Optimization of the operating parameters of microbial electrolysis cell assisted anaerobic digester for generating bioenergy from an ethanol stillage

P. G. Velichkova*, M. R. Popova, A. T. Angelov

Department of Engineering Geoecology, University of Mining and Geology "St. Ivan Rilski", Sofia 1700, Bulgaria

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In order to improve the process of biomethanation, a hybrid system anaerobic digester - microbial electrolysis cell (AD-MEC) was created. The influence of different technological parameters on the operation of the installation in the purification of ethanol stillage was studied. It was found that 0.8 V is the optimal external load at which 80 % of methane in the biogas and a yield of 18.10 l CH_4/kg COD is reached. The applied external voltage of 1.0 V did not promote the yield of methane (14.13 l CH_4/kg COD), but the amount of methane in the biogas was 70 %, which is higher than the 52 % obtained for a stand-alone process. The influence of working pH and temperature was studied at different values for the biomethanation process. The best results for the hybrid AD-MEC system were obtained at pH 7.5 and temperature 35 ˚C. Such values are characteristic of the biomethanation process, as methanogenic bacteria are very sensitive to abrupt changes in the environment (pH below 6.8, presence of oxygen, very low or high temperatures, etc.).

Keywords: anaerobic digester, microbial electrolysis cell, ethanol stillage, bioenergy, parameters

INTRODUCTION

Anaerobic digestion (AD) is a key technology for converting organic matter into methane-rich biogas. However, there are still limitations such as destabilization and poor decomposition of some substrates, as well as low biogas production [1-3]. This is mainly due to the accumulation of volatile fatty acids (VFAs), which rapidly lower the pH of the medium and the process becomes unstable.

A microbial electrolysis cell (MEC) system is similar to that of a microbial fuel cell and overcomes the thermodynamic barrier by means of small applied voltages (0.5-1.0 V). This makes the process independent of the reactor surface area, which benefits the economic feasibility. The biocatalyzed electrolysis achieves this by utilizing electrochemically active microorganisms, which convert dissolved organic material to bicarbonate, protons and electrons. Externally, the anode and the cathode are connected to the power supply using an electrical circuit. The power supply drives the released electrons from the anode to the cathode. At the cathode, protons and electrons combine to form hydrogen [3-6]. Electromethanogenesis synthesizes methane in two ways, either by direct uptake of electrons from the electrode, called direct electromethanogenesis, or mediated by hydrogen and other compounds such as acetate, formate which are produced and combined with carbon dioxide to form methane, called mediated or indirect electromethanogenesis [7, 8]. MEC is a promising technology for the removal of organic pollutants and for biogas production. Many studies have revealed higher rates of degradation of different substrates in AD-MEC systems than in a single AD system [9-12]. The integration of MEC into an anaerobic reactor stabilizes the process by helping the decomposition of the substrate and thus leads to the production of hydrogen and methane. In addition, the rate of degradation of inflexible compounds or complex wastewater is higher in AD-MEC [3, 13, 14]. So, integrated AD-MEC systems have the ability to not only simultaneously produce biogas but also upgrade it. The combination of wastewater treatment along with biomethane production may help in compensating the cost of wastewater treatment, making the MEC technology more sustainable.

There are literature data on the study of the influence of one or two operating parameters on the work of AD-MEC, but there is not enough generalized data on the optimal operating conditions of such a system. This is extremely important as it saves time and money, especially when scaling up the installation. In both the single anaerobic digestion process and the AD-MEC hybrid system, the operating conditions must be optimal in order to obtain the maximum amount of biogas with a high methane content. In the present work, the influence of several technological parameters will be studied - the magnitude of the applied external voltage, temperature and pH. The variation of the external voltage can indirectly affect the solution pH and alkalinity due to abiotic reactions on the electrode surface of MEC and

*To whom all correspondence should be sent:
E-mail: polina.velichkova@mgu.bg

plays a key role in CH_4 generation and COD degradation [15, 16].

EXPERIMENTAL

Integrated AD-MEC system

Scheme and picture of a laboratory installation are shown on Figure 1. The anaerobic reactor is a Plexiglas tube with a diameter of 150 mm, a height of 400 mm and a working volume of 2.7 dm^3. Two graphite plates measuring 100 × 100 × 6 mm were used for the electrodes and the distance between them – 20 mm, which were fastened with pins to the cover. Recirculation pumps moved the flow. The reactor system was filled with ethanol stillage and 10 % of volume of substrate inoculum from a mixed methanogenic consortium (activated sludge).

