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# A METHOD FOR ESTIMATION OF BIOMASS ENERGY UTILISATION BY BIOGAS PRODUCTION

***Abstract.*** *Currently, about 10% of the energy in the world is biofuel energy from plant biomass. Anaerobic fermentation is a sustainable technology in waste processing and energy production. First-generation biofuels are made from dedicated feedstocks and conversion technology bioenergy crops. Second-generation biofuels are bio-based products derived from non-food feedstocks, which are agricultural and forestry feedstocks. Third-generation biofuels are produced from aquatically cultivated feedstocks. To assess the output of biogas from biomass, it is necessary to perform calculations of anaerobic fermentation processes. The well-known Buswell model allows for the theoretical determination of the amount of biomethane from a substrate with organic substances. The method estimates the output of anaerobic fermentation products based on theoretical stoichiometric evaluation. Theoretical Biochemical Methane Potential considers all organic substances as biodegradable. The amount of biomethane (*$nCH_4$*) is a parameter that depends on the elementary composition of organic matter. To determine *$nCH_4$*, measurements and calculations based on elemental analysis are required. The empirical formula of organic matter can be determined using stoichiometric equations. Higher values are obtained for grains and lignin - from 698.6 to 705.4 dm³/kg, for wood and straw the biogas yield is from 476.5 to 514.2 dm³/kg. Solid wastewater sludge - 570 dm³/kg. Biogas from* *anaerobic fermentation not only represents a clean energy source but also contributes to reducing the volume of solid waste and greenhouse gas emissions. Anaerobic fermentation can also be integrated into various agricultural and industrial processes.*

***Key words:*** *Biogas, Biomethane, Anaerobic Fermentation, Biothermodynamics*.

**Introduction.** EU goals determine the decarbonization of the Member States. One of the directions for decarbonization is the projects of renewable gases (biogas, biomethane) and biofuels. The potential of the renewable gases industry, according to European Biogas Association (EBA) exceeds the prospects for using hydrogen. Biomethane is a biogas that is brought to a gas quality containing 95 % to 98 % of methane. The production of biomethane is carried out by the technology of anaerobic fermentation of waste and residues of agricultural biomass. Biomethane can be used for the production of thermal and electricity, as fuel for compressed and liquefied transport, as well as as a raw material for the chemical industry. In 2020, the production of biomethane in EU countries will be up to 32 TW·h. In the period up to 2050, the production of biomethane will increase from 1000 to 1400 TW·h, which will replace 20 % of the need for natural gas, according to EU plans. According to EBA, the number of biomethane plants in EU countries is 729. Germany has the highest proportion of biomethane installations (232), France-131, UK-80 [1-5].

Electricity production with biomass is possible by thermochemical technologies: burning, rapid pyrolysis and gasification. Direct combustion is the simplest way to produce thermal energy with efficiency of about 75 % and electricity with efficiency of about 8-13 %. Rapid pyrolysis is the process of rapid heating of fuel and waste in a boiling layer to high temperature in the absence of air. Charcoal particles and pyrolysis gas come out at the outlet. The electrical efficiency of technology is from 20 to 30 %, and the thermal efficiency of modern installations reaches 91-93 %. The technology of gasification of woody and plant waste is sold in high temperature and pressure with restriction of air access. The electrical efficiency is 40 %, and thermal efficiency is 40-45 %.

Gasificationis is thermal oxidation occurning at high temperature (750-900 °C) in the environment (steam, air, oxygen, or a mixtuie of them). Gasification products are gases-$H_2$, CO, $CH_4$, and $CO_2$. There are also solid product (char), inorganic contaminants ($H_2S$ and HCl) and organic contaminants (tar). Anaerobic Digestion (AD) is process whereby microorganisms break down biomass in the absence of oxygen. AD for biogas production involves four processes called hydrolysis, acidogenesis, acetogenesis, and methanagenesis. Hydrolysis breaks down polymers like cellulose, starch, and proteins into monomers by exoenzymes. Acetate, $H_2$, $CO_2$, and volatile fatty acids (VFA) are produced during acidogenesis while acetogenesis produces acetic acid. The final process, methanogenesis runs parallel to the third to transform the $CO_2$ and $H_2$ into methane.

The basics of biogas energy generation and thermodynamic principles

(The role of thermodynamics in enhancing anaerobic digestion efficiency)

By applying thermodynamic principles to biogas energy generation, we can enhance the overall efficiency and maximize the benefits. The following are key consideration:

-Heat exchange,

-Exergy analysis,

-Entropy optimization,

-Utilizing thermodynamics for maximizing energy generation from biogas

**Relevance of the research**. Biogas is the promising technology of decreasing natural gas usage. Its burning simply returns the sequestrated $CO_2$ by plants and, possibly, converted by animals. Thus, it doesn't influence the $CO_2$ balance in the nature instead of using fossil fuels releasing the $CO_2$ deposits accumulated dcuring billion years. Biogas is a renewable resource. Thus, effective usage of it is one of the solution of global warming problem.

