BIOGAS SPECIFIC HEAT CAPACITY VARIATIONS DURING UPGRADING

Revik Vardanjan[1], Aigars Laizans[2], Andris Jakovics[3], Stanislavs Gendelis[3]
[1]Armgate LLC, Latvia; [2]Latvia University of Agriculture; [3]University of Latvia
revik@armgate.eu, aigars laizans@llu.lv, andris.jakovics@lu.lv, stanislavs.gendelis@lu.lv

Abstract. The research paper presents theoretic analysis and simulation results of biogas specific heat capacity and density dependence on biogas content and temperature. The research results indicate that methane content has inverse impact on density – the density decreases by 16..19 % when the methane concentration increases from 50 % to 75 %. Specific heat capacity of biogas increases, when the methane concentration increases – by 17 % when the methane concentration increases from 50 % to 75 %. When biogas is being upgraded using a passive drier – a heat exchanger, and water vapor is removed, both the density and specific heat capacity decrease. The knowledge gathered is important for designers calculating biogas heat exchangers and passive driers.

Keywords: biogas density, specific heat capacity, methane content, biogas drying, water content in biogas.

Introduction

Biogas production is becoming a more and more important part of renewable resources based energy supply system, as it helps develop more independent economy and at the same time reduces environment pollution. The major biogas production systems are using the anaerobic mesophilic process [1] and different biomaterials, including wild growing (grass, reed [2]), specially grown (maize, sugar beet) and even waste, are being used as raw materials. At the same time biogas differs substantially from natural gas as it includes not only methane CH_4 as the main component, but also carbon dioxide CO_2, water vapor H_2O, and minor components, which can be rather aggressive (like H_2S, SO_2, NH_3) [3].

Removal of some contaminates is requested by further usage of gas, especially if it takes to be used for co-heating plants (CHP) using internal combustion engines (ICE) [4]. The process called biogas upgrading has lot of variations depending on the quality of the final product and components to be removed [5].

Major parts of all biogas upgrading processes require additional energy consumption, which at the end increase the overall costs, but there are solutions, which do not require additional energy to drive (so called passive biogas upgraders), rather just investments in equipment and temperature difference between biogas and cooling environment, e.g., air, water or ground [6]. Such passive biogas upgrader (heat exchanger) allows to remove water vapor and decrease concentration of aggressive components H_2S, SO_2, NH_3, as they dissolve at some extent in the water condensate.

The aim of the research was to evaluate the thermal properties of biogas before it enters the passive biogas upgrader (PBU), with the biogas thermal properties after the PBU. Understanding the specific heat and density changes will allow to create optimized construction of PBU.

Specific heat capacity concept

Specific heat capacity c is is the amount of heat required to change a unit mass of a substance by one degree in temperature. It can be expressed as:

$$c = \frac{Q}{m\Delta T}, \tag{1}$$

where: c – particular substance specific heat capacity, $J \cdot kG^{-1} \cdot K^{-1}$
Q – amount of heat supplied to or removed from the substance, J;
m – mass of the substance, kG.
ΔT – temperature difference when cooling or heating the object, K.

Biogas is a substance with variable concentration of the main components, and depends on numerous external factors, including the biomass type and preprocessing level, microbiological composition in the digester, technological process particularities (mixing intensity, temperature, etc.). In line with concentrations fluctuation, the thermodynamic properties of biogas are fluctuating, but this process is not linear as there are several components which change their volumes.

The additional challenge for passive biogas upgrader developers, which use temperature differences between biogas and outside environment, is related to the water vapor condensation within the heat exchanger of PBU. This process is the major for water vapor removal from biogas, and needs some energy, but at the same time decrease of water vapor and few additional component concentration in biogas changes the biogas specific heat capacity.

Biogas at the exit of the digester has 100 % relative moisture content, and absolute moisture content depending on temperature (if the mesophilic biodegradation process is used, biogas temperature is around 38 ºC). With the decrease of biogas temperature instant water condensation takes place, and if only temperature is decreasing, at the exit of the PBU heat exchanger the relative moisture content is still 100 %, but the absolute moisture content decreases substantially. Water content in the air is 46.1 $g \cdot m^{-3}$, when biogas temperature is +38 ºC, but decreases to 8.16 $g \cdot m^{-3}$, when biogas temperature decreases to +10 ºC (Fig.1, and (1) equation developed from [7], $R^2 = 0.9996$).

$$M = 0.0006T^3 + 0.0014T^2 + 0.3304T + 4.4721 \, , \tag{2}$$

where M – mass of water in the air, $g \cdot m^{-3}$;
T – temperature,, ºC.

