12th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2008, Istanbul, Turkey, 26-30 August, 2008

APPLICATION EXPERIENCES OF MEASUREMENT DEVICES OF METHANE AND CARBON DIOXIDE CONCENTRATION

Radek Sedlačík, Marie Dvořáčková
Tomas Bata University
Faculty of Technology
Department of Environmental Protection Engineering
Nam. TGM 275, Zlin 76001
Czech Republic

František Hruška
Tomas Bata University
Faculty of Applied Informatics
Department of Electronic and Measurement
Nad Stranemi 4511, Zlin 76005
Czech Republic

ABSTRACT
Methane fermentation is a biotechnology capable of converting many types of waste biomass (including polymeric materials) to methane and carbon dioxide under anaerobic conditions. The aim of this work was to choose and verifies appropriate sensors for measuring methane and carbon dioxide concentrations in middle-sized laboratory fermenter during anaerobic bioprocesses. There were chosen two sensors based on infra-red spectrophotometry measurement procedure, which require specific arrangement of gas measurement loop. In this paper is described development in designing and testing of this loop under anaerobic conditions. Results and experiences of several carried experiments are included in this paper.
Keywords: methane, carbon dioxide, infra-red spectrophotometry, anaerobic bioprocess, fermenter

1. INTRODUCTION
Recently, there has been growing interest in using renewable energy sources. One of these sources, bioenergy, has great potential because of low carbon dioxide emission. Unfortunately, producing energy from biomass generates dangerous competition between food and "energy" crops. The best way to avoid this situation is to utilize waste biomass. Nowadays, the most studied method for waste to energy conversion is anaerobic digestion, which can convert broad scope of waste, for instance agricultural animal and plant waste and municipal waste water, into energy full product – biogas. Biogas is a mixture of carbon dioxide and methane which can be use for producing electricity or heat.

Many studies have been concentrated on biogas production [1, 2]. Biogas is usually produced under controlled conditions in large tanks inside sewerage plant. Waste is converted into huge quantum of biogas, which is hot (35-75°C), wet and under pressure. There were developed different methods to determine the quantity and quality of biogas, however the most frequently biogas measurement methods (in technological praxis and in the laboratory) are volumetric measurement (simple for almost every gas flow [3]) and IR spectrophotometry [4].

This contribution is, contrary to previously research [5], focused on modifying and testing gas measurement loop under anaerobic conditions. There is described a development of this loop including data from liquid phase sensors (to give complex view on the anaerobic bioprocesses).

2. EXPERIMENTAL

2.1. Materials

Mixture (8 litres) of anaerobic activated sludge and a bio-medium ($MgSO_4$; $CaCl_2$; $FeCl_3$; $(NH_4)SO_4$; phosphoric buffer; trace elements: B^{3+}, Fe^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Mo^{6+}) were utilized in all four experiments. Acid (0.1M HCl) and alkali (0.1M NaOH) solutions were dosed via peristaltic pumps automatically according to the requested pH value. Glycerol (12g) was batched manually as a substrate for microorganisms.

2.2. Methods

Figure 1 shows the scheme of gas measurement loop connexions in four experiments. The arrangement had been changing to improve results of biogas determination. First, the output gas flowed through outlet valve, drying jars and gas sensors (GASCARD II, Edinburgh Instruments, UK). In safety valve, it continued to a pump or, if pressure achieved adjusted level, turn to flow meter (Bronkhorst, Holland) and then into the atmosphere. Behind the pump, the carried gas was piped into fermenter vessel under level of suspension (A). In the second experiment, the arrangement was almost the same as in the first experiment, but the gas was piped above the level of suspension (B). Tube between the safety valve and the pump was closed off in the third experiment (C).