**Latest research and publications.**

***The basics of biochemical processes of carbohydrate breakdown***. There are two processes of carbohydrate breakdown - anaerobic breakdown of carbohydrates (glucolysis) and aerobic breakdown (oxidation) of carbohydrates. The anaerobic process of carbohydrate breakdown can be analyzed on the multi-stage process (12 intermediate stages) of the conversion of glucose into lactic acid according to the reaction [6-7] with the difference in the Gibbs energy $\Delta G_0$ [kJ/mol]:

$$C_6H_{12}O_6 = 2CH_3\text{–}CHOH\text{–}COOH,\ \Delta G_0 = -\ 115.137\ \text{kJ/mol} \qquad (1)$$

Glucose breakdown efficiency is 40% (cucumbers). Another direction of the process is the transformation with the participation of acetylcoenzyme and the formation of acetic acid $CH_3COOH$ (vinegar fermentation).

Aerobic decay (oxidation) of carbohydrates and glycolysis pass equally to the stage of formation of pyruvic acid. In the presence of oxygen, the process of converting pyruvic acid into lactic acid is inhibited and the process of oxidation of pyruvic acid, which leads to several times more release of the amount of free energy (up to 1250 kJ/mol). Fermentation refers to intracellular mechanisms. Due to fermentation, many organisms receive chemical energy from glucose and other subtractic without molecular oxygen. Fermentation is a life without air.

In 1857, the biological nature of the fermentation process caused by living cells of microorganisms was proved by Louis Pasteur. He found that in aerobic conditions, yeast is formed from sugar 20 times more a small substance than in anaerobic. He found that oxygen suppresses fermentation (Louis Pasteur effect). The process of methane fermentation was studied at work [8]. The fermentation process was considered from two phases. In the first phase of complex organic substances acids (acetic, anthill, lactic, oil and others), alcohols (ethyl, propyl, butyl and others), gases (carbon dioxide, hydrogen, hydrogen sulfide, ammonia), amino acids, glycerin and others) are formed. The first phase is called acidic or hydrogen fermentation, because In the process, the excretion of acids and pH is reduced to 5-4.5.The second phase (alkaline or methane fermentation) - there is a further decomposition of substances with the release of gases consisting of methane, carbon dioxide, hydrogen and nitrogen. The Barker scheme is convenient for practical use. Other works distinguish three and four phases of decay of organic matter and different groups of bacteria. There are the following phases of methane synthesis from the substrate:

1. Hydrolysis phase. High molecular weight organic substances (protein, cellulose, carbohydrates, fats) by hydrolysis bacteria are converted to low molecular weight water-soluble compounds (monosaccharides, amino acids, fatty acids and water). The polymers turn into monomers.
2. Acid-forming phase. Organic monomers are decomposed into acids (acetic, propionic, oil), alcohols and aldehydes and compounds: $H_2$, $CO_2$, $N_2$, $H_2S$. Anaerobic conditions are created necessary formation of methane bacteria.
3. Acetogenic phase. This phase is carried out by acetogenic bacteria. This forms acetate with hydrogen and acetic acid by using hydrogen to restore $CO_2$.
4. Methanogenesis.

Acetic acid is decomposed into methane, carbon dioxide and water according to the reaction:

$$CH_3COON \rightarrow CH_4 + CO_2 + H_2O. \tag{2}$$

Hydrogen and carbon dioxide turn into methane and water:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \, – \tag{3}$$

stimulate the process of synthesis of biogas supplement of green amaranth plants, corn and melafen.

Acetogenation - the process of converting fatty acids, amino acids and alcohols into acetic acid at a temperature of 25ºC. The duration of the process is about 24 hours with the formation of acetic acid. Methanogenic phase - methane and carbon dioxide. The duration of the process is about 14-20 days. Most bacteria form methane of molecular hydrogen and carbon dioxide according to the reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O. \tag{4}$$

Some types of bacteria form methane from acetic acid.

$$CH_3CON = CH_4 + CO_2 \tag{5}$$

The processes of methane formation of cellulose and formic acid, methanol and methylamine, carbon monoxide are known. Processes in the acid phase and methanogenic phase occur at different speeds. Acid bacteria (aerobic) double the mass for 5-10 hours. Methanogenic bacteria develop slowly and double the mass in 3-5 days.

The known McCarthy scheme [9], according to which the process of anaerobic substance occurs in three phases:

- in the first phase, complex organic substances biological polymers (proteins, lipids, polysaccharides) are subjected to hydrolysis with the formation of organic acids (oil, propionic, dairy), under the influence of microorganisms, hydrolysis of monosaccharides, organic acids and alcohols occurs, and, as a result, hydrogen, ammonia, acids are formed.
- the second phase is acetogenic microorganisms – anaerobic bacteria that convert organic acids into acetic acid, hydrogen, carbon dioxide;
- in the third phase, meta-forming bacteria break down organic matter using metabolites formed in the first phases.

