were between 176–278 L kg^{-1} VS. The highest methane content of 63.2 % was reached when OLR was increased from 2.8 till 6.0 kg VS m^{-3}. However, higher OLR (6.4 kg VS m^{-3}) did not let to achieve higher methane yields which could be explained with potential ammonia or long chain fatty acids inhibition. Hidraulic retention time was in range 8-10 days.

The study showed that anaerobic digestion at mesophilic and pH-controlled (7.2 ±0.2) conditions is a potential technology for treatment of undiluted acid whey. Relatively low fluctuations in microbial counts still showed that elevated *Archaea* counts are observed at the same time when biogas yields tend to increase.

2. AM characterisation

Capacity of AM produced by using activator with different M_s modules to dissolve base in distilled water was measured (Fig.8).

The optimal releasing velocity was found for AAM 12.5, because up to 24th day base released gradually with similar rate. Material with higher alkali concentration provides lower density, higher porosity and more stable and more gradual NaOH release velocity.

mIn the first day 56.5 and 59.0 % of NaOH compared with 10th day was released in the media with AAM 7.5 and 10, in contrast to AAM 12.5, where in the first day only 38.1% was released.

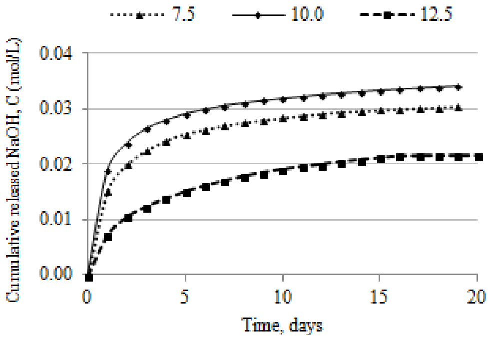


Fig. 8. Cumulative released base curves for different AM – 7.5, 10.0, 12.5.

For AM 12.5 releasing velocity was very stable from the second day till the 24th day. In Fig. 9 it was shown, that pH value for every day displaced distilled water was in range 11.45-10.55 till day 10th, but even till day 27th material AM 10 provide stable pH increase around 10.2. The other two materials showed similar behavior up to day 20th.

AM has a high porosity and low density, what leads to slow dissolution of NaOH to the fermentation media. As the pore volume and density could be controlled by alkali concentration in the solution, different materials with specific base release rate for different purpose could be used. For long fermentations and high initial pH increase necessity material AM 12.5 could be produced by changing alkali concentration during material production. For short fermentations with high initial pH materials AM 10 and 7.5 could be used. Materials provide possibility to increase pH even till day 20th.

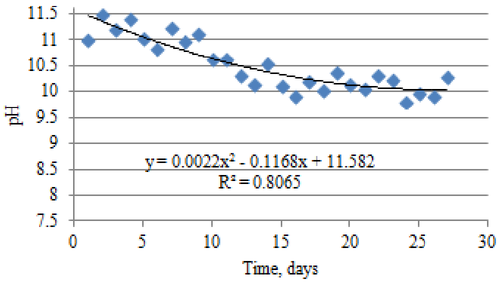


Fig. 9. pH values every day for granule of AM 10.

3. AM immobilisation properties

The mineralogical changes of the AM during the fermentation process were also examined. The alkaline material has a fairly amorphous structure. The AM before and after the fermentations was subjected to the analyses using SEM (Fig. 10).

