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TREATMENT OF SEWAGE SLUDGE FOR FUEL CELLS SUPPLY

Abstract

Sewage sludge represents the main fraction of municipal waste generated in Poland. Since its production increases rapidly, an effective method for its decomposition needs to be found. Due to conventional energy sources depletion, new solutions allowing for renewable energy production are recommended. One of the methods for conversion of sewage sludge into green energy is application of the fuel cells feeding with gaseous residuals of sewage sludge, obtained as a result of different thermal or biological processes. Such a system can be easily modified and adjusted to the individual needs, which makes this solution very promising. The article analyses biological and thermal processes that can be used in converting sewage sludge into a useful input for various types of fuel cells.

Key words

Sewage sludge, fuel cells, hydrogen, energy

Introduction

In 2010 sewage sludge production in Poland was about 520 000 tDS/a, and the most popular way for its utilization was deposition on the landfills [1]. This trend seems to be observed today, with the huge and significantly increasing sewage sludge quantities. In a few months Poland will face the real problem connected with the new legislation. As a result of the Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste [2], deposition of sewage sludge directly on landfills is prohibited. In Poland it will have to be applied starting from January 1st, 2016. It means that soon the volume of sludge will increase rapidly and the techniques for an effective sewage sludge utilization will be sought for.

The main component of sewage sludge is water (ca. 70-90%), and the remaining part is represented by organic matter (50%) and mineral fraction (50%) [3], which makes this waste material interesting for several industrial applications. High probability of releasing some toxic compounds like heavy metals into environment, practically excludes agriculture utilization of sewage sludge. However, a substantial organic load allows for converting this material into the form useful for energy generation.

To achieve this goal, in most cases the organic solids must be transformed into either gaseous or liquid phase, which is then used in special installation to energy production. Few processes allow for applying the organic matter directly in its raw, natural form (i.e. combustion). The techniques for final energy generation differ and depending on the expected results a concrete equipment should be applied. For both heat and electricity generation it will be a CHP unit (combined heat and power), for sole heat production it may be a simple engine, and for sole electricity some kind of turbine can be used. One of the newest devices applied for power generation based on the electro-chemical reactions is fuel cell (FC).

Fuel Cells

The general purpose of fuel cells is to convert the energy included in the ions into electrical power through chemical reaction. Fuel cell acts like battery, which does not need to be previously loaded. Fuel cells are built from two electrodes: cathode and anode, separated by the electrolyte membrane, which enables cations or anions flow between electrodes. The scheme of typical fuel cell is presented at Figure 1.

Six basic types of fuel cells are recognized [4-5]: phosphoric acid fuel cell (PAFC), polymer electrolyte membrane fuel cell (PEM), direct methanol fuel cell (DMFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). Simple characteristics of these systems are given in Table 1.

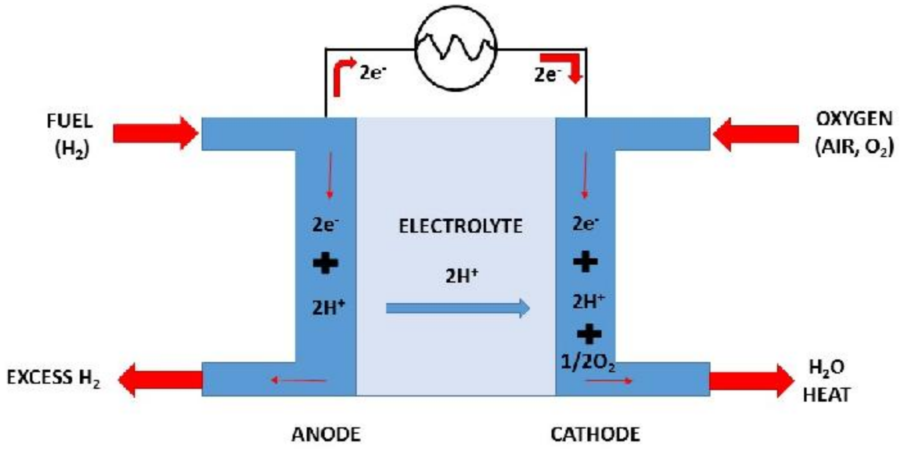

Fig. 2 Typical fuel cell.
Source: Author's

Table 1. Differences between basic types of fuel cells

FC type	Mobile ion	Operating temperature	Applications
PAFC	H^+	220°C	CHP units, about 200 kW
PEM	H^+	30-100°C	Mobile applications, vehicles, low power CHP units
DMFC	H^+	20-90°C	Low power portable electronic systems
AFC	OH^-	50-200°C	Space vehicles
MCFC	CO_3^{2-}	650°C	Large scale CHP units (up to 1MW)
SOFC	O^{2-}	500-1000°C	Wide range of CHP units (2kW-multi MW)

