Thermodynamics of combustion gases from biogas

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Abstract

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Biogas as a respected source of renewable energy is used in various areas for heating or in power cogeneration units. It is produced by anaerobic fermentation of biodegradable materials. The utilization of biogas is wide – from process of combustion in order to obtain thermal energy, combined heat and power production, gas combustion engines, micro turbines or fuel cells up to trigeneration. Biogas composition depends on the raw material. The aim of this paper was to develop a new methodology; according to this methodology, by means of gas mixture thermodynamics and tabular exact parameters of individual gaseous components, all the necessary thermodynamic and operating values of biogas composition were calculated. The mathematical model of biogas combustion was elaborated. For an accurate realization of calculation, a computing program was designed.

Keywords: renewable resource; gaseous fuel; stoichiometry; characteristic indexes; Wobbe number

Biogas can be considered as a globally significant source of renewable energy that is produced by anaerobic fermentation of biological materials (Haitl et al. 2012; Fodora et al. 2013). At Slovak University of Agriculture in Nitra, a modern device for production of biogas from agricultural materials was developed and has been successfully used (Gaduš et al. 2011; Janíček et al. 2012). Biogas composition is quite widely varied according to the type of used material. It depends also on the specifications of the country where the material was produced (Jablonický et al. 2013; Surendra et al. 2014; Zhang et al. 2015; Iglinski et al. 2015). Therefore, determination of its parameters is a real challenge (Vitázek et al. 2009; Jandačka et al. 2011). Authors of this article introduce a method that enables to calculate all the necessary thermodynamic and operating values of biogas composition by means of gas mixture thermodynamics and tabular exact parameters of individual gaseous components. In addition, a computing program for fast and accurate calculation of all required parameters was designed.

MATERIAL AND METHODS

Identification of the system. Simple diagram of combustion device for combustion of gaseous fuel with excess air was developed. It indicates the movement of mass and energy. To analyse the process, the following aspects were considered:
– thermodynamics of ideal gases;
– thermodynamics of ideal gases mixtures;
– thermodynamics of moist air (moist gas);
– tables of actual specific enthalpy and individual gases and linear regression of these values.

All analyses and calculations were performed for identical weight of gases (1 kg), since these re-
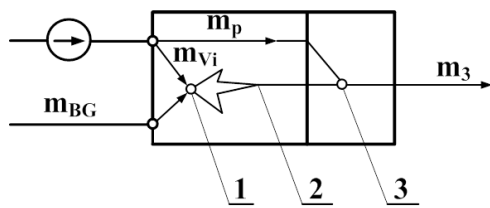
Fig. 1. The diagram of mass and energy movement in a combustion device

lationships are the simplest. Fig. 1 shows the diagram of mass and energy movement during biogas combustion with excess air in combustion device at constant pressure.

Fig. 2 shows the course of substance changes during the process of hot mixture production in *i-x diagram* of moist air (moist gas). The combustion of biogas and production of hot exhaust mixture is being analysed as three individually gradually running actions at constant pressure.

The points:

0 – the state of atmospheric air serving as combustion air;

1 – combustion mixture m_1 as a mixture of stoichiometric mass of combustion air and biogas;

2 – the state of stoichiometric hot exhaust m_2;

3 – the final state of hot exhaust mixture, which is produced by mixing of stoichiometric exhaust m_2 (2) and the excess of combustion air m_p (0).

The actions:

0–1 – shows the process of combustion mixture production at constant temperature and pressure;

1–2 – shows the biogas combustion at constant pressure, but it does not show it thermodynami-
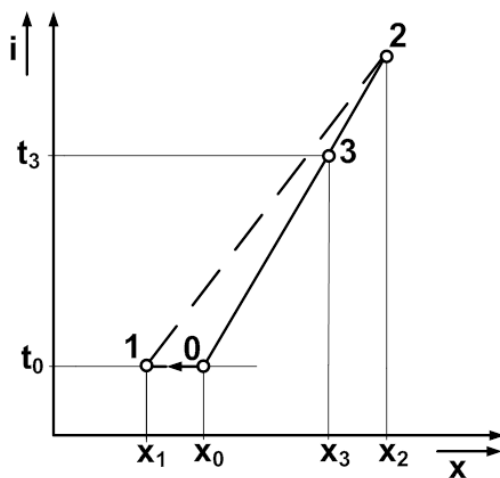