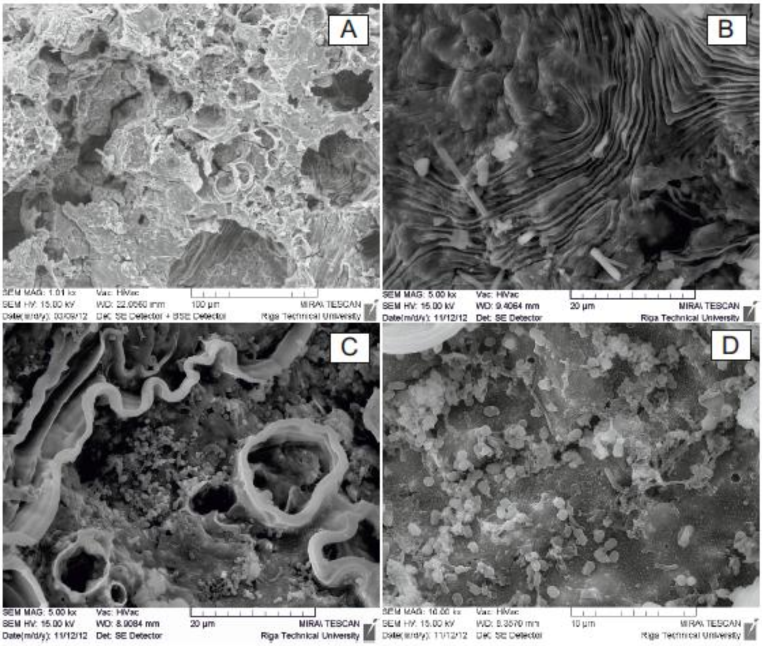


Fig. 10. Microstructure of AM studied with SEM. The AM before the fermentation is shown in a) and b). The material after the fermentation is shown in c) and d). Photographs were taken at 1000 (a), 5000 (b,c), 10 000 (d) × amplification.

The AM displays a porous material structure with wide range of pore diameter. EDX results indicate that compounding elements as Al, Si, Na and O were present at material structure however these elements should not affect the growth of microorganisms negatively. The crystals of NaOH were visible on the material before the fermentation (Fig. 10, A and B) and the SEM analyses showed that they disappear after the fermentation. It was also demonstrated that a biofilm was present on the granules at the end of the experiments (Fig. 10, C and D). The immobilization of microorganisms on solid materials has been claimed to be beneficial on expanding the possibilities to support the process [20]. In our study during cultivation over 30 days, two dominant cell morphologies were observed - mainly coccoid forms microorganisms with dimensions of approximately 0.6 µm in diameter and rod-shaped forms microorganisms in lenght of approximately 2 µm similar to those observed in the initial inoculum. With the increase of

population density on the given support, there is a greater chance of cross-feeding, co-metabolism and interspecies hydrogen and proton transfer, which may further stimulate the growth of microcolonies [21]. As AAM contain different concentrations of trace metals (Mg^{2+}, Ca^{2+}, Fe^{2+}, K^{+} cations), it is able to enhance microbial activity [22].
To compare microbiological diversity between biofilm on SM and granular inoculum, the microbiological analysis was performed with inoculum, too. Epifluorescent staining of the granules showed high variability in cell size and shape (Figure 11, left). The same observation was supported with SEM analyses (Figure 11, right). Cell size ranged from 0.2 to several micrometers and included long and short rods, cocci, coccobacilli and clubs. No visual presence of sarcina type cells was observed in the inoculums granules. FISH analysis showed that 42% of all cells belonged to the domain Archaea, 28% belonged to the Eubacteria and 30% were either too small for correct identification or did not bind to the fluorescent probes used in the study.

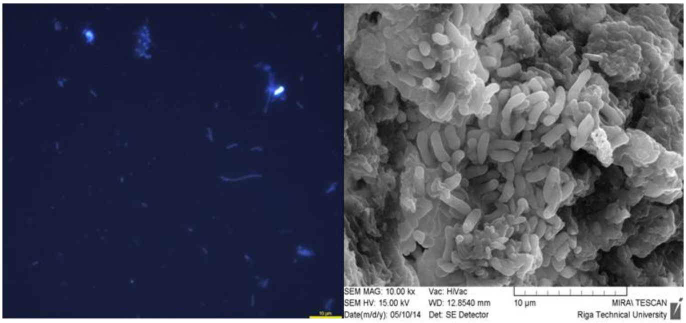


Fig. 11. Granular sludge visualized with epifluorescence microscopy (left) and SEM (right).