Source: [5]

Using fuel cells as an energy generator brings many benefits, including increased efficiencies and the lack of dangerous pollutants emissions [6]. Apart from hydrogen, which is employed in FCs most often and directly, there are other chemical compounds that can be used for fueling FCs and for hydrogen generation by reforming. These are: methane (CH_4), ammonia (NH_3), methanol (CH_3OH), ethanol (C_2H_5OH) or gasoline (C_8H_{18}) [5]. The examples of the reforming reactions are presented below ((1)-(3)) [5]. Depending on the type of fuel cell used for energy production, different requirements for fuel content are considered. For gaseous fuels they are summarized in Table 2.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$C_nH_m + nH_2O \rightarrow nCO + \frac{m}{2} + n\ H_2 \quad (2)$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (3)$$

Table 2. Fuel requirements in its application for different fuel cells

Gaseous compounds	PEM	AFC	PAFC	MCFC	SOFC
H_2	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (>10ppm)	Poison	Poison (>5%)	Fuel[a]	Fuel[a]
CO_2 and H_2O	Diluent	Poison[b]	Diluent	Diluent	Diluent
CH_4	Diluent	Diluent	Diluent	Diluent[c]	Diluent[c]
S (H_2S and COS)	unknown	unknown	Poison (>50ppm)	Poison (0.5ppm)	Poison (>1.0ppm)

[a] CO reacts with H_2O producing H_2 and CO_2, CH_4 with H_2O reforms to H_2 and CO faster than reacting as a fuel at the electrode.

[b] The fact that CO_2 is a poison for AFC rules out its use with reformed fuels

[c] Fuel in the internal reforming MCFC and SOFC.

Source: [5]

There are many processes and technologies that allow to provide conversion of solids into gaseous phase. It can be done by either thermal or biological processes. Among thermal processes both pyrolysis and gasification can be performed. Biological procedures that can be utilized for gas fuels production are anaerobic digestion or direct fermentation to biohydrogen.

Thermal processes

Gasification is the process in which solid fuel is converted into gas in the presence of oxygen or other oxidizing agent like air or steam [7]. At high temperatures of 800-1400°C, oxidation of carbon and cracking of tars and gases take place [8]. As a result of these processes, a high-quality flammable gas is produced. Its calorific values range from 4 MJ/m^3 (when air is used as gasifying agent) to even 10 MJ/m^3 (in the case of oxygen utilization); therefore, it can be used for heat and power generation [8]. The gas obtained after gasification of sewage sludge contains mainly carbon monoxide and hydrogen [7, 9]. Thus, it is considered for fueling the fuel cells for electricity production. Other gaseous compounds are: methane, ethane, ethene, nitrogen, and various contaminants. Nipattummakul and co-workers [10] in their work showed that steam gasification of sewage sludge might be very perspective and the hydrogen yield for the process conducted at 1000°C is 0.076 $gH_2\,g^{-1}$. Results of the other work [11] confirm this finding and indicate that the presence of water vapour and some catalysts like dolomite, alumina or olivine increases the content of hydrogen in obtained syngas. Some data are available that presents the optimal process condition for the efficient syngas production. These recommendations include: low (110-165°C) temperature in the dryer, proper grinding of the sludge prior gasification and utilization of indirectly heated dryer [8].

Latest research in the field of sewage sludge gasification concerns to increasing the hydrogen content in producer gas. It can be done by applying the two-stage gasifier [12]. Moreover, the tar and ammonia content after the process can be significantly reduced by using of the Ni-coated distributor. The tar removal was also a subject of other investigation [13]. It occurred that using a dolomite as a primary catalyst can increase the tar removal efficiency up to 71%. In the same study it was proven that the throughput influences the producer gas composition and the higher throughput is the lower hydrogen content in syngas.