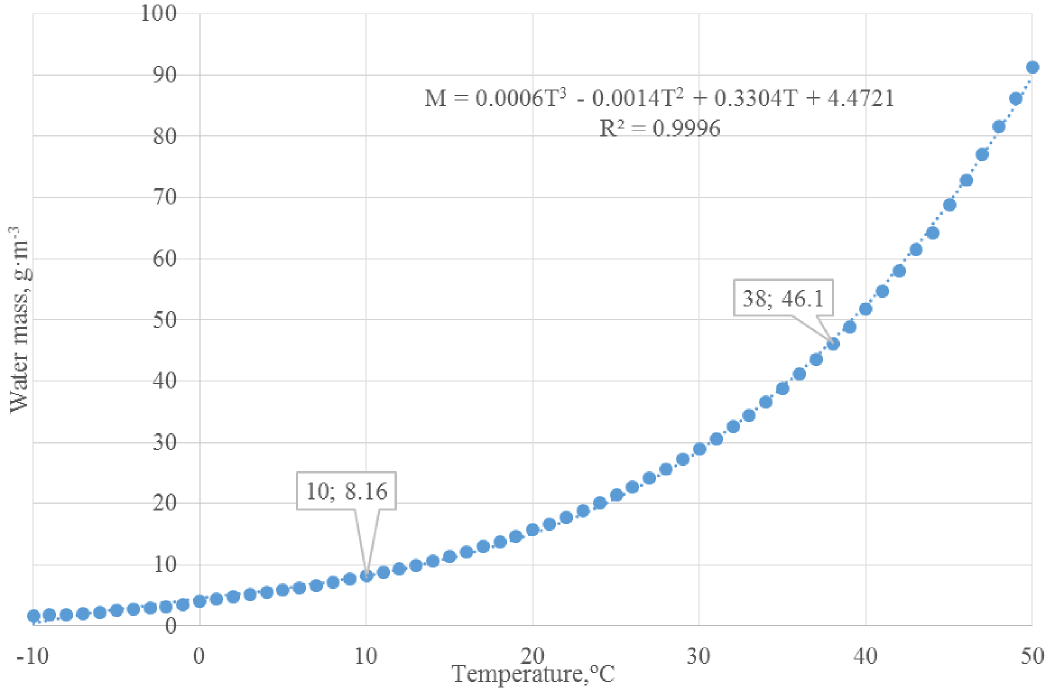

Fig. 1. **Content of water in the air with different temperatures (100 % relative moisture)**

Thus, when biogas is cooled from +38 ºC to +10 ºC, water condensate with the mass $M = 46.1$-$-8.16 = 38.94$ g is removed from each cubic meter of biogas.

Biogas transfer through the heat exchanger cannot be described either as an adiabatic process, because water condensate is being removed instantly after it occurs, or a purely isochoric process, because the biogas volume after water condensation changes both the density and volume. In this research, the isochoric approach was explored.

Specific heat capacity of biogas can be calculated using weighted average formula:

$$C_V^{biogas} = \sum x_i C_V^i \, , \tag{3}$$

where C_V^{biogas}– specific heat capacity of biogas;
x_i – volume fraction of each biogas component i;
C_V^i – specific heat capacity of each biogas component i.

Materials and methods

Theoretic analysis using available information about specific heat capacity of different gases was carried out. Simulation of specific heat capacity and specific weight for different biogas compositions, where the main changing components are methane and carbon dioxide, as well as water vapor variation due to condensation, was provided. Two main measurement points – the first before biogas enters the passive dryer – heat exchanger, and the second at the exit of the heat exchanger, were set. Biogas is entering and exiting the heat exchanger with 100 % relative moisture content, entrance temperature +38 ºC, exit temperature +10 ºC.

Biogas composition and densities of each component used in the simulations are presented in Table 1.