Fig. 2. The course of substance changes during the process of hot mixture production in *i-x* diagram of moist air

cally, because the composition of mixture of gases considerably varies;

2–3, 0–3 – shows the production of hot exhaust mixture (3) resulting from mixing of stoichiometric exhausts (2) and excess of air (0);

The methodology of calculation. Biogas is a mixture of several gases. Biogas composition is expressed by the volume parts x_{vi} that are numerically equal to the molar parts x_i. Molar weight of mixture M is calculated:

$$M = \frac{m}{n} = \frac{\sum n_i \times M_i}{n} = \sum x_i \times M_i \quad \text{(kg/mol)} \qquad (1)$$

where: m – weight of the mixture (kg); n – amount of component of the mixture; x_i – molar fraction of component; M_i – molar weight of component

Universal gas constant of mixture r is calculated:

$$r = \frac{R_m}{M} = \frac{8,314}{M} \qquad \text{(kJ/kg)} \qquad (2)$$

where: R_m – molar gas constant; M – molar weight of the mixture

The mass part of individual gas components σ_i is calculated from x_i value:

$$\sigma_i = \frac{m_i}{m} = \frac{n_i \times M_i}{n \times M} = x_i \frac{M_i}{M} \qquad (3)$$

where: m_i – weight of the component (kg); m – weight of the mixture (kg)

Heating power of biogas Q_n, based on 1 kg of the mixture is calculated:

$$Q_n = \sum \sigma_i \times Q_{ni} \qquad \text{(J/kg)} \qquad (4)$$

where: σ_i – mass part of particular component; Q_{ni} – heating power of the component

The density of biogas ρ_{BG} at basic conditions ($t = 15°C$ (288.15 K), $p = 101.325$ kPa) is calculated by the equation of state for an ideal gas:

$$\rho_{BG} = \frac{1}{v} = \frac{p}{r \times T} \qquad \text{(kg/m}^3） \qquad (5)$$

where: v – specific volume of the mixture, T – thermodynamic temperature

The heating power of biogas Q_n, based on 1 m³ of mixture at basic conditions is calculated:

$$Q_n = Q_n \text{ (J/kg)} \times \rho_{BG} \text{ (kg/m}^3) \qquad \text{(J/m}^3) \qquad (6)$$

Relative density – the density of biogas d is calculated as the ratio of gas density ρ_{BG} and density of atmospheric air ρ_a at basic conditions:

$$d = \frac{\rho_{BG}}{\rho_a} \qquad (7)$$

Biogas. Biogas is produced from raw materials by anaerobic bacteria activity without excess air. Biogas composition depends on the raw materials. The literature presents several different compositions of biogas. According to Trávníček et al. (2015), the composition of biogas is in % of volume as follows:

Methane CH_4 $x_{CH_4} = 50 \div 70$ (% vol)
Carbon dioxide CO_2 $x_{CO_2} = 30 \div 45$ (% vol)
Water vapour H_2O $x_{H_2O} = 1 \div 5$ (% vol)
Nitrogen N_2 $x_{N_2} = 0 \div 5$ (% vol)
Oxygen O_2 $x_{O_2} = < 1$ (% vol)
Ammonia NH_3 $x_{NH_3} = 0 \div 0.05$ (% vol)
Hydrogen sulphide H_2S $x_{H_2S} = 0 \div 0.5$ (% vol)
Hydrocarbons C_nH_{2n+2} $x_{C_nH_{2n}} = < 1$ (% vol)

Essential part of the weight of biogas is formed by methane CH_4 and carbon dioxide CO_2. Other gases are present in such small quantities that are not relevant for the calculations. Therefore, model calculations for the composition of biogas only with methane and carbon dioxide composition were performed. In order to provide sufficient amount of data, the calculated values of minimum and maximum state of methane are presented.