Methanogens use water to recover $CO_2$ to $CH_4$

$$4H2 + CO2 = CH4 + 2H2O \tag{6}$$

***Biomass resources.*** The energy efficiency of plant biomass is determined by its yield and annual production [10, 11]

Let us perform the the analysis of the influence of pyrolysis parameters in thermal destruction on the composition of biofuels when using various raw materials.

*Fundamental hydrolysis of cellulose from extraordinary wood.* Using pre-treatment of corn cobs with a deep eutectic solvent fraction of hemicellulose and lignin of raw biomass, cellulose content increases by 140 %. Corn straw was pre-treated with microorganisms and a microbiological agent helps to reduce the process of biogas production. This reduces the content of lignin and cellulose, gas formation increases.

Table 1. Energy characteristics of biomass

| Biomass | Yield/Dry matter [t/hm$^2$] | Energy efficiency | |
|---|---|---|---|
| | | GJ/hm$^2$ | TOE/hm$^{2*}$ |
| Cereal straw | 2,6/2,2 | 40,3 | 1,38 |
| Potato buds | 1,7/1,3 | 19,5 | 0,67 |
| Straw rapeseed | 2,5/2,1 | 38,2 | 1,30 |
| Potato tubers | 21,2/5,3 | 85,9 | 2,93 |
| Beet | 38,7/9,7 | 155 | 5,3 |
| Corn stems | 55/15 | 274,5 | 9,37 |
| Jerusalem artichoke stems | 95,7/27,5 | 495 | 16,9 |

* TOE – Ton of Oil Equivalent 29.3 GJ/T

*Anaerobic Biomass Conversion in Methane.* The output of biogas from vegetable biomass is given in Table 2 [12].

Table 2. Biogas exit from vegetable biomass

| Type of raw material | Gas output, m$^3$ per 1 kg of dry matter | Methane content, % |
|---|---|---|
| Tree leaves | 0,219 – 0,29 | 58 |
| Corn stalks | 0,38 – 0,46 | 59 |
| Oat straw | 0,29 – 0,31 | 59 |
| Barley straw | 0,25 – 0,30 | 59 |
| Rye straw | 0,20 – 0,30 | 59 |
| Wheat straw | 0,20 – 0,30 | 59 – 60 |
| Beet tops | 0,40 – 0,50 | 85 |
| Potato tops | 0,28 – 0,49 | 60 – 75 |

The energy intensity (energy) of biogas is 22.3 MJ/m$^3$ [13]. 0.30 m$^3$ of biogas, or 180 dm$^3$ of methane at a concentration of 60 %, can be obtained per 1 kg of dry biomass. The energy consumption of dry biomass is 15...18 MJ/kg. When burning biogas with an energy consumption of 6.7 MJ/kg.

Processing of plant biomass is determined by technological processes or exergy. Analyzing various technologies and losses of exergy of vegetable fuel we get the following:

1. Grinding, drying and pressing, packaging (98-99 % of output energy), seal 5-10 times.
2. Fermentation (liquid fuel energy) efficiency - 30 %, low concentration of fuel components in substrates; expensive technologies;
3. Methane fermentation (methane), efficiency 30...40 %, low gas formation;
4. Thermolysis (gas synthesis, CO + $H_2$, efficiency 20...40 %), the disadvantage is high temperatures.

Comparing technological processes, it can be seen that solid fuels can be obtained with low loss of degradation energy and are the most promising. Experimental studies of the efficiency of transformation of aerobic fermentation products into biogas and electrical power showed that the efficiency of biomass conversion in plant was 59.87 %. The efficiency of energy products in relation to the overall energy energy reaches a low value of 27.66 %. Degradation of energy intensity is observed.

More effective is the production of animal manure (40-50 $m^3$/10 $m^3$ per day) or biogas (Landfillgas) from dumps [15].

The elemental composition of vegetable biomass and the highest combustion heat are shown in Table. 3. In Table 4, there are compositions of organic waste (manure). And in Table 5, there is a biogas production for different substrates and additives.

Table 3. Elementary composition of vegetable biomass
and higher combustion heat

| Elementary composition | Wood | Lignin | Straw | Crops |
|---|---|---|---|---|
| C, мах. % | 47...51 | 65,9 | 42...47 | 43...60 |
| H, мах. % | 5,7...6,3 | 4,9 | 5,1...6,0 | 6,4...7,2 |
| O, мах. % | 39...44 | 23,0 | 39,1...43,8 | 24...46 |
| N, мах. % | 0,13...0,54 | 0,7 | 0,4...1,1 | 1,7...3,9 |
| Ashiness | 0,5...4,0 | 5,1 | 3,8...12,2 | 2,0...4,6 |
| Higher combustion heat $Q^{в}$, MJ/kg | 18,4...19,2 | 20,6 | 15,8...17,7 | 17,0...26,5 |