One of the newest ideas for sewage sludge gasification is a method called supercritical water gasification (SCWG) technology, which involves the sludge hydrolysis in supercritical water followed by gasification of released oligomers [14]. Numerous studies have been performed both without and with the use of different catalysts [15-19]. Zhang and co-authors (2010) [15] investigated the influence of the type of sludge on hydrogen production during SCWG performed at 500°C and 37 MPa for 2 hrs. Their results show that the primary sludge gives more energy in the form of hydrogen (32%) than either secondary sludge (20% of H_2) or digested sludge (20% of H_2). Other research presents the comparison of the efficiency of SCWG of sewage sludge performed with or without K_2CO_3 as catalyst [16]. In this case the catalyzed gasification occurred to be less effective (47% of H_2) than the non-catalyzed process (47% of H_2). Some research were performed to improve the efficiency of the SCWG of sewage sludge by application different catalysts. Xu and Antal in their work used a coconut shell and activated carbon as a catalysts and obtained the syngas with the hydrogen content of 42% [17]. Other work [18] shows that sodium hydroxide is much better catalyst for SCWG of sludge and allows to product the gas with the hydrogen content higher than 76%. Another method studied recently for improving the gasification efficiency regarding H_2 yield is the conditioning the sludge with lime (CaO) prior to the thermal process [19]. The results obtained in discussed work indicate that the increase in the hydrogen production is caused by complete conversion of CaO into $Ca(OH)_2$ and its further distribution over the sludge matrix.

Second thermal process that allows for producing gaseous compounds used for feeding fuel cells is pyrolysis. In this process organic fraction of sewage sludge is thermally decomposed. The typical process conditions are: temperatures between 300 and 900°C, ambient pressure and oxygen-free atmosphere [7, 8, 20]. As a results of the pyrolysis different products are generated, depending on process conditions and method used. These are: solid char, water, water-soluble organics, tars and pyrolytic gas [20]. The final products may be grouped into three fractions [7]:

- solid (pyrolytic coke), charcoal including inert substances, dust, heavy metals;
- liquid, a mixture of oils, tars, water and organic compounds;
- gas (pyrolytic gas).

The efficiency of gas production is related to moisture content in sewage sludge. To achieve a high-calorific fuel drying procedure should be performed prior to pyrolysis [8]. Usually the gas includes: H_2, CH_4, CO, CO_2, N_2. Such pyrolytic gas can be utilized as a gas fuel itself [20].

Decomposition of sewage sludge during pyrolysis was a subject of many investigations. One of them [21] proved that the calorific value of gas produced as a result of such thermal process is about 23 MJ/m^3. Moreover, the composition of pyrolytic gas was determined as CO, CO_2, H_2 and C_1-C_4 hydrocarbons like CH_4, C_3H_3, C_2H_2, CH_2CO. The Authors showed that the share of gaseous form of final products increases with increasing the temperature of reaction. The changes of gas composition during pyrolysis were studied also by Conesa and co-workers [22]. They specified the three stages of pyrolysis by both temperatures and generated gaseous compounds. The first stage takes place at 250°C and leads to releasing such products as methane, carbon dioxide, acetic acid and water. Second one is performed at 350°C and brings also other compounds, which are prevalent. During the last stage (at 550°C) hydrogen, methane, carbon dioxide, alcohols and hydrocarbons are produced. This shows the importance of temperature of pyrolysis and its influence on further gas composition for its utilization in fuel cells. One of the recently published study concerns the flash pyrolysis of sewage sludge in a conical spouted bed reactor [23]. In this study the influence of the process condition on the product yields was investigated. It was proved that the liquid is the main product of the thermal process conducted at high temperatures, with the maximum at 500°C. Further increasing of the temperature led to the secondary reactions like cracking, which caused the decrease in the liquid yield and the increase in gas products yield. The highest concentration of H_2 in the gaseous phase was obtained at temperatures between 500 and 600°C as a result of both cracking reaction and dehydrogenation promoted by the catalytic effect of the inorganic fraction.

In other study Fan and co-workers [24] also investigated the influence of process temperature on the products yields during the pyrolysis of different municipal sewage sludges in a gas sweeping fixed-bad reactor. The results of their work confirmed that the main product of the sewage sludge pyrolysis is liquid (above 40% wt at 700°C), and the maximum gas production equals ca. 27.5 % wt takes place at temperature of 700°C. Hydrogen releasing started at 450°C and the rate increases vigorously from 600 to 700°C indicating sharp dehydrogenation and decarbonylation reactions.