Poor biogas:

$x_{CH_4} = 40\%$ vol $x_{CO_2} = 60\%$ vol $M = 32.822$ kg/mol
$r = 253.3$ J/(kg.K) $\sigma_{CH_4} = 0.195$ $\sigma_{CO_2} = 0.804$
$Q_n = 9.764$ MJ/kg

Rich biogas:

$x_{CH_4} = 75\%$ vol. $x_{CO_2} = 25\%$ vol $M = 23.033$ kg/mol
$r = 360.1$ J/(kg·K) $\sigma_{CH_4} = 0.522$ $\sigma_{CO_2} = 0.478$
$Q_n = 26.1$ MJ/kg

Flammable component of biogas (methane – CH_4) contains the elements (carbon – C) and (hydrogen – H) according to the formula:

$$12.011 \text{ kg of C} + 4 \times 1.008 \text{ kg of } H_2 = 16.04 \text{ kg of } CH_4 \qquad (8)$$

where:

$$1 \text{ kg of } CH_4 = 0.74868 \text{ kg of C} + 0.251325 \text{ kg of } H_2 \qquad (9)$$

For stoichiometric calculations, these weight proportions are used:

Carbon C $c = 0.74868 \times \sigma_{CH_4}$ (10)
Hydrogen H $h_2 = 0.25132 \times \sigma_{CH_4}$ (11)
Carbon dioxide CO_2 $co_2 = \sigma_{CO_2}$ (12)

Atmospheric air. Atmospheric air serves as a source of oxygen in the process of combustion of biogas.

Mass composition of atmospheric air is defined as (Vitázek 2012):

Dry air:

nitrogen N_2 $\sigma_{N_2} = 0.75524$
oxygen O_2 $\sigma_{O_2} = 0.23144$
argon + inert gas Ar_+ $\sigma_{Ar+} = 0.0005$
carbon dioxide CO_2 $\sigma_{CO_2} = 0.01282$
molar weight $M_a = 28.96$
universal gas constant $r_a = 287.04$ J/(kg.K)

The density of atmospheric air ρ_a at basic conditions is $\rho_a = 1.225$ kg/m³.

Stoichiometric derivation. Ideal stoichiometric combustion of biogas is described by chemical equations for oxidation of individual flammable components.

For 1 kg of biogas:

$$C + O_2 = CO_2 \qquad (13)$$

$$1 \text{ kg of C} + 2.26642 \text{ kg of } O_2 = 3.6642 \text{ kg of } CO_2 \quad (14)$$

$$2 H_2 + O_2 = 2 H_2O \qquad (15)$$

$$1 \text{ kg of } H_2 + 7.9365 \text{ kg of } O_2 = 8.9365 \text{ kg of } H_2O \quad (16)$$

Stoichiometric oxygen mass for ideal combustion of 1 kg of biogas is as follows:

$$m_{O_2i} = 2.6642 \times c + 7.936 \times h \qquad \text{(kg)} \quad (17)$$

where: c, h – weight proportions of carbon and hydrogen

Relevant smallest stoichiometric mass of dry air for ideal combustion of 1 kg of biogas is as follows:

$$m_{Vi} = m_{O_2i}/\sigma_{aO_2} = m_{O_2i}/0.23144 \qquad \text{(kg)} \quad (18)$$

where: m_{O_2i} – stoichiometric mass of oxygen O2 for ideal combustion of 1 kg of biogas (relation 17); σ_{aO_2} – weight proportion of oxygen in the air

New gases formed by oxidation at stoichiometric combustion of 1 kg of biogas are as follows:

Carbon dioxide CO_2 $\Delta m_{CO_2} = 3.6642 \times c$ (kg)   (19)
Water vapour H_2O $\Delta m_w = 8.9365 \times h$ (kg)   (20)

When burning 1 kg of biogas, the weight of inert gas remains as follows:

Carbon dioxide CO_2 $m_{CO_2} = \sigma_{BCO_2}$ (kg)   (21)

where: σ_{BCO_2} – weight proportion of CO_2 in biogas

Mathematical model of combustion – Stoichiometric combustion gases from 1 kg of biogas

Fan sucks atmospheric air m_0 for stoichiometric combustion of biogas.