Table 4. Chemical composition of organic waste (manure)

| | Content, %, of | | | | |
|---|---|---|---|---|---|
| Substrate type | C | O | S | H | N |
| Cattle Manure | 61 | 12 | 1 | 8 | 18 |
| Litter | 82 | 9 | 0,9 | 1 | 7 |
| Pig Manure | 81 | 11 | 0,08 | 7 | 0,92 |
| Horse Manure | 77 | 13 | 0,07 | 9 | 0,75 |
| Cattle Manure and Corn Grains | 71 | 16 | 1 | 8 | 19 |
| Pig Manure and Corn Grains | 91 | 4 | 9 | 7 | 4 |
| Horse Manure and Corn Grains | 82 | 9 | 15 | 1 | 0,8 |

The decomposition of manure occurs through the process of anaerobic decomposition – urease urobacteria – according to the reaction:

$$CO(NH_2)_2 + H_2O = (NH_4)_2\,CO_3 \tag{7}$$

Table 5. Biogas yield from different types of substrate
with active biological additives

| Substrate | Biogas yield [$m^3$/10 kg of substrate] | | |
|---|---|---|---|
| | without additives | with the addition of corn | with the addition of the drug Medosfon |
| Cattle Manure | 9,19 | 9,8 | 10,92 |
| Horse Manure | 7,31 | 9,9 | 11,59 |
| Pig Manure | 13,92 | 14,8 | 16,66 |
| Chicken Manure | 7,7 | 9,33 | 10,38 |

Ammonium carbonate decomposes:

$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O \tag{8}$$

The complete decomposition of fresh cattle manure according to the conditional formula (in mass fractions of organic matter) is written as:

$$C_{0.61}\ H_{0.08}\ O_{0.12}\ N_{0.18}\ S_{0.01} + 0.77\ H_2O \rightarrow$$
$$\rightarrow 0.275\ NH_4^+ + 0.5HCO_3^- + 0.413CO_2 + 0.571CH_4 + 0.011H_2S \tag{9}$$

Hence, 0.413 g of $CO_2$ and 0.571 g of $CH_4$ will be released per 1 g of ashless substance.

*Chemical composition of the degraded waste to predict methane production*. The formation of methane from decomposed waste (fermentation products) can be determined from the chemical reaction as

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4. \tag{10}$$

where $C_nH_aO_b$ – organic matter; $a$, $b$ – stoichiometric coefficients.

This model did not include the production of hydrogen. In the process of glucose decomposition, according to the reaction equation, methane can be obtained in the amount of: from 1.0 g $C_6H_{12}O_6$ we'll obtain 0.25 g $CH_4$, 0.69 g $CO_2$, 0.06 cell mass, and 632 kJ energy or (from 1 mole of glucose, 2.8 moles of $CH_4$ and 2.6 moles of $CO_2$ are obtained [15]).

**The aim of the work** is to estimate the possibilites of biogas production from different sources.

**Main part.** Currently, about 10 % of the energy produced in the world is biofuel energy obtained from the fermentation of plant biomass. Biofuels from biomass have been widely implemented: sugar cane ethanol in Brazil, corn ethanol in the United States. Anaerobic digestion is a sustainable technology used in waste treatment and bioenergy production.

First generation biofuels are produced from dedicated on the feedstock and conversion technology bioenergy crops. Second-generation biofuels are bio-based products that that come from non-food feedstock. That is agriculture and forestry feedstock. Third-generation biofuels are produced from aquatic cultivated feedstock.

The Buswell model [16] allows for the theoretical determination of the amount of biomethane from an organic substrate. The model combines chemistry, biology, mathematics and thermodynamics in a biosystem.

The stoichiometric Buswell's equation ($BE_q$) plays a paramount role in counting quantity of biomethane either in pure or mixed organic matters.

The equation can be written as follows:

$$C_xH_yO_z+\left(x-\frac{y}{4}-\frac{z}{2}\right)H_2O=\left(\frac{x}{2}+\frac{y}{8}-\frac{z}{4}\right)CH_4+\left(\frac{x}{2}-\frac{y}{8}+\frac{z}{4}\right)CO_2. \qquad (11)$$

Theoretical biochemical methane potential (TBMP) considers all organic matters are biodegradable. Quantity of biomethane ($nCH_4$) is a parameter which depends on the elemental composition of organic matters.

To determine $nCH_4$, measurements and calculations are necessary based on elemental analysis, the empirical formula of an organic matter can be determined using stoichiometric *BEq*.

The most organic matters their C/H/N/S contents are analysed using elemental analysis. The mass fraction $w_i$ [%] of elements *i* and of ash $w_{ash}$ [%] in samples are in Table 6.