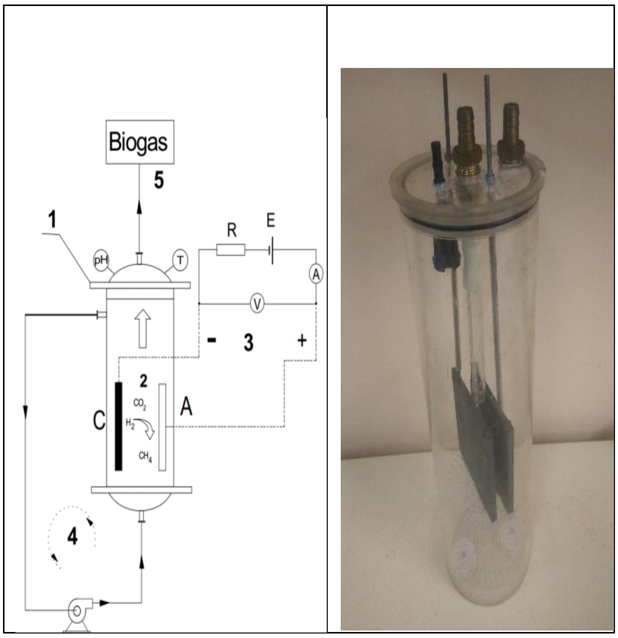

Fig. 1. Scheme of laboratory installation and pictures of AD-MEC. 1 - anaerobic bioreactor (UASB), 2 - MEC, 3 - MEC load chain, 4 - recirculation flow, 5 - biogas.

Wastewater and activated sludge

Wastewaters were from “Almagest”, Verinsko Village, Bulgaria. They are obtained after the separation of ethanol obtained by enzymatic hydrolysis of maize. After obtaining the ethanol stillage, it was stored in a cool place at 4 °C. Before use the wastewater was neutralized to pH 7.5 with NaOH.

Activated sludge was also from “Almagest”. The culture is granulated in the form of spherical flocs (soft pellets). The particles have diameters varying in the range of 2-3 mm. The pellets displayed good mechanical stability, maintaining its intact structure at low stirring speeds, especially if no direct mechanical impact was applied.

Analytical methods

Chemical oxygen demand (COD) was measured with a HANNA INSTRUMENTS kit. The contents of CO_2, CH_4, O_2, H_2S and H_2 in the emitted gas were measured using a portable gas analyzer "Draeger X-am 7000". The sulfate concentration was determined using a spectrophotometric method at λ 420 nm using $BaCl_2$ as reagent. Reducing sugars were determined as glucose using dinitrosalicylic acid (DNS) reagent by the method described by Miller [17]. The protein content was determined according to the method of Lowry *et al.* [18]. Dry weight was measured using a Kern DAB moisture analyzer balance.

RESULTS AND DISCUSSION

Characterization of the ethanol stillage

The values of the main parameters of ethanol stillage are shown on Table 1. As can be seen from the results, the ethanol stillage has a high organic load (COD 60-88 g/l), low pH (3.88) and relatively high contents of protein (9.4 g/l) and sugar (4.55 g/l, of which 0.28 g/l glucose). However, the best method for purification of this wastewater is its biochemical transformation accompanied by the generation of additional energy, i.e. the process of biomethanation. In addition, it was assumed that the stillage has a relatively good ratio of micro- and macronutrients necessary for the development of microorganisms in methanogenic consortia. For the fully balanced composition of the substrate both ammonium and phosphate salts are added [19].

Table 1. Characterization of the ethanol stillage

Parameter	Value
pH	3.88
Dry matter, %	4.15
COD, g O_2/l	60-88
SO_4^{2-}, mg/l	288
Total protein, g/l	9.4
Reducing sugars, g/l	4.55
Glucose, g/l	0.28
Fructose, g/l	0.53
Maltose, g/l	3.34

Influence of the magnitude of the applied external voltage

According to Choi *et al.* [20], increasing the external voltage from 0.5 to 1.0 V improves the decomposition while voltage higher than 1.0 V has a negative effect. Linji *et al*. [21] found that 0.8 V is the optimal external voltage. Lee *et al.* [22] found that high voltages kill microorganisms. They also proved that there are different dominant populations in the anaerobic digestion reactor and the hybrid system. This means that the optimal external voltage is different for specific substrates in the AD-MEC system. The study will compare the kinetics of biogas production from an ethanol stillage without external voltage (independent process of anaerobic digestion) and at external voltages of 0.8 and 1.0 V in the AD-MEC system. The other conditions were kept the same - pH 7.5 and temperature 35 °C. The hydraulic retention time (HRT) required to be 10 days. The effect of external supplemental voltage of 0.8 and 1.0 V was tested on the CH_4 generation by using ethanol stillage. The cathode and anode electrodes were connected to the power supply, with an external resistance of 10 Ω. Figure 2 shows the graphs of the kinetics of a process without external voltage (only process of biomethanation), and at external voltages of 0.8 V and 1.0 V.