Composition of m_0:

dry portion $m_{OS} = m_{Vi}$ (22)
wet portion $m_{OW} = m_{OS} \times x_0 = m_{Vi} \times x_0$ (23)
total weight $m_{OC} = m_{OS} + m_{OW} = m_{Vi}(1 + x_0)$ (24)

where: x_0 – specific humidity of atmospheric air

In convertor, the biogas m_{BP} is added to the air. This forms an explosive mixture m_1:

Composition of m_1:

dry portion	$m_{1S} = m_{OS} + m_{BG}$	(25)
wet portion	$m_{1W} = m_{OS} \times x_0 = m_{Vi} \times x_0$	(26)
total weight	$m_{1C} = m_{IS} + m_{1W} = m_{Vi}(1 + x_0) + m_{BG}$	(27)
specific humidity	$x_1 = m_{1W}/m_{1S}$	(28)
enthalpy	$I_1 = m_{1S} \times i_{1V} + m_{1W} \times i_{1W} + m_{BG} \times i_{BG}$	(29)

If:
specific heat capacity of air
$$c_{pv} = 1.01 \text{ kJ/(kg·K)}$$
specific heat capacity of water vapour
$$c_{pw} = 1.84 \text{ kJ/(kg·K)}$$
specific heat capacity of biogas
$$c_{BG} = \sigma_{CH4} \times 2.2 + \sigma_{CO_2} \times 0.83 \text{ kJ/(kg·K)} \quad (30)$$

where: i_{1V} – specific enthalpy of dry air; i_{1W} – specific enthalpy of humidity; i_{BG} – specific enthalpy of biogas

Combustion mixture m_1 burns in the combustion chamber and hot stoichiometric gases m_2 are formed. The weight is constant.

Composition of m_2:

dry portion	$m_{2S} = m_{OS} - m_{O2i} + \Delta m_{CO_2} \times \sigma_{BCO_2}$	(31)
wet portion	$m_{2W} = m_{1W} + \Delta m_W$	(32)
total weight	$m_{2C} = m_{2S} + m_{2W} (\equiv m_{1C})$	(33)
specific humidity	$x_2 = m_{2W}/m_{2S}$	(34)

Chemical composition of m_2: stoichiometric combustion – all O_2 is spent:

$$m_{2N_2} = m_{OS} \times \sigma_{aN_2} \quad (35)$$
$$m_{2Ar} = m_{OS} \times \sigma_{aAr} \quad (36)$$
$$m_{2CO_2} = m_{OS} \times \sigma_{aCO_2} + \Delta m_{CO_2} \times \sigma_{BCO_2} \quad (37)$$
$$m_{2W} = m_{OS} \times x_0 + \Delta m_W \quad (38)$$
$$m_{2C} = m_{2N_2} + m_{2Ar} + m_{2CO_2} + m_{2W} \quad (39)$$

Enthalpy of the hot exhaust gases m_2:

$$I_2 = I_1 + m_{BG} \times Q_n \times \eta_h \quad (40)$$

where: η_h – efficiency of the burner (includes all the losses during combustion)

Final mixture

The final gas mixture m_3 is a mixture of ideal exhaust gases m_2 and additional atmospheric air m_p. The total mass of intake air is as follows:

$$m_{VS} = m_{OS} + m_{ps} = m_{Vi} + m_{ps} \quad (41)$$

where: m_{ps} – weight of dry portion of additional air

The excess air coefficient α is as follows:

$$\alpha = \frac{m_{VS}}{m_{Vi}} \quad (42)$$

Subsequently:

$$m_{VS} = \alpha \times m_{Vi} \quad (43)$$
$$m_{ps} = m_{VS} - m_{Vi} = m_{Vi}(\alpha - 1) \quad (44)$$
$$m_{pw} = m_{ps} \times x_0 = m_{Vi}(\alpha - 1) \times x_0 \quad (45)$$

where: m_{pw} – weight of wet portion of additional air

Composition of m_3:

dry portion	$m_{3S} = m_{2S} \times m_{ps}$	(46)
wet portion	$m_{3w} = m_{2w} \times m_{pw}$	(47)
total weight	$m_{3C} = m_{2S} \times m_{3w}$	(48)
specific humidity	$x_3 = m_{2w}/m_{3s}$	(49)