Table 1

Biogas components, volume, %

Component	volume in biogas, %		Density, $kG \cdot m^{-3}$
	min	max	
Methane CH_4	50	75	0.688
Carbon dioxide CO_2	25	45	1.842
Water vapor H_2O	2	7	0.0463
Oxygen O_2	1	2	1.33
Nitrogen N_2	1	2	1.165
Ammonia NH_3	0.5	1	17.031
Hydrogen H_2	0.5	1	2.016
Hydrogen sulfide H_2S	0.5	1	34.076

Specific heat capacity calculation formulas for the major biogas components were obtained. Methane specific heat capacity can be calculated, using the equation [7]:

$$C_{CH4} = 0.628326\frac{T_K}{T} + 0.752532 + 0.582779\left(\frac{T}{T_K}\right) + 0.082044\left(\frac{T}{T_K}\right)^2 - 0.010773\left(\frac{T}{T_K}\right)^3, \quad (4)$$

where T_K – critical temperature for methane, T_K = 190.65 K;
T – methane temperature, K.

Specific heat capacity for water vapor can be calculated, using the equation [8]:

$$C_{H2O} = (143.05 - 183.54\cdot\theta^{0.25} + 82.751\cdot\theta^{0.5} - 3.6989\cdot\theta)/18, \quad (5)$$

where θ – critical temperature coefficient, $\theta = T / 100$.

Specific heat capacity for carbon dioxide can be calculated, using the equation [8]:

$$C_{O2} = (-3.7357 + 30.529\cdot\theta^{0.5} - 4.1034\cdot\theta + 0.024198\cdot\theta^2)/44 \quad (6)$$

Specific heat capacity for oxygen can be calculated, using the equation [8]:

$$C_{O2} = (37.432 + 0.020102\cdot\theta^{1.5} - 178.57\cdot\theta^{-1.5} + 236.88\cdot\theta^{-2})/32 \quad (7)$$

Specific heat capacity for nitrogen can be calculated, using the equation [8]:

$$C_{N2} = (39.06 - 512.79\cdot\theta^{-1.5} + 1072.7\cdot\theta^{-2} - 820.4\cdot\theta^{-3})/28 \quad (8)$$

Specific heat capacities of other minor components will be used as constant values, not depending on temperature, thus C_{NH3} = 2.19 $kJ\cdot kG^{-1}\cdot K^{-1}$, C_{H2} = 14.32 $kJ\cdot kG^{-1}\cdot K^{-1}$, and C_{H2S} = 1 $kJ\cdot kG^{-1}\cdot K^{-1}$.

Results and discussion

The simulation results of biogas density in two measurement points and different methane concentrations are presented in Fig. 2.

The chart shows that biogas density strongly depends on the methane concentration – with methane share in the biogas increase from 50 % to 75 % biogas density decreases by 16.8 % at the heat exchanger entrance, and by 19.5 % at the heat exchanger exit. The difference between the two numbers is because of water condensation within the heat exchanger and partial soluble gases removal together with water. The observation also shows that the density of biogas with a higher methane concentration is decreasing by larger extent – by 16.68 %, if the methane concentration is 75 % in comparison with 13.87 % for biogas with 50 % methane concentration.