To improve the yield of hydrogen in gaseous phase obtained as a result of sewage sludge pyrolysis new methods has been developed recently. One of them called biophysical drying (BDS) coupled with fast pyrolysis was described by Han and co-workers [25]. In this process good moisture removal rates are obtained and the energy consumption is decreased significantly compared to the traditional thermal drying. In consequence, the syngas and char yields of BDS pyrolysis were higher than those achieved for traditional process. Maximum syngas yield with H_2 content of 42.6% reached 33.4% for BDS pyrolysis performed at 900°C.

As it is described above both thermal processes: gasification and pyrolysis might be used for the conversion of sewage sludge into a valuable, gaseous product, which can be then used in fuel cells for electricity production. These processes are similar and have many benefits compared to incineration. Many ideas are presented that combine both the process for increasing the efficiency of sewage sludge degradation and its conversion into energy. One of them is Thermoselect Technology, which involves pyrolysis of solids and then gasifying of the obtained coke into syngas [26]. Another process – Noelle Conversion – is performed at high temperatures (>2000°C) and pressures (>3.5 MPa) [27]. Some works describe pyrolysis gasifiers as an equipment adequate for sewage sludge into energy conversion [20]. Very promising method being a combination of both pyrolysis and gasification (MWDPG – microwave-induced drying, pyrolysis and gasification) was described by Menéndez and co-workers [28]. Data related to an application of these thermal processes for electricity production in fuel cells is still very limited. An interesting work concerning two-step process has been shown recently by Sattar et al [29]. The investigators gasified different biochars formed via intermediate pyrolysis performed at 500°C obtaining high-quality syngas. The results suggest that the hydrogen production for all tested chars except woods was the highest at temperatures in range from 700 to 750°C and for the sewage sludge biochars it increased sharply once again after reaching 850°C. For sewage sludge biochars the highest H_2 yield (ca. 57 %) was observed at 850°C, however, this kind of chars occurred to be the least efficient for steam gasification compared to other tested materials. In the research presented by Jayaraman and Gökalp [30] it is stated that the pyrolysis, combustion and gasification of the dried sewage sludge may be considered as a primary pyrolysis and secondary reaction and the material is converted into tar, char and gas during the first step of the process performed at all tested ambiences (steam, argon, oxygen or their mixtures). The complete burn out of sewage sludge chars took place at 950°C and the gasification temperatures are lower than those obtained for *miscanthus* samples.

Biological processes

A second group of methods applied for feeding fuel cells by different gaseous compounds obtained from sewage sludge conversion is represented by biological processes. The most popular and perspective nowadays is application of anaerobic digestion (AD) as well as dark fermentation. First one is a multistage conversion of organic matter in which fermentative processes play the most important role. Second one in turn can be considered as a one of the stages of the previously mentioned AD. As a result of these processes different products are obtained. While dark fermentation leads mainly to hydrogen generation, its extension with further steps gives in consequence biogas – the gaseous mixture of two main compounds, namely methane and carbon dioxide.

Anaerobic digestion has been used successfully for sewage sludge degradation for many years. It is a conversion of organic matter into gaseous phase by metabolism of some specialized species of anaerobic microorganisms. The presence of oxygen is thus unwelcome. This process is carried out both at mesophilic (ca. 35-40°C) or thermophilic (ca. 55°C) conditions [30]. During several complex biochemical reactions organic structures like carbohydrates, lipids and proteins are transformed first to simpler compounds (sugars, fatty acids and amino-acids, respectively), subsequently to acetic acid and hydrogen, and finally to methane and carbon dioxide [32]. This biological process may be performed as a mono-substrate digestion (when only sewage sludge is used as a feedstock) or as a co-digestion (when the mixture of sewage sludge with other organic matter(s) is utilized) [33]. Both ways are beneficial and effective from the economical point of view, but co-digestion may bring additional advantages, like higher methane content in produced biogas or higher efficiency in biogas production.