4. Influence of different AM modifications on AD process

In the research porous AM granules with fraction sizes 2-4 and 4-5.6 mm were investigated as materials for enhancement of methane production during anaerobic digestion process. The age factor of AM granules was researched to obtain material structural changes and its usage in fermentations. Alkaline materials with names: CMA (aged for 6 month in room conditions) and CMN (fresh) were used.
The cumulative methane graphs (Fig. 12) showed no significant difference in digesters with 10% whey. However, in digesters with 15 % whey higher methane production showed fresh AM. During the first 40 h 80-87% of total methane amount was released for digesters with 10% whey and 87-90 % for digesters with 15% whey. Comparing digesters with 15% whey with aged

AM provided 9% more methane release compared to new AM. Overall digesters with 15% whey produced 21-30% more methane comparing to digesters with 10%.
pH of substrate for the second and final day and both AM fractions is given in Fig. 12. There is no significant difference between the second day data; however final pH values are higher with aged AM for the digesters with 10 % whey.

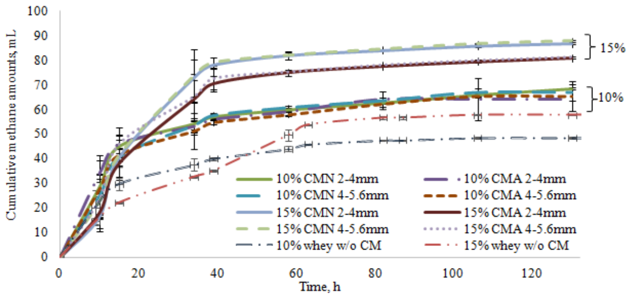


Fig. 12. Cumulative methane amounts from 10 or 15% cheese whey with new (CMN) and aged (CMA) alkaline composite material of fractions 2-4 and 4-5.6 mm.

For comparison, pH increased up to 7.82 with aged AM fraction 2-4 mm, while with fresh AM increased only up to 7.31. This could be explained by more effective digestion process and higher level of the substrate conversation to methane. The final pH for 10% digester and with AM fraction 2-4 mm showed slightly higher values.

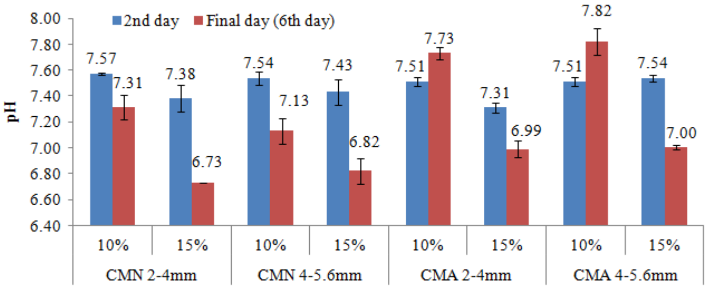


Fig. 13. pH values of digestate on the 2nd and final (6th) day.

As the most effective material for cheese whey anaerobic digestion were obtained aged AM with both fractions. It could be proven by much higher

end pH value compared with the 2nd day value. The higher end pH value in 15% whey digester was reached with aged AM.
AM addition increased biochemical methane potential (BMP) by 1.9-2.5 times (Table 1). The higher potential value was observed for the digesters with 10% whey and aged material addition. With fresh AM BMP was almost by 25% lower.
The higher BMP values were observed with fresh AM in digesters with 15 % whey. It could be explained by necessity for higher base content because of the higher substrate addition.