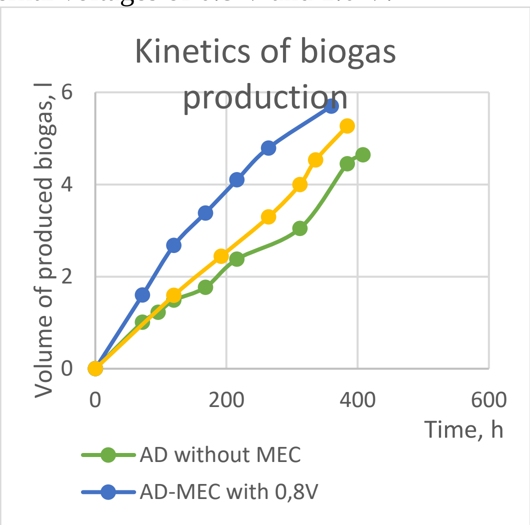

Fig. 2. Graphs of biogas production using different technology modes.

The biogas production was almost doubled by MEC with 0.8 V external voltage on the 240th hour, (10th day) compared to the other two modes. Therefore, the process is faster at MEC with 0.8 V. The relatively even release of biogas in the hybrid installation with 0.8 V is impressive, which is a prerequisite for a more stable process.

The data in Table 2 show that despite the higher organic load in the system with MEC, degradation is achieved up to about 74 % at 0.8 V and 59 % at 1.0 V external voltage. In the system without MEC, the degradation is 48 %. This means that the integration of MEC into AD improves the absorption of the substrate and speeds up the process. Methane yield per 10 days (required contact time) is also highest with a 0.8 V system (18.10 l CH_4/kg COD), followed by a MEC-free process (16.48 l CH_4/kg COD) and finally a 1.0 V AD-MEC system (14.13 l CH_4/kg COD). The amount of sulfates also decreases at the output of the system, the greatest reduction being in a 0.8 V AD-MEC system (from 287 to 120 ppm). The biogas composition produced under the three modes is shown on Table 3. As can be seen, the biogas richest in methane was generated by the MEC-AD system with 0.8 V (80 %), followed by the system with 1.0 V (70 %) and without MEC (52 %).

Influence of operating temperature

Operating temperature is well known as one of the most effective factors for microbial kinetics and is therefore important for the identification and evaluation of the bacterial activity. Anaerobic digestion usually develops in the mesophilic (30–40 °C) and thermophilic state (45–60 °C) [23, 24].

Thermophilic operating temperature leads to an increase in the reaction rate, which increases the production of biogas and the rate of destruction of organic material; however, thermophilic bacteria are more sensitive than mesophilic ones to changes in the environment [25].

Table 2. Input and output parameters of the installation

Parameter \ System	AD without MEC	AD-MEC with 0.8 V	AD-MEC with 1.0 V
COD_{input}, g/l	61	88	86
COD_{output}, g/l	32.10	23.25	35.20
SO_4^{2-} $_{input}$, mg/l	289	287	288
SO_4^{2-} $_{output}$, mg/l	174	120	122
Methane yield, l CH_4/kg COD on 10th day	16.48	18.10	14.13

Table 3. Composition of produced biogas

System / Composition of biogas	CH_4, vol. %	CO_2, vol. %	H_2S, ppm	H_2, vol. %
AD without MEC	52	31	496	> 4
AD-MEC with 0.8 V	80	12	306	0.8
AD-MEC with 1.0 V	70	24	320	0.9

Kyazze *et al*. [26] reported that the optimum temperature of acetate-fed two-chamber MEC was about 30 ºC. Production of biogas decreased at temperatures below 25 ºC or above 40 ºC due to lower activity of electroactive bacteria (EAB). In another study [27], the maximum current density generated by a single-chamber MEC was obtained at a temperature of 29-31 ºC and also the decrease in COD shows a similar trend in the system. According to the results by Feng *et al.* [28], the performance of the AD-MEC under 25 ºC and that of the AD system at 35 ºC was almost similar. In a previous study the optimal temperature was determined as 35 ºC for the same consortium for biomethanation of vinasse [29]. Meta-analysis presented by Amin *et al.* showed the established optimal temperature intervals and found that for AD-MEC it is between 30 and 40 ºC [30]. They also found that the optimal activity of acidogenic, acetogenic and electrogenic bacteria is at a lower pH than the optimal pH for methanogenic bacteria. Methanogens, which are sensitive to changes in pH, have optimal activity in the pH range of 6.8–7.2. As a result, it is logical that the optimal temperature conditions to improve methane yield be different from the TCOD removal rate. According to the result, the choice of a temperature range of 30-40 ºC, as made in many studies, has the best impact on methane yield. Therefore, the processes of biogas production from an ethanol stillage with AD-MEC at 25, 35 and 45 ºC were studied at 0.8 V external voltage and pH 7.5.