In 2010 Dubrovskis with co-workers [34] compared biogas yield and methane production from different types of sludge. They determined that both biogas and methane production depend on the kind of sludge and the highest energetic efficiency can be expected when fresh sludge is utilized (biogas – 397 dm^3 kg_{VSd}^{-1}; methane – 233 dm^3 kg_{VSd}^{-1}). The worst results were obtained for longterm stored sludge (biogas – 264 dm^3 kg_{VSd}^{-1}; methane – 122 dm^3 kg_{VSd}^{-1}). In other research [31] the influence of temperature condition on methane production was studied. It was shown that mesophilic single-stage AD of sewage sludge is more effective than thermophilic process, though the differences are insignificant (451.1 and 416.0 cm^3 CH_4 g_{VSrem}^{-1}, respectively). These Authors confirmed also that co-phase process (meso- and thermophilic) may bring similar results to those for single-stage mesophilic process, with methane yield between 424 and 468 cm^3 CH_4 g_{VSrem}^{-1}. Recently published work of Liao et al. [35] indicates that the role of thermal pre-treatment in biogas production from sewage sludge is significant. Such technique can improve the solid-state anaerobic digestion efficiency both increasing biogas yield by 11% and decreasing the fermentation time from 22 to 15 days.

Possibility of an effective co-digestion of sewage sludge with other organic wastes was investigated by Sosnowski and co-workers [33]. In their studies organic fraction of municipal solid waste (OFMSW) was used as a co-substrate. The obtained results indicated that co-digestion was more efficient than single digestion of sewage sludge (460 and 240 dm^3, respectively), and that the cumulative biogas production in the case of co-digestion increased with increasing the proportion of OFMSW. Recently Nghiem and co-workers [36] have analyzed co-digestion of sewage sludge with glycerol. In the pilot-scale experiments they proved that crude

glycerol can be used as a co-substrate for on-demand biogas production from sewage sludge, and that the additional volume of methane produced was 1.3 m^3 dm^{-3} of glycerol. This is in agreement with the other studies on such co-digestion [37] that showed an efficiency increase in biogas production with the increase of the volume of glycerol added, until its critical concentration of 1% (v/v) in the feedstock. On the other hand there are some works showing that crude glycerin may influence the biogas production negatively when mixed with sewage sludge [38]. Negative effect of co-digestion of sewage sludge with different microalgae species was described recently by Caporgno et al. [39]. Both biogas and methane production observed in co-digestion were significantly lower than for sole sewage sludge digestion. These results were the same for the mesophilic and thermophilic conditions.
There are at least a few papers describing either today existing power plants combining anaerobic digestion with fuel cells or their lab-scale simulations. De Arespacochaga et al. [40] in their work described the pilot-scale plant for sewage biogas production and fueling SOFC. The system was operated at O/C ratio of 2, stack temperature of 800°C and reforming temperature of 550°C. The obtained efficiency for co-generation was about 60%, and the heat-to-power ratio was 0.8. The preliminary result suggest that afterburning of some volume of biogas is necessary to achieve thermal self-sufficiency. The example of the simulation of the system with MCFC is the paper presented by Verda and Sciacovelli [41]. These authors used the experimental data from the digester to build the model of such system and to investigate some variations. The obtained results indicate that the costs of such unit are comparable with market prices of electricity and the expected efficiency should not be lower than 50%. One of the latest work concerning the system of fuel cells feeding with biogas is simulation study written by de Arespacochaga et al. [42]. These Authors compared the economic and technical aspects of different FC systems with traditional cogeneration combining micro-turbine and internal combustion engine. MCFC occurred to be the most efficient with the capability of improving the electrical self-sufficiency of the industrial-scale power plant by 60%. Although the systems consisting of SOFC were characterized by technical performance similar to those systems with combustion engines, their industrial deployment is still unprofitable economically. The general conclusion of this work is that both biogas producers and fuel cells manufacturers should work together on the field of such combining systems to overcome the limitations and improving existing small-scale power plants.

Hydrogen production via fermentation (dark-fermentative H_2 production) is the other way to convert sewage sludge into feedstock for fuel cells. This method is environmentally friendly and economically reasonable, so it is attracting more and more attention. The process is carried out by fermentative microorganisms like facultative (*Klebsiella pneumoniae, Enterobacter* and *Bacillus sp.*) and strictly anaerobic bacteria (*Clostridium butyricum*) [43]. The overall aim is to keep the electron balance between donors and acceptors. A key role in this process is played by the group of enzymes (hydrogenases), which either oxidize H_2 to protons or reduce protons to release molecular hydrogen [44]. H_2 production during dark fermentation can be described with two equations, (4) and (5), given below:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{4}$$

$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2CO_2 + 2H_2 \tag{5}$$

The theoretical maximum hydrogen yield in the above reactions is 4 moles of H_2 per one mole of glucose [44]. Moreover, simultaneously either acetate or butyrate is formed. Similarly to anaerobic digestion, the process can be performed in mesophilic or thermophilic conditions. Other important parameters are pH of the fermentation broth and C/N ratio. Due to the fact that different VFAs are generated, the pH should be continuously monitored to avoid rapid decrease and further inhibition of microorganisms' growth.