The mathematical relationship for ultimate analysis is shown:

$$w_{Ash}+\sum w_i=100\%.$$

For $C_xH_yO_zCl_sN_vS_u$ matters [%]:

$$\sum w_i=w_{\mathrm{C}}+w_{\mathrm{H}}+w_{\mathrm{O}}+w_{\mathrm{Cl}}+w_{\mathrm{N}}+w_{\mathrm{S}}.$$

For $C_xH_yO_zCl_sN_vS_u$ matters [%]:

$$\sum w_i=w_{\mathrm{C}}+w_{\mathrm{H}}+w_{\mathrm{O}}+w_{\mathrm{Cl}}+w_{\mathrm{N}}+w_{\mathrm{S}}.$$

Mass fraction of the ash is calculated by the equation:

Table 6. Mass fraction of elements

| Sample | Element/Component | | | | | | |
|---|---|---|---|---|---|---|---|
| | C | H | O | Cl | N | S | Ash |
| | Atomic mass $\mu_i$ [g/mol] | | | | | | |
| | 12.011 | 1.008 | 15.999 | 35.453 | 14.007 | 32.065 | – |
| | Mass fraction $w_i$ [%] | | | | | | |
| Chicken litter | 45.32 | 5.85 | 27.38 | 0.35 | 5.16 | 0.45 | 15.49 |
| Feedlot manure | 45.39 | 5.35 | 30.98 | 1.16 | 0.96 | 0.29 | 15.87 |
| Wood | 47-51<br>(50) | 5.7-6.3<br>(5.7) | 39-44<br>(39) | – | 0.13-0.54<br>(0.13) | – | 0.5-40<br>(5.17) |
| Lignin | 65.9 | 4.9 | 23 | – | 0.7 | – | 5.1 |
| Straw | 42-47<br>(47) | 5.1-6.0<br>(5.5) | 39.1-43.8<br>(40) | – | 0.4-1.1<br>(1.0) | – | 3.8-12.2<br>(6.5) |
| Cereals | 43-60<br>(60) | 6.4-7.2<br>(7.2) | 24-46<br>(24) | – | 1.7-3.9<br>(3.0) | – | 2.0-4.6<br>(5.8) |

Note: in parentheses, there are values considered for calculations in this work

$$w_{Ash} = 100 - \sum w_i.$$

The values taken into account in the calculations are indicated in Table 7 in parentheses.

We can convert the element to mole by dividing the mass of element per it's atomic mass. Thus, the mole $n$ relation

$$n_C : n_H : n_O : n_{Cl} : n_N : n_S = \frac{w_C}{\mu_C} : \frac{w_H}{\mu_H} : \frac{w_O}{\mu_O} : \frac{w_{Cl}}{\mu_{Cl}} : \frac{w_N}{\mu_N} : \frac{w_S}{\mu_S} = x : y : z : s : v : u \qquad (12)$$

Let the mass of a waste be 100.0 g then the elemental ratios in chicken litter and feedlot manure are counted (Table 7). The empirical formulas and masses are in Table 8.

Stoichiometric coefficients $BE_q$ are determined from the equation:

$$C_x H_y O_z Cl_s N_v S_u + \frac{4x - y - 2z + s + 3v + 2u}{4} H_2O \rightarrow$$
$$\rightarrow \frac{4x + y - 2z - w - 3v - 2u}{8} CH_4 + \frac{4x - y + 2z + s + 3v + 2u}{8} CO_2 +$$
$$+ sHCl + vNH_3 + n H_2S \qquad (13)$$

Table 7. Elements ratios

| Sample/mole | $n_C = x$ | $n_H = y$ | $n_O = z$ | $n_N = v$ | $n_S = u$ | $n_{Cl} = s$ |
|---|---|---|---|---|---|---|
| Chicken litter | 3.773 | 5.804 | 1.711 | 0.368 | 0.014 | 0.90 |
| Feedlot manure | 3.779 | 5.308 | 1.936 | 0.069 | 0.009 | 0.033 |
| Wood | 4.167 | 5.655 | 2.437 | 0.009 | - | - |
| Lignin | 5.492 | 4.861 | 1.437 | 0.050 | - | - |
| Straw | 3.917 | 5.456 | 2.500 | 0.071 | - | - |
| Cereals | 5.000 | 7.143 | 1.500 | 0.214 | - | - |

Table 8. The empirical formulas and empirical masses

| Sample | Empirical formula, $C_xH_yO_zCl_wN_vS_u$ | Empirical mass, $\mu(C_xH_yO_zCl_wN_vS_u)$ |
|---|---|---|
| Chicken litter | $C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$ | 84,510 |
| Feedlot manure | $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$ | 84,130 |
| Wood | $C_{4.167}H_{5.655}O_{2.437}N_{0.09}$ | 94,83 |
| Lignin | $C_{5.492}H_{4.861}O_{1.437}N_{0.050}$ | 94,5 |
| Straw | $C_{3.917}H_{5.456}O_{2.500}N_{0.071}$ | 93,5 |
| Cereals | $C_{5.000}H_{7.143}O_{1.500}N_{0.214}$ | 94,2 |