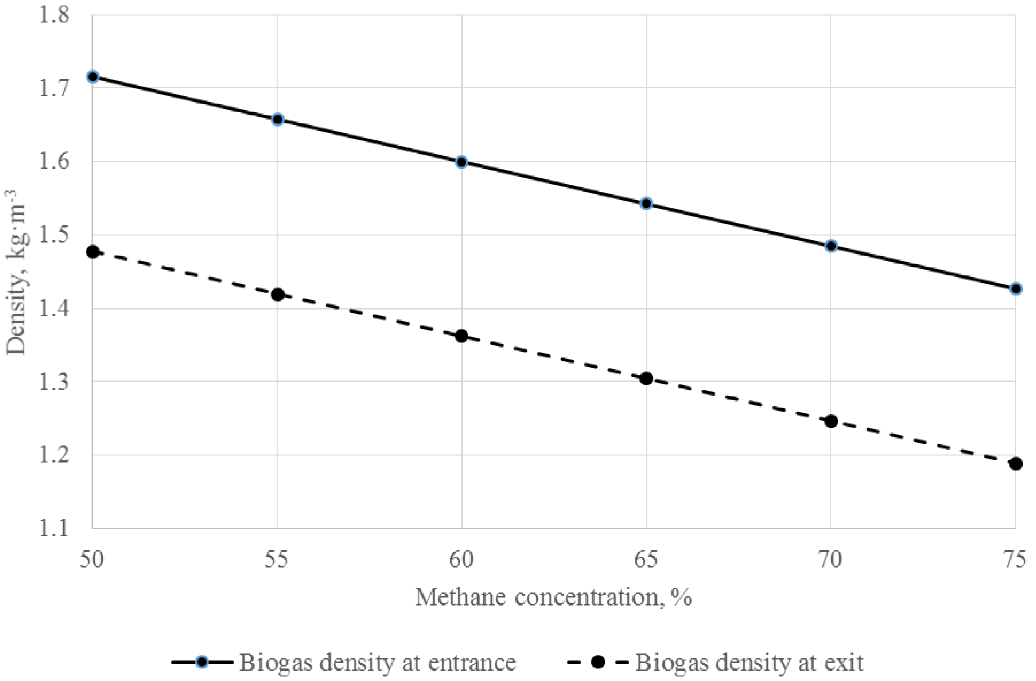

Fig. 2 **Biogas density dependence on methane concentration at dryer entrance and exit**

The simulation results of the specific heat capacity of biogas with different methane concentrations are presented in Fig. 3.

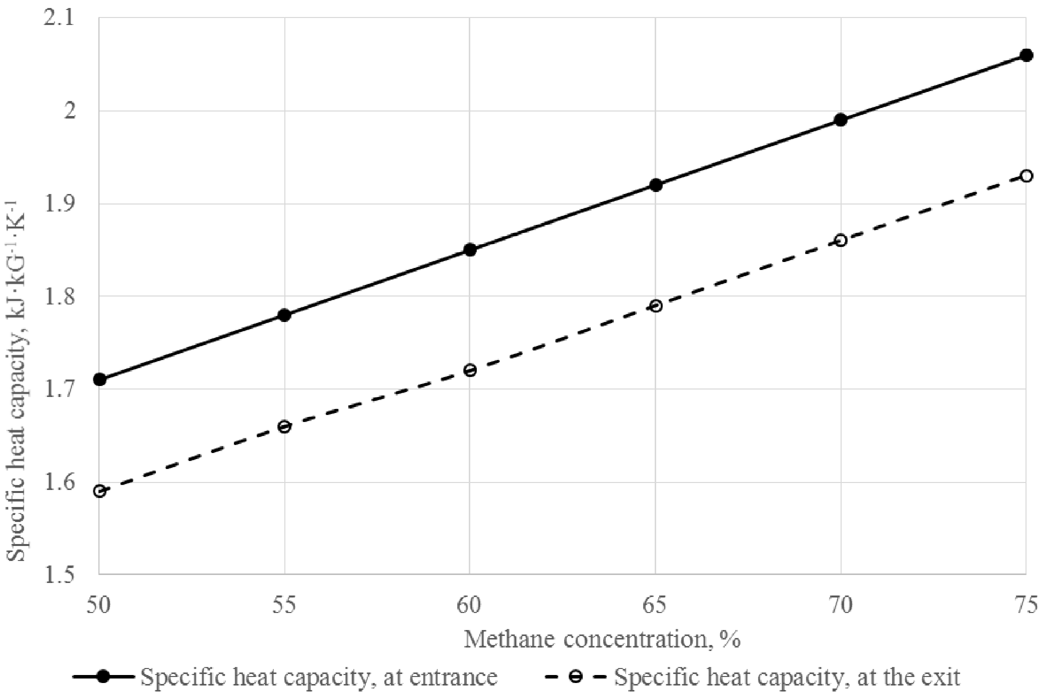

Fig. 3 **Biogas specific heat capacity dependence on methane concentration at dryer entrance and exit**

The simulation results show that biogas specific heat capacity strongly depends on the methane concentration – with methane share in the biogas increase from 50 % to 75 % the biogas specific heat capacity increases by 16.99 % at the heat exchanger entrance, and by 17.61 % at the heat exchanger exit. Biogas at the entrance from the dryer has by 6..7 % higher specific heat capacity than at the exit – so it will take less energy to heat up the biogas after the passive dryer before entering other steps of the upgrading system.