Although its expected potential is high, the available data on biohydrogen production from sewage sludge is very limited. Some of the sources claim that dark fermentation of sewage sludge in insufficient (0.16 mg H_2 g^{-1} of dried solids (DS)); on the other hand others recommend a pre-treatment step for increasing the efficiency of biohydrogen production [45-46]. Cai and co-workers in 2004 [47] stressed the importance of alkaline pre-treatment and initial pH for further H_2 production. High initial pH value for raw sewage sludge (pH>10) was beneficial for renewable energy production. The highest H_2 yield was obtained for alkaline pre-treated sewage sludge at initial pH of 11.0 (16.9 cm^3 g^{-1} DS). Moreover, it occurred that the higher initial pH led to slower consumption of this gaseous bioproduct, which makes the process more stable. Similar investigation of the influence of sewage sludge pre-treatment on further H_2 production was performed by Xiao and Liu [48], who applied sterilization as a pre-treatment step. The results indicated that such operation accelerate biohydrogen production and reduce methanogens activity. The observed increase in H_2 generation was very high (16.3 cm^3 g^{-1} volatile solids (VS) in comparison with 0.35 cm^3 g^{-1} VS obtained for untreated sewage sludge). Additionally, due to NH_4^+ production, only small decrease of pH took place; volatile acids were neutralized with the ammonia. Apart from the pre-treatment step prior to sewage sludge dark fermentation, also co-fermentation of sewage sludge with different organic wastes for biohydrogen production is also considered. Zhu and co-workers [49] found this process very beneficial for H_2 production, when the mixture of primary sludge, activated sludge and food wastes is used. All combinations of these wastes led to an increase in hydrogen production potential, and the maximum yield of 112 cm^3 g^{-1} VS was obtained for co-digestion of all three wasted components. According to the Authors, such improvement was a consequence of the increase in the buffer capacity. Similar investigation was conducted by Kim et al. [50], who showed that co-fermentation of food waste with sewage sludge brings better results than H_2 production from food waste only. Tyagi and co-workers [51] also studied the potential of co-fermentation of sewage sludge with OFMSW (organic fraction of municipal solid waste). The process performed at thermophilic conditions occurred to be much more efficient in hydrogen production than sole anaerobic digestion of sludge. The maximum yield of 51 cm^3H_2 g^{-1} VS consumed was obtained at OFMSW to mixed sludge ratio of 5:1 and at TS concentration of 20%. Another work in the field of co-digestion of sewage sludge for hydrogen production was presented by Kim et al. [52]. These Authors used the mixture of the sludge and rice straw in two different systems: one-stage for methane production and two-stage for combined generation of hydrogen and methane. The results showed the great potential of the two-stage system for bioenergy production (H_2 production of 21 cm^3H_2 g^{-1} VS at the first stage and CH_4 production of 266 cm^3CH_4 g^{-1} VS at the second stage of the process). The total bioenergy yield obtained for the combined system was almost 60% higher than the yield for one-stage system.

Summary and conclusions

The presented short review of potential applications of sewage sludge for feeding fuel cells confirms the significance of research in this field and its potential impact on closing the material and energy loop, promoted among others by the European Commission's strategy "Innovating for Sustainable Growth: a Bioeconomy for Europe". Several knowledge gaps have been identified, including new catalysts for the efficient syngas generation or new bacterial strains for hydrogen fermentation. Taking into account the fact that the global volumes of sewage sludge will be increasing, good practices in sewage sludge management will become more and more important as well. Due to the low efficiency of some of the techniques analyzed, further engineering work is also necessary, with new methods for sewage sludge utilization designed and tested in the field. Application of safe, economics and ecological products based on sewage sludge in microbial fuel cells is a viable technological solution, which offers also promising industrial prospects by providing solutions to the acute problems resulting from the increasing quantities of sewage sludge production. Reinventing the current approach to this waste through its processing and feeding into the fuel cells seems to be an economic and safe method of waste disposal and can be performed in different ways or systems.

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