The values of stoichiometric coefficients are given in table 9

Table 9. Values stoichiometric coefficients

| Sample | $n_{H_2O}$ | $n_{CH_4}$ | $n_{CO_2}$ | $n_{HCl}$ | $n_{NH_3}$ | $n_{H_2S}$ |
|---|---|---|---|---|---|---|
| Chicken litter | 1,752 | 2,042 | 1,732 | 0,010 | 0,368 | 0,014 |
| Feedlot manure | 1,549 | 2,037 | 1,742 | 0,033 | 0,069 | 0,009 |
| Wood | 6,166 | 2,177 | 1,989 | - | 0,009 | - |
| Lignin | 3,595 | 2,976 | 2,516 | - | 0,050 | - |
| Straw | 1,356 | 1,989 | 1,928 | - | 0,071 | - |
| Cereals | 2,625 | 2,938 | 2,062 | - | 0,214 | - |

$BE_q$ for wood:

$$C_{4,167}H_{5.655}O_{2.437}N_{0.009} + 6.166H_2O \rightarrow 2.177CH_4 + 1.989CO_2 + 0.009NH_3 \quad (14)$$

$BE_q$ for lignin:

$$C_{5,492}H_{4,861}O_{1,437}N_{0.050} + 3,595H_2O \rightarrow 2.976CH_4 + 2,516CO_2 + 0.05NH_3 \quad (15)$$

$BE_q$ for straw:

$$C_{3.917}H_{5.456}O_{2.500}N_{0.071} + 1.356H_2O \rightarrow 1.989CH_4 + 1.928CO_2 + 0.071NH_3 \quad (16)$$

$BE_q$ for cereals:

$$C_{5.000}H_{7.143}O_{1.500}N_{0.214} + 2.625H_2O \rightarrow 2.938CH_4 + 2.062CO_2 + 0.214NH_3 \quad (17)$$

$BE_q$ has the form for chicken litter:

$$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014} + 1.752H_2O \rightarrow 2.042CH_4 + 1.732CO_2 + 0.010HCl + 0.368NH_3 + 0.014H_2S. \quad (18)$$

$BE_q$ has the form for feedlot manure:

$$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009} + 1.549H_2O \rightarrow 2.037CH_4 + 1.742CO_2 + 0.033HCl + 0.069NH_3 + 0.009H_2S. \quad (19)$$

Biomethane and biogas can be calculated by the following formula:

$$n_C = x = n_{CH_4} + n_{CO_2}$$

For mole of biomethane

$$n_{CH_4} = \frac{4x + y - 2z - s - 3v - 2y}{8}$$

Mole of biogas

$$n_{CH_4} + n_{CO_2} + n_{HCl} + n_{NH_3} + n_{H_2S} = x + s + v + n.$$

The calculation results are in table 10.

The percentage parameters of anaerobic digestion can be determined by the following two relations in per cents:

$$100 \cdot \frac{n_{biomethane}}{n_{biogas}} \quad (20)$$

$$100 \cdot \frac{n_{CH_4}}{n_{CH_4} + n_{CO_2}} \quad (21)$$

Table 10. Calculation results

| Sample | Mol of biogas $n_{biogas}$ | Mol of biome-thane $n_{biomethane}$ | $100 \times \times \frac{n_{biometha}}{n_{biogas}}$ [%] | $100 \times \times \frac{n_{CH_4}}{n_{CH_4}+n_{CO_2}}$ [%] | Volume, $dm^3$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $CH_4$ | $CO_2$ | $NH_3$ | biogas |
| Chicken litter | 4.165 | 2.042 | 49.03 | 54.12 | 541.11 | 459.0 | – | 1103,96 |
| Feedlot manure | 3.971 | 2.037 | 51.30 | 53.90 | 542.29 | 463.8 | – | 1035.73 |
| Wood | 4.176 | 2.177 | 52.1 | – | 514.2 | 469.0 | 2.1 | 986.1 |
| Lignin | 5.542 | 3.013 | 54.4 | – | 705.4 | 596.4 | 11.8 | 1313.2 |
| Straw | 3.988 | 1.989 | 49.9 | – | 476.5 | 461.9 | 17.0 | 955.4 |
| Cereals | 5.214 | 2.937 | 56.3 | – | 698.6 | 490.3 | 50.9 | 1239.8 |

Using the values of elemental composition (*x*, *y*, *z*, *s*, *v*, *u*) or stoichiometric coefficients ($n_{H_2O}$, $n_{CH_4}$, $n_{CO_2}$, $n_{HCl}$, $n_{NH_3}$, $n_{H_2S}$) we obtain [$dm^3$]:

$$V_{CH_n} = \frac{22400(nCH_4)}{nC_xH_yO_zCl_SN_vS_n}. \tag{22}$$

$$V_{biogas} = V_{CH_4} + V_{CO_2} + V_{HCl} + V_{NH_3} + V_{H_2S}. \tag{23}$$

In biotechnological systems, there are two kind of processes:

- isochoric in sealed apparatus;
- isobaric in open-type apparatus.