Table 1. Biochemical methane potential with different AM

AM type	Substrate and AM size	BMP, [mL CH_4/g COD]
New AM	15% whey + 4-5.6 mm	199.2 ± 7.7
	15% whey+ 2-4 mm	196.5 ± 6.6
	10% whey + 4-5.6 mm	239.8 ± 16.2
	10% whey + 2-4 mm	232.4 ± 6.0
Aged AM	15% whey+ 4-5.6 mm	184.1 ± 0.7
	15% whey + 2-4 mm	183.3 ± 5.1
	10% whey + 4-5.6 mm	306.1 ± 6.6
	10% whey + 2-4 mm	298.9 ±4.8
w/o AM	10 % whey	122.3± 6.8
w/o AM	15 % whey	104.5 ± 1.8

5. Influence of different AM compositions

Two AM modifications with (AMS1) and without (AMS0) glass were tested with a fraction size of 2-4 mm. AMS1 contained sodium silicate glass waste from fiberglass production with total mixture content of SiO_2/Al_2O_3 ratio 1.7, SiO_2/Na_2O ratio 3.3 and Na_2O/Al_2O_3 ratio 0.5. AMS0 without silica glass waste contained SiO_2/Al_2O_3 ratio 0.9, SiO_2/Na_2O ratio 3.5 and Na_2O/Al_2O_3 ratio 0.2 respectively.
AMS1 contained higher amount of SiO_2 and Na_2O compared to AMS0, therefore higher alkali diffusion was achieved. pH of daily displaced water was tested during the leaching test. High initial pH level was detected for both AM, however, slightly higher pH was for AMS1 granules – pH 11.6 and 11.4 respectively. The pH level decreased during leching test and with decrease of leached alkali pH level decreased to pH 6.8 after 25 day test.
The cumulative methane production with 10% whey and AMS1 are given in Fig. 14. The results indicated that the concentration 0.5 g AMSI/g VS showed slightly higher methane production rates, hovever, cumulative

methane yield at the end of experiment with AM addition didn't show significant difference. Methane yields with AM additive were similar at the end of the fermentation period, but were 11% higher than in the digesters without AM.

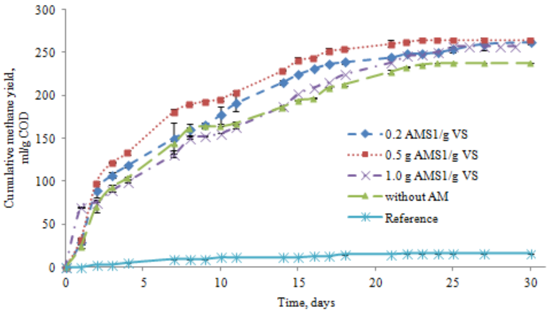


Fig. 14. Cumulative methane production with 10 vol% whey concentration and 0.2, 0.5, 1.0 g AMS1/g VS during 30 days.

The cumulative methane production with 15% whey and AMS1 are given in Fig. 15. Rapid methane production rate increase was observed for the digesters with 1.0 g AMS1/g VS from the 7th day while for the digesters with lower concentration and without AM had long inhibition periods. Total CH_4 yield for the digesters with 1.0 g AMS1/g VS on day 16 provided an overal increase of 140% when compared to the digester without AM while the digesters with lower concentrations provided 40-41% increase. The digesters with lower AM concentration provided continuous CH_4 production rate increase after day 16, however delayed digestion was observed for the digester with the lowest AM concentration.

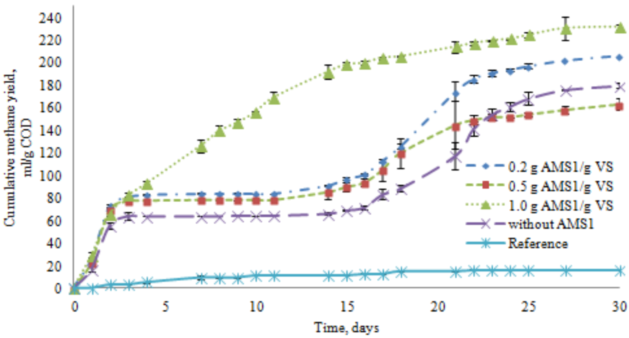


Fig. 15. Cumulative methane production with 15 vol% whey concentration and 0.2, 0.5, 1.0 g AMS1/g VS during 30 days.