Raw biogas coming out from the digester is denser and with higher specific heat capacity – it has higher overall enthalpy. Processing using a simple heat exchanger, which upgrades biogas – reduces water vapor content and contamination with soluble aggressive gases, reduces also the specific heat capacity of biogas. Even a small multistage heat exchanger installed on the exit of the biodigester can remove substantial amounts of water vapor if condensed water is being removed.

As the described biogas upgrading process is close to isochoric, biogas pressure after heat exchanger decreases, and power requirements for biogas pumps decrease as the density decreases also. These are very important factors to take into account when biogas heat exchangers are designed.

Conclusions

1. Biogas density depends on the methane concentration – it is inversely proportional to the methane amount in biogas. When water vapor is removed, the biogas density decreases also – by 13..16 %, if biogas is being cooled from +38 ºC to +10 ºC.
2. Specific heat capacity of biogas is calculated as weighted average of all component specific heat capacities, which are non-linearly depending on biogas temperature. With temperature decrease from +38 ºC to +10 ºC, the specific capacity decreases by 6..7 %, thus in line with water vapor removal the energy needed to heat biogas up will decrease.
3. Biogas density and specific heat capacity changes must be taken into account when passive biogas upgraders – heat exchangers are being designed.

Acknowledgement

This research has received financial support of the European Regional Development Fund according to the agreement between LLC “Environment, Bioenergetics and Biotechnology Competence Centre” and Investment and Development Agency of Latvia as of April 11, 2011 regarding implementation of the project # L-Kc-11-0005, project No. 3.6.

References

1. Blumberga D., Dzene I., Al Sedi T., Rucs D., Prasls H., Ketners M., Finstervalders T., Folka S., Jansens R., “Biogāzes rokasgrāmata”, 2007, – 155 lpp.
2. Veli-Matti J., Kask Ü., Laizāns A. Biogas Production from Reed. In: Guidebook of reed business. Tallinn University of Technology, Tallinn, Estonia, 2013. pp.88-96. ISBN 978-9949-484-91-1
3. Niesner J., Jecha D., Stehlik P. Biogas upgrading technologies: State of art review in European region Chemical Engineering Transactions, Volume: 35, 2013
4. Scott S., Turra F. Six Reasons to Dry Biogas to a Low Dewpoint Before Combustion in a CHP Engine. Internet. Available at: http://www.parker.com/literature/United%20 Kingdom/PAR6841_Whitepaper_v3.pdf
5. Petersson A. Wellinger A. “Biogas upgrading technologies – developments and innovations”, 2009, – 19 lpp. [online][11.10.2015] Available at http://www.iea-biogas.net/files/daten-redaktion/download/publi-task37/upgrading_rz_low_final.pdf
6. Jakovics A., Gendelis S., Laizans A., and Vardanjans D. Multiphysical mathematical modelling of counterflow heat exchanger with condensation. In: Inter-Academia 2014. Proceedings of 13th International Conference on Global Research and Education, Riga, Latvia, September 10-12, 2014.
7. Tanishita I., Watanabe K., Kondo H., Nakashima A. Thermodynamic properties of gaseous methane. The Review of Physical Chemistry of Japan (1973), 42(2): 125-134, Internet. Available at http://hdl.handle.net/2433/46977
8. Modeling temperature variations in a pilot plant thermophilic anaerobic digester. Valle-Guadarrama S; Espinosa-Solares T; López-Cruz IL; Domaschko M, Bioprocess and Biosystems Engineering, ISSN: 1615-7605, 2011 May; Vol. 34 (4), pp. 459-70; Springer-Verlag.
9. Brizi F., Silveira J.L, Desideri U., dos Reis J.A., Tuna C.E., de Queiroz Lamas W. Energetic and economic analysis of a Brazilian compact cogeneration system: Comparison between natural gas and biogas. Renewable and Sustainable Energy Reviews 38, pp. 193-211.