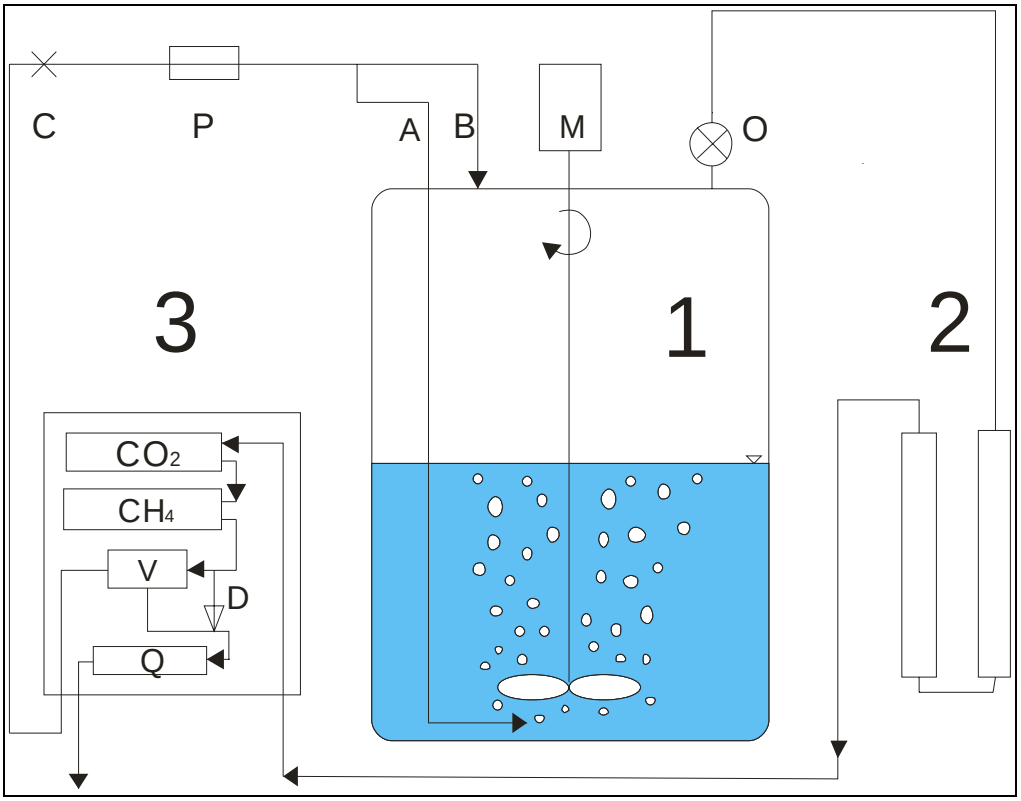

Figure 1. Scheme of the gas measurement loop.1-bioreactor vessel; 2-drying jars; 3-measuring box; A,B,C,D-variations of connexion; CH_4-methane sensor; CO_2-carbon dioxide sensor; M-motor; O-gas-outlet valve; P-air-pump; Q-small flow meter; V-safety valve.

Finally, the safety valve was passed and the measured gas went directly to the flow meter (D) in the fourth experiment. The outlet valve was staying closed. From time to time, researcher opened it via the Internet and reduced recording period. Overpressure in the bioreactor vessel forced produced biogas through sensors. If the pressure decreased, operating staff closed the outlet valve.

3. RESULTS AND DISCUSION

Figure 2 presents fluctuations in the level of oxidation-reduction potential (ORP) and in dissolved oxygen concentration during the first experiment. Measured biogas was pumped under the suspension level. Unfortunately, the gas measurement loop was not enough pressure-tight and as a result, the air (with oxygen) contaminated the flowing gas. Due to this contamination, concentration of dissolved oxygen increased. The level of ORP is strong dependent on concentration of dissolved oxygen (if oxygen is the main oxidation agent). Decreases of both values were caused by striping with nitrogen gas by liquid sampling. Level of dissolved oxygen was too high for anaerobic bioprocesses, thus, it was necessary to rearrange the gas measuring loop.

The second and the third experiments were more convenient, from dissolved oxygen point of view; however, there were problems with safety valve and sensors connection. These problems disable balancing of biogas production. Furthermore, all experiments took more than 100 hour. This long time and quite short recording period produce huge quantity of data. For instance, data from the second experiment takes more than 4600 line and 16 columns in spreadsheet MS Excel®. On the other hand, if the recording period is longer than a minute, balance of biogas production get less correct. One possible solution is using of special software, for instance Statistika®, but not everybody (especially students) have these expensive programs installed on its computer. This complication was solved in the last experiment by changing operating procedure.