At 30th day of the experiment the cumulative CH_4 production was 206 ml/g COD for 0.2 g AMS1/g VS, 163 ml/g COD for 0.5 g AMS1/g VS, 231 ml/g COD for 1.0 g AMS1/g VS and 177 ml for the digester without AM. The cumulative CH_4 production increase at the end of experiment was 14 to 29% higher for the digesters with AM compared to digesters without AM. The cumulative methane production for digesters with AMS0 is given in Figure 6. The amount of AM was increased due to lower buffering capacity of AMS0 compared to AMS1. The results indicate that increased CH_4 production was detected at day 2. Increase in CH_4 production was 17-52% when compared to the digesters without AM. Continuous digestion was observed for digesters with AM, however, an inhibition period was observed for digesters with 0.5 g AMS0/g VS and without AM. The adaption period was prolonged until day 16. The digester with 1.0 g AMS0/g VS had no inhibition period, however, the digester with 2.0 g AMS0/g VS had low inhibitory effect until day 7 and then methane production rate increase was observed. At the end of experiment on day 30 the average volume of CH_4 was 216 ml/g COD for the digesters with 0.5 g AMS0/g VS, 207 ml/g COD for 1.0 g AMS0/g VS, 242 ml/g COD for 2.0 g AMS0/g VS and 117 ml/g COD for the digesters without AM. The total increase in CH_4 yields from the digesters with AM was from 76 to 106 % compared to the digesters without AM.

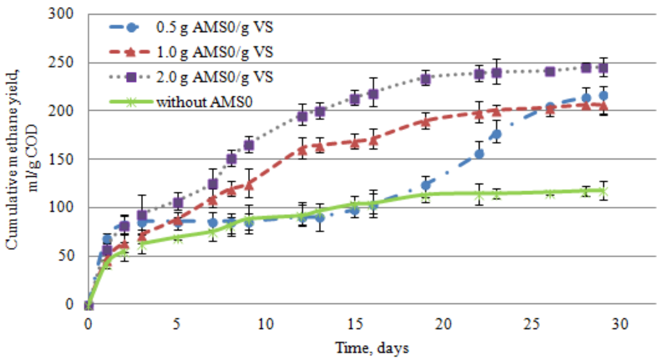


Figure 16. Cumulative methane production with 15 vol% whey concentration and 0.5, 1.0, 2.0 g AMS0/g VS during 30 days.

AM addition in the digesters with 10% whey increased BMP by 10.2 % when compared with digesters without alkaline material additive (see Table 2). The highest potential value (264.6 mL CH_4/g COD) was observed for the digesters with 0.5 g AMS1/g VS. The highest BMP value (231.2 mL CH_4/g

COD) with 15% whey and AMS1 addition was observed with concentration 1.0 g AMS1/g VS. The BMP value was increased to 37.1% with AMS0 additive when compared to the digesters without AM additive.
It was observed that AMS0 had slightly higher BMP values (6%), comparing BMP results in the digesters with 15% whey and both material modifications, but as cumulative methane curves showed more unstable process, AMS1 additive was chosen as more appropriate for biogas production.