In isochoric processes, the volume is constant disregarding the volume change due to heating or cooling the vessel. The heat amount amount

$$Q_V = \int_1^2 (dU + pdV) = \int_1^2 dU = U_2 - U_1 = \Delta U, \tag{24}$$

where $U$ – internal energy [J]; $p$ – pressure [Pa]; $V$ – volume [$m_3$]; $U_1$ – the internal energy at the beginning of a process [J]; U2 – the internal energy at the end of the process [J]; $\Delta U$ – change of the internal energy [J].

In isobaric processes, the pressure is constant disregarding the barometric pressure change during the process. The heat amount

$$Q_p=\int_1^2 dU+\int_1^2 pdV=U_2-U_1+pV_2-pV_1=$$

$$=\left(V_2+pV_2\right)-\left(V_1+pV_1\right)=H_2-H_1=\varDelta H, \tag{25}$$

where $V_1$ is the volume at the beginning of the process; $V_2$ is the volume at the end of the process; $H_1$ is the enthalpy at the beginning of the process [J]; $H_2$ is the enthalpy at the end of the process [J]; $\Delta H$ is the enthalpy change [J].

Hence, the heat of the process at $p$ = const or $V$ = const is a function of the state of the system. This is a consequence of the first law of thermodynamics is the theoretical basis of thermochemistry and is called Hess law.

According to the Hess's law, the thermal effects of different physicochemical processes are calculated: biochemical reactions, phase transitions, dissolution processes, etc., when there are no experimental data. In biochemical transformations there is a change in the internal energy of the system, due to the fact that the internal energy of the reaction products differs from the internal energy of the substances that reacted (the source products).

Hess's law can be formulated as: the thermal effect of a reaction that occurs at constant pressure or constant volume, does not depend on the path of the reaction, and is determined only by the condition of the starting substances and reaction products.

The thermal effect of isochoric reaction is equal to the increase in the internal energy of the system [J]:

$$Q_V = \Delta U. \tag{26}$$

The thermal effect of an isobaric reaction is equal to the increase in the enthalpy of the system [J]:

$$Q_p = \Delta H. \tag{27}$$

The thermal effect of the endothermic reaction (which occurs with heat absorption) is taken positive, and for the exothermic reaction, the thermal effect will be negative (reaction with heat release).

When streamlining thermochemical equations of reactions, the aggregate state of reagents should be indicated: (T) - solid, (P) - liquid, (d) - gaseous.

Using the consequences of Hess's law, it's possible to calculate the value of thermal effects for biochemical reactions.

For comparison and use in calculations, thermal effects are calculated under standard conditions: pressure $p$ = 101325 Pa and temperature $T$ = 298.15 K (25 °C).

The thermal effect under standard conditions is denoted as $\Delta_R H^0$ ($R$ means "reaction").

The standard thermal effect of the reaction is equal to the difference of standard heat formation of reaction products and starting substances (taking into account the steichiometric coefficients):

$$\Delta_r H^0 = \Sigma \left( V_i \Delta H_i^0 A_i \right) - \Sigma_j \left( V_j \Delta H_j^0 A_j \right), \tag{28}$$

where $i$ is the number of each initial material and $j$ is the number of each final products.

The standard heat (enthalpy) of the formation of a substance $\Delta H_f^0$ [J] ($f$ means "formation") is the thermal effect of the reaction of the formation of one mole of this substance from simple substances (or elements) taken in the thermodynamically stable state at $T$ = 298.15 K and $p$ = 101325 Pa.

The heat of the formation of simple substances in thermodynamically stable state under standard conditions is taken equal to zero ($\Delta H_f^0(O_2) = 0$).

Knowing the thermal effect of the formation of a chemical compound in one aggregate state, it is possible to calculate the thermal effect of its formation in another aggregate on the basis of Hess's law:

$$\Delta H_f(d) = \Delta H_f(P) + \Delta H_{evaporation}, \tag{29}$$

$$\Delta H_f(P) = \Delta H_f(d) + \Delta H_{melting}, \tag{30}$$

where $\Delta H_{evaporation}$ – the enthalpy of evaporation [J]

There are three kinds of information that we must have for biochemical engineering: balances, kinetics and thermodynamics.