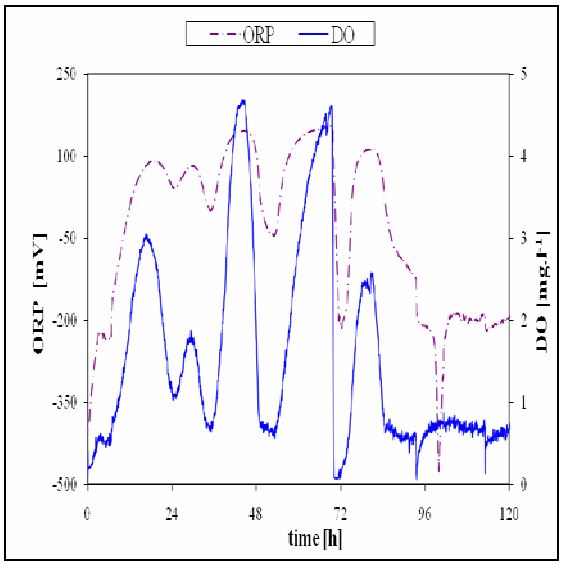

Figure 2. Variation of oxidation-reduction potential (ORP) and concentration of dissolved oxygen (DO) during the first experiment.

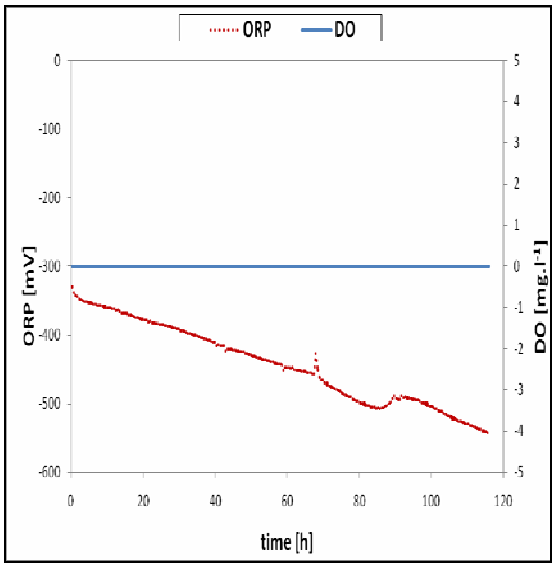

Figure 3. Variation of oxidation-reduction potential (ORP) and concentration of dissolved oxygen (DO) during the last experiment.

As can be seen in Figure 3, concentration of dissolved oxygen remained constant (zero) during the last experiment. The ORP level, which was deep under the zero level, went down owing to growing production of by- and end products of really anaerobic bioprocesses. These ideal anaerobic conditions were achieved due to new arrangement in measuring box (D) and modified operating practice. The bioreactor vessel was staying isolated from surrounding environment, except the moment of batching glycerol and liquid sampling at 70th hour. Moreover, the temperature 35±1°C stimulated the biogas production, which sustained a small overpressure preventing oxygen contamination from air.

Figure 4 displays carbon dioxide and methane production through the fourth experiment. Carbon dioxide and methane are important products of these bioprocesses and pass to gas phase forming biogas. Carbon dioxide is less concentrated because it is reabsorbed into the liquid phase and its production by microorganisms is under anaerobic condition lower than methane production.