Table 2. Parameters at the end of the batch experiment

No	Whey concentration, %	Material modification	AM addition, g/g VS	pH	TS, %	VS, %	BMP, mL CH_4/g COD
1	15	AMS1	0.2	7.29±0.08	0.46±0.09	0.20±0.02	203.58
2			0.5	7.54±0.12	0.48±0.13	0.21±0.01	204.66
3			1.0	7.85±0.28	0.38±0.04	0.17±0.05	231.21
4		AMS0	0.5	7.14±0.02	0.58±0.06	0.23±0.07	219.15
5			1.0	7.32±0.08	0.55±0.11	0.22±0.06	209.63
6			2.0	7.48±0.19	0.48±0.12	0.18±0.07	245.49
7		without	0.0	6.65±0.21	1.24±0.14	0.79±0.08	179.23
8	10	AMS1	0.2	6.71±0.05	0.32±0.09	0.21±0.03	262.92
9			0.5	6.98±0.18	0.26±0.06	0.12±0.01	264.59
10			1.0	7.21±0.09	0.15±0.08	0.09±0.02	258.36
11		without	0.0	6.95±0.17	1.05±0.09	0.59±0.15	237.54

pH values at the end of experiment showed clear trend – with increased AM addition pH values increased but remained in the range optimal for anaerobic consortia.

6. Active NaOH releasing test

Three water flows 1.9, 2.7 and 6.0 L/h were provided throught filter filled with AM (Fig. 17, left).

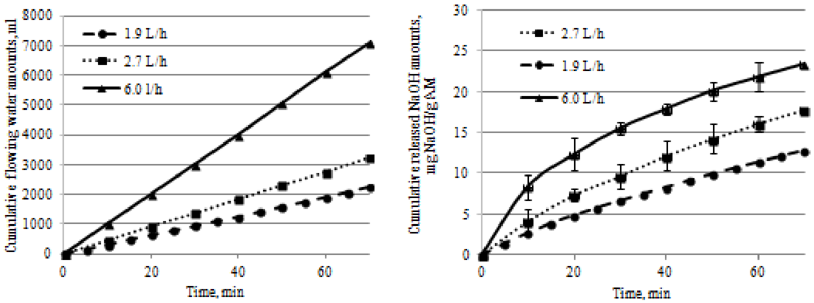


Fig. 17. Analyse of water flows in active system for AM capacity determination and cumulative released NaOH amounts

It is seen that flows 1.9 and 2.7 L/min provides very stable base release rate and could be used in continuous fermentation.

7. Continuous fermentation

The novel material is produced from recycled wastes, so even if it requires activation with NaOH and temperature (80 °C), the total cost of material is expected to be lower than for other technologies, which are used in producing methane from acid whey. AAM added to the reactor system before the start of experiments requires no additional pH adjustment, which allows to use less sophisticated pH control. pH was maintained in range 7.2±0.05.

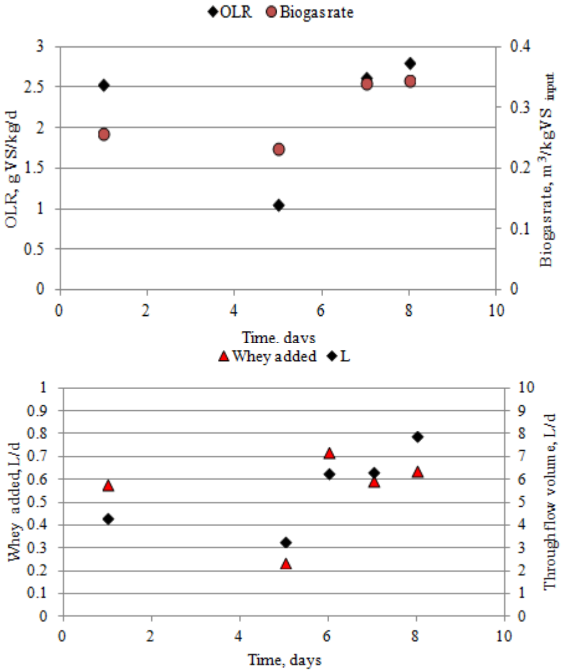
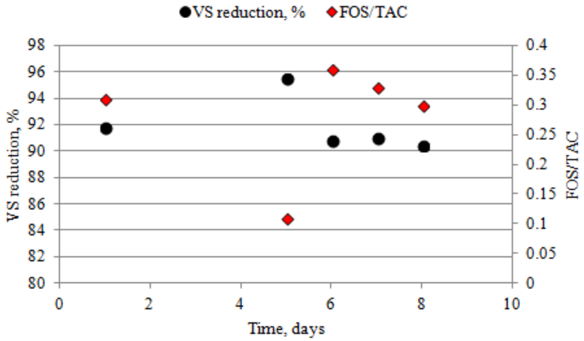


Fig. 18. Biogas rate for different OLR and volumes of added whey and digestate volumes flowing through filter with AM.