Chemical composition of m_3:

$$m_{3N_2} = m_{2N_2} + m_{ps} \times \sigma_{aN_2} \quad (50)$$
$$m_{3O_2} = m_{ps} \times \sigma_{aO_2} \quad (51)$$
$$m_{3Ar} = m_{2Ar} + m_{ps} \times \sigma_{aAr} \quad (52)$$
$$m_{3CO_2} = m_{2CO_2} + m_{ps} \times \sigma_{aCO_2} \quad (53)$$
$$m_{3W} = m_{2W} + m_{ps} \times \sigma_{aN_2} \quad (54)$$
$$m_{3C} = m_{3N_2} + m_{3O_2} + m_{3Ar} + m_{3CO_2} + m_{3W} \quad (55)$$

The molar mass M_3:

$$M_3 = \frac{1}{\Sigma \sigma_i/M} = \frac{m_{3C}}{\Sigma m_{3i}/M_i} \quad (56)$$

where: m_{3C} – total weight of the mixture; m_{3i} – weight of the component; M_i – molar weight of the component; σ_i – weight proportion of the component

Universal gas constant r_3:

$$r_3 = 8,314/M_3 \quad (57)$$

Enthalpy of the mixture m_3:

$$I_3 = I_2 + m_{ps}(1.01 + x_0 + 1.84)t_0 \quad (58)$$
$$i_3 = I_3/m_{3C} \quad (59)$$

where: x_0 – specific humidity of atmospheric air; t_0 – temperature of air

The temperature t_3 is calculated using the equation for i_3. The real enthalpies of individual gases are listed by the Ražnievič tables as follows (if $t = 0°C$ so $i = 0$). Linear regression for temperature section from 1,600 to 2,400°C is used.

$$i_i = b_i \times t + a_i \quad (60)$$

where: a_i, b_i – constants of linear equation

From this:

$$I_3 = \Sigma\sigma_{3i} \times i_{3i} = \Sigma\sigma_{3i}(b_i \times t_3 + a_i) \qquad (61)$$

After modification:

$$i_3 = \Sigma\,(m_{3i}\,(b_i \times t_3 + a_i))/m_{3C} \qquad (62)$$

From this, it is possible to determine the temperature t_3:

$$I_3 = \frac{i_3 \times m_{3C} - \Sigma\,m_{3i} \times a_i}{\Sigma\,m_{3i} \times b_i} \qquad (63)$$

RESULTS AND DISCUSSION

Using the presented methodology, there is an example of thermodynamic parameters of biogas, whose composition equals to the average value for basic state ($t = 15^{\circ}$C, $p = 101.325$ kPa).

Composition:

Methane	CH_4 57% vol
Carbon dioxide	CO_2 43% vol

Calculated parameters:

Molar mass		$M = 28.067$
Universal gas constant		$r = 296.2$ J/(kg·K)
Mass share:	CH_4	$\sigma_{CH_4} = 0.3257$
	CO_2	$\sigma_{CO_2} = 0.67425$
Density		$\rho_{BG} = 1.187$ kg/m^3
Heating value		$Q_n = 16.27$ MJ/kg
		$Q_n = 19.31$ MJ/m^3
Relative density		$d = 0.969$
Wobbe No.		$W_n = 19.62$ kJ/m^3
Chemical composition		$c = 0.243$
		$h = 0.0818$
		$co_2 = 0.6743$

Stoichiometric weight of dry air for 1 kg of biogas is $m_{Vi} = 5.61$ kg. For quick and accurate calculation of all the necessary thermodynamic exhaust parameters of biogas, a calculation program was developed.

Characteristic indicators

Measured biogas consumption V_{BG} is given.