The graphs on Figure 3 show that the highest biogas production is at 35 ˚C, followed by 45 ˚C and 25 ˚C, respectively. After 240 hours, (10 days) biogas production is almost doubled at 35 ˚C (4.5 l) *vs* 25 ˚C (2.1 l). At 45 ˚C, the produced biogas is 3.3 l. Low temperatures such as 25 ˚C have no positive effect on the biomethanation process, even when there is an integrated MEC. Higher temperatures such as 45 ˚C reduce biogas production, but manage to keep the process stable. This may be related to the type of methanogenic consortium which is immobilized on activated carbon and protects it from adverse external influences.

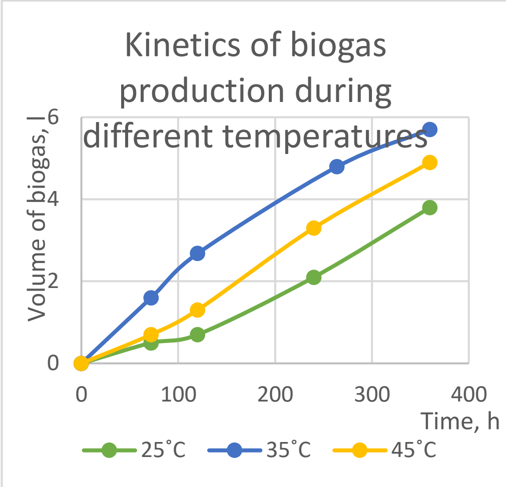

Fig. 3. Graphs of biogas production at different temperatures in AD-MEC.

Perhaps maintaining a high temperature in the reactor for a long time will also lead to negative effects and inactivation of microorganisms. It is also economically unprofitable. Huang *et al.* [31] suggested that because of decreasing of methanogens activity, operation of anaerobic digesters under 25 ºC could lead to an accumulation of VFAs. These results showed that the AD-MEC system could be a suitable alternative to elevate methane production at ambient temperature. Therefore, the optimal temperature for the combined AD-MEC system is 35 ˚C.

Influence of operating pH

The ideal conditions for methanogenic microorganisms are in a narrow pH range: 6.8-7.2. For systems, the optimal pH during hydrolysis and acidogenesis was reported to be between 5.5 and 6.5, while for methanogenesis the optimal pH was 7.0. In anaerobic bioreactors, pH defines the balance between carbonic acid, bicarbonate alkalinity and carbonate alkalinity, as well as between ammonia and ammonium ions [32, 33]. The process of biogas production with AD-MEC at pH 6.5, 7.5 and 8.5 was studied by keeping constant the other conditions - 0.8 V external voltage and 35 ˚C.

The graphs on Figure 4 show that the highest biogas production is at pH 7.5, followed by 8.5. As expected, at pH 6.5 almost no biogas was produced because processes of hydrolysis and acidogenesis instead of methanogenesis took place. Therefore, the optimal pH for the combined AD-MEC system is the same as that for methanogenesis (7-7.5).

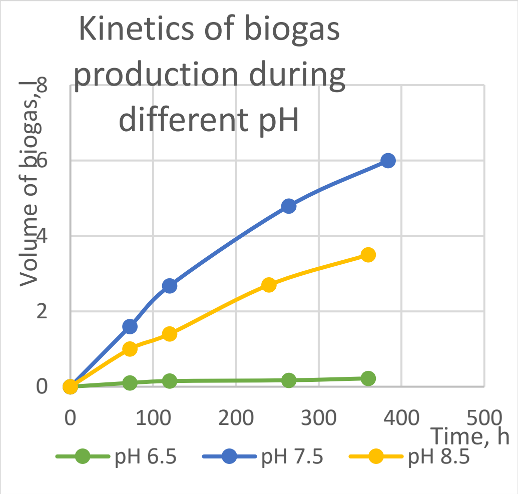

Fig. 4. Graphs of biogas production at different pH in AD-MEC

CONCLUSION

The influence of different parameters on the operation of the hybrid system AD-MEC was studied. The optimal values of these parameters were established. The optimal external load is 0.8 V at which 80% methane in the biogas and yield of 18.10 l CH_4/kg COD is reached. Unfortunately, at the applied external voltage of 1.0 V, the methane yield turned out to be even lower (14.13 l CH_4/kg COD) compared to a stand-alone biomethanation process (16.48 l CH_4/kg COD). Increasing the applied voltage above 1.2 V can lead to electrolysis of water and oxygen production, which not only affects electron transfer, but also has a negative effect on methanogenic bacteria. We found that low temperatures and low pH negatively affect the AD-MEC system, so the optimal values are 35 ˚C and pH 7.5.

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