Anaerobic treatment of acid whey using system with alkaline materials for the controlling of pH showed an HRT from 5-7 days, corresponding to an OLR of 1.7-2.7 g VS/kg/d, with a VS reduction of 84-96% and biogas yield of 0.25-0.32 m^3/kg VS/d. Achieved methane content was 64 % (Fig. 19, right).



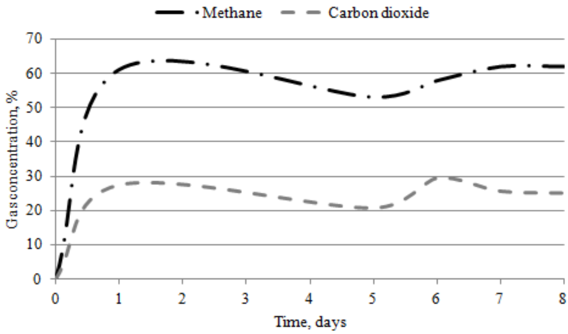


Fig. 19. FOS/TAC ratio and VS reduction according average methane and carbon dioxide content per day.

Activity of AM was one week. The average digestate flow through a filter was 1L per gVS per kg AM, the corresponding added whey and digestate volume ratio was 1:10.

CONCLUSIONS

1. Dairy waste, like whey, is an attractive substrate for anaerobic treatment, because it of high energetic value, it is easily biodegradable and accessible for microorganisms.
2. It is possible to obtain biogas production rate of 0.35 $m^3/kg_{VS}/d$ with OLR of 2.8 $kg_{VS}/m^3/d$ in a continuous reactor with automatic pH system, and to achieve methane concentration of 52%.
3. The alkali-releasing material produced from aluminium and glass fibre production waste is a very attractive material for pH control in anaerobic digestion systems and can also be used as a support for microorganism immobilisation.
4. The optimal alkaline material concentration with whey additive of 10% is 0.5 g_{AM}/g_{VS}, but with whey additive of 15% - 1.0 g_{AM}/g_{VS}, because of higher biomethane yield up to 22% compared to experiments without AM additive.
5. Influence of technological parameters on base-releasing rates and ability to increase pH were evaluated and it was concluded, that, in whey anaerobic digestion process, it is recommended to use AM fraction of 2-4 mm with SiO_2/Al_2O_3 ratio of 1.7, SiO_2/Na_2O ratio of 3.3 and Na_2O/Al_2O_3 ratio of 0.5, using 1 kg AM per 0.03 m^3 reactor volume.
6. Material's ability to control pH was evaluated in range of 7.2±0.05 in a continuous reactor and it was concluded, that digestate flow through a filter, that contains AM, should be 3 $L/g_{VS}/d$ while OLR is 1.7-2.7 kg $VS/m^3/d$ and obtained average biogas rates are 0.25-0.32 m^3/kg VS/d; material should be changed every seven days.

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1. A method of anaerobic digestion of acidic whey in four-chamber system. E.Skripsts, K. Rugele, J. Rubulis, V. Dubrovskis. EU patent No. EP13198723.2, 2014 (*Accepted*).

2. Method of using alkali-activated non-cement binders for producing biogas from cheese whey. K. Rugele, E.Skripsts, D.Bajare, T. Juhna, S. Larsson. EU patent No. EP12199477.6, 2013 (*Accepted*).

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