Volumetric flow of biogas:

$$v_{BG} = V_{BG}/3{,}600 \qquad (\text{m}^3/\text{s}) \qquad (64)$$

Mass flow of biogas – basic state:

$$\dot{m}_{BG} = v_{BG} \times \rho_{BG} \qquad (\text{kg/s}) \qquad (65)$$

Volumetric flow of intake air – basic state:

$$v_a = \frac{m_{Vi} \times \alpha(1 + x_0) \times \dot{m}_{BG} \times r_a \times T_0}{p_a} \quad (\text{m}^3/\text{s}) \qquad (66)$$

Heating performance of the combustion unit:

$$P = \dot{m}_{BG} \times Q_n \times \eta_h \qquad (\text{W, kW, MW}) \quad (67)$$

Volumetric flow of the hot exhaust mixture 3 at temperature t_3 and pressure p_a:
Volumetric flow of intake air – basic state:

$$v_3 = \frac{m_{3C} \times \dot{m}_{BG} \times r_3 \times T_3}{p_a} \qquad (\text{m}^3/\text{s}) \qquad (68)$$

Volumetric share of O_2 and CO_2 in mixture 3:

$$O_2\text{: } x_{O_2} = \sigma_{3O_2}\frac{M_3}{M_{O_2}}100 = \frac{m_{3O_2}}{m_{3C}}\ \frac{M_3}{M_{O_2}}100 \quad (\%) \quad (69)$$

$$CO_2\text{: } x_{CO_2} = \sigma_{3CO_2}\frac{M_3}{M_{CO_2}}100 = \frac{m_{3CO_2}}{m_{3C}}\ \frac{M_3}{M_{CO_2}}100 \quad (\%) \quad (70)$$

Mass flows of individual gases in mixture 3:

$$\dot{m}_{3i} = m_{3C} \times \dot{m}_{BG} \times \sigma_{3i} \qquad (\text{kg/s}) \qquad (71)$$

Wobbe number W_n, which expresses conditions of gaseous fuel exchangeability:

$$W_n = \frac{Q_n}{\sqrt{d}} \qquad (\text{kJ/m}^3) \qquad (72)$$

where: Q_n – heating capacity on 1 m^3 (for basic state); d – relative density (for basic state)

Biogas as a source of renewable energy has been widely used recently. Its composition varies according to the input material. The article (Vítěz 2015) analyses methods of biogas production from rye grass. Biogas production from other materials is examined in the works of (Haitl et al. 2012; Janíček et al. 2012; Zhang et al. 2015) and others. Diversity, which is apparent in the biogas composition, can be also found in the methods of determination of the necessary parameters. Therefore, the whole process is rather challenging. Thermodynamic analysis is dealt with in the article (Chawla, Ghost 1992), where the calculation of parameters in generating hydrogen from biogas for fuel cells is described. Production of gaseous components in biofuel combustion is studied also in the work (Jandačka et al. 2011; Haitl et al. 2012). Usage of biogas as a fuel for combustion engines is described in the work of (Jablonický et al. 2010). The article (Ashrafi et al. 2008) is aimed at the thermo-

dynamic optimization in steam reforming of biogas. The calculations have shown higher efficiency and lower NO$_x$ production when using modified biogas in combustion engines. The presented method enables calculation of all the necessary thermodynamic and operating values of biogas with particular composition by means of gas mixture thermodynamics and tabular exact parameters of individual gaseous components. Entering of input values enables to distinguish the composition of exhaust gases for the particular devices (e.g. spark ignition engines, micro turbines, gas burners in boilers etc.). Our results correspond with the authors mentioned above.

CONCLUSION

Biogas is produced from different materials even at the same device. Accordingly, its composition varies. Available literature indicates that it varies in a considerable extent. Therefore, it is not easy to determine the parameters of biogas. Biogas and its exhaust create a mixture of six different gases and the composition of the mixture changes substantially during combustion. Therefore, identification of individual composition is challenging. All exhaust components from biogas with an increase of temperature, will increase its specific heat capacity. In this article, linear regression for selected temperature section from accurate tables was used, while all formulas showed a correlation coefficient higher than 0.999. Elaborated computing program enables the calculation of all parameters according to this methodology without its detailed knowledge. It is necessary to specify the content of the main components of biogas. Direct usage of biogas is not possible because of various impurities that have to be removed – water vapour, carbon dioxide, hydrogen sulphide, oxygen, nitrogen, hydrocarbons, halogen derivatives of hydrocarbons, silicon or organosilicon compounds. This may increase the cost for the utilization of biogas.

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