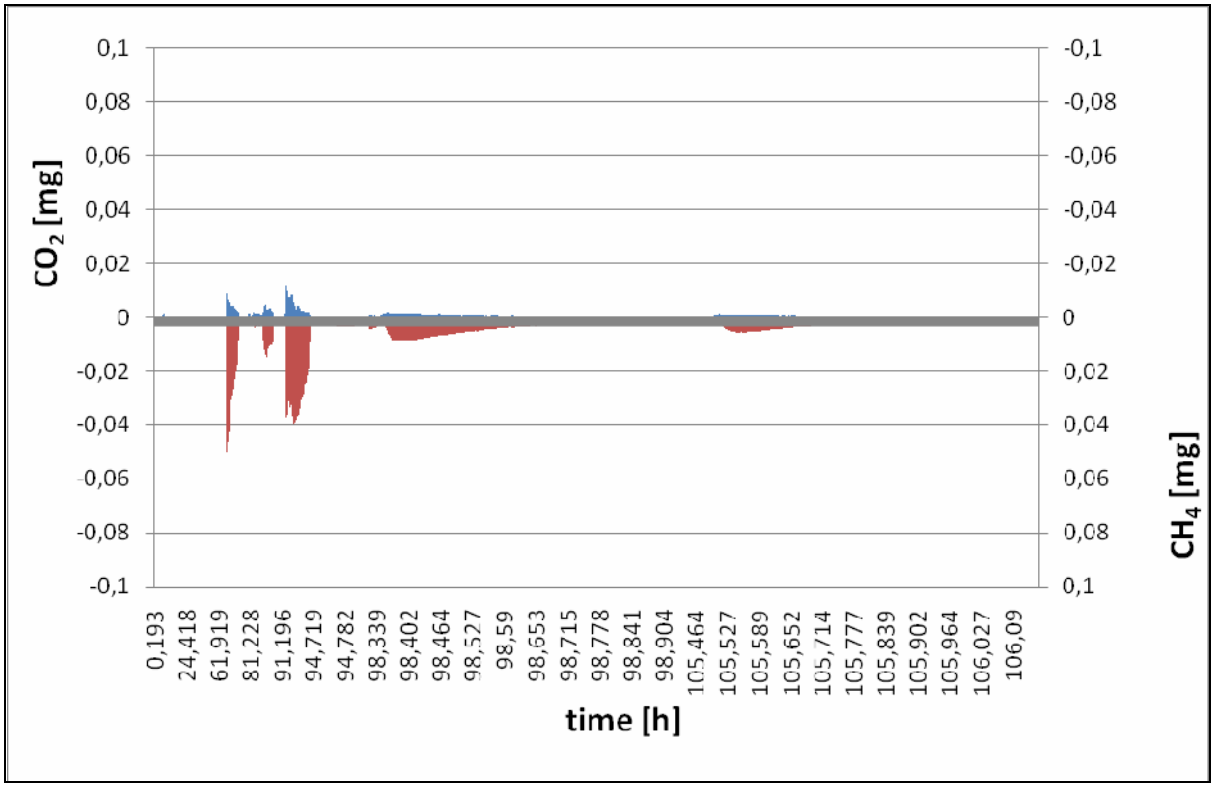

Figure 4. Production of carbon dioxide (CO_2 ↑ up) and methane (CH_4 ↓ down) during the last experiment.

4. CONCLUSION

This report presents data and experiences from four experiments operated under anaerobic conditions. There is briefly described a development of gas measurement loop arrangement. Problems with connection and data handling were solved successfully. Nevertheless, the problem with gas tightness of fermenter vessel has not been satisfactorily worked out. Further research will be focused on software modification to calculate actual concentration of carbon dioxide and methane in bioreactor vessel (not only in the outlet biogas).

5. ACKNOWLEDGEMENT

This work was supported in part by the Ministry of Education, Youth and Sports of the Czech Republic under grant FRVS, No. MSM 281100001 and MSM 7088352101.

6. REFERENCES

[1] Weiland P.: Production and energetic use of biogas from energy crops and wastes in Germany, Applied Biochemistry and Biotechnology, Humana Press Inc., Totowa (USA), 2007

[2] Berglund M., Börjesson P.: Assessment of energy performance in the life-cycle of biogas production, Biomass and Bioenergy, Pergamon-Elsevier Science ltd, 2005

[3] Liu J., Olsson G., Mattiasson B.: A volumetric meter for monitoring of low gas flow rate from laboratory-scale biogas reactors, Sensors and Actuators B: Chemical Elsevier Science Bv, 2003

[4] Dvořáčková, M.; Julinová, M.; Hoffmann, J.; et al.: New Trends of Characterisation of Polymers Biostability under Aerobic and Anaerobic Conditions. In TMT. 10th International Research/expert Conference: "Trends in the Development of Machinery and Associated Technology". Barcelona-Lioret de Mar (Spain), 2006

[5] Sedlačík R., Dvořáčková M., Hruška F.: Preparation and Verification of Laboratory Fermenter for Instalation of Gas Sensors, In TMT. 11th International Research/expert Conference: "Trends in the Development of Machinery and Associated Technology", Hammamet(Tunisia), 2007