The standard molar enthalpy of combustion $h_c^o$ [kJ/mol] of organic matter is proportional to the number of electrons that it transfers to oxygen during combustion [7, 17]

$$h_c^o = -111.19 \cdot E \tag{31}$$

Where 111.19 kJ/mol is the energy amount per electron; $E$ is the number of electrons transferred to oxygen during combustion to $CO_2$(g), $H_2O$(l), $N_2$(g), $P_4O_{10}$(s), $SO_3$(g) [kJ/mol]:

$$\left(\overline{h}_f^o\right)_{bio} = n_c\left(\overline{h}_f^o\right)_{CO_2} + \frac{1}{2} n_H \left(\overline{h}_f^o\right)_{H_2O} - \overline{h}_c^o$$

$$\overline{h}_{f(bio)}^o = n_{CO_2} \cdot \overline{h}_{f(CO_2)}^o + n_{H_2O} \cdot \overline{h}_{f(H_2O)}^o - n_C \cdot \overline{h}_{f(C)}^o \qquad (32)$$

or

$$\overline{h}_{f(bio)}^o = \frac{\overline{h}_{f(bio)}^o}{M_{r(bio)}} \qquad (33)$$

for the reaction

$$C_{nc} H_{nH} O_{nO} + \left(n_c + \frac{1}{4} n_H\right) O_2 \rightarrow n_c CO_2 + \frac{1}{2} n_H H_2 O \qquad (34)$$

Standard molar entropy can be determined according to the equation [7].

$$\overline{S}_{bio}^o = 0{,}187 \sum_i \frac{\overline{S}_i^o}{a_i} n_i, \quad (33)$$

Where $n_i$ is the number of atoms of element in the empirical formula of the biomass, $\overline{S}_i^o$ – standard molar entropy of element $i$ [kJ/mol], $a_i$ – the number of atoms per molecule of element $i$ in its standard state elemental form.

The standard state elemental form of carbon is graphite, which is simply written as C, which makes $a_C = 1$. The hydrogen, oxygen and nitrogen are in their standard state in elemental forms. All diatomic gasses $H_2$, $O_2$ and $N_2$, respectively, which implies that $a_\mathrm{H} = a_\mathrm{O} = a_\mathrm{N} = 2$.

Equation (34) can be used to predict standard specific entropy of a wide range of organic substances.

The equation for $\overline{S}_{bio}^o$ looks like:

$$\overline{S}_{bio}^o = 0{,}187\left(\overline{S}_C^o n_C + \frac{\overline{S}_{H_2}^o}{2} n_H + \frac{\overline{S}_{O_2}^o}{2} n_O + \frac{\overline{S}_{N_2}^o}{2} n_N\right) \qquad (35)$$

Since the empirical formula contains $n_c = 1$ carbon atoms, $n_H = 1.770$ hydrogen atoms, $n_O = 0.490$ oxygen atoms, $n_N = 0.240$ nitrogen atoms.

The standard molar entropies [18] are:

$$\overline{S}_c^o = 5.51\ \mathrm{J/mol \cdot K};\ \overline{S}_{H_2}^o = 130{,}68\ \mathrm{J/mol \cdot K};\ \overline{S}_{O_2}^o = 205.15\ \mathrm{J/mol \cdot K};$$

$$\overline{S}^o_{N_2} = 191.61\ \mathrm{J/mol \cdot K}.$$

Specific enthalpy and specific entropy depending on temperature can be calculated as:

$$h^t_f = h^o_f + h_{cor} = h^o_f + C_p\left(T - T_o\right), \quad (35)$$

$$S^t = S^o + S_{cor} = S^o + C_p \ln\left(\frac{T}{T_o}\right), \quad (36)$$

where $C_p$ – specific heat capacity; $h_{cor}$ and $S_{cor}$ are corrections that need to be made from $T_0 = 298.15$ K to $T$.

The specific heat capacity of dry biomass is 1.308 J/(g·K) [7].

Using the values $\overline{h}^o_{f,bio}$ and $\overline{S}^o_{f,bio}$ determines the standard molar Gibbs free energy of formation using the Gibbs equation [J/mol]:

$$g^o_{f.bio} = \overline{h}^o_{f.bio} - T_o \cdot \overline{S}^o_{f.bio}, \quad (37)$$

Table 12. Standard molar enthalpy, entropic, Gibbs free energy

| Substance | $\Delta H^0$ [KJ/mol] | $\Delta G^0$ [KJ/mol$^{-1}$] | $\Delta S^0$ [J/(mol·K)] |
|---|---|---|---|
| $H_2$(g) | 0 | 0 | 130.6 |
| $H_2O$(c) | -285.9 | -237.2 | 70.0 |
| $H_2O$(g) | -241.8 | -228.6 | 188.7 |
| CO(g) | -110.5 | -137.3 | 197.9 |
| C(s) | 0 | 0 | 5.7 |
| $CO_2$(g) | -393.7 | -394.6 | 213.8 |
| N(g) | 0 | 0 | 191.4 |
| $O_2$(g) | 0 | 0 | 205.0 |
| S(g) | 0 | 0 | 31.9 |
| $CH_4$(g) | -74.6 | -50.5 | 186.3 |
| $CH_3CHOHCOOH$(T) | -694.08 | -522.92 | 142.26 |
| $CH_3COCOOH$(P) | -584.5 | -468.38 | 179.5 |
| $C_{12}H_{22}O_{11}$(T) | -222.1 | -1544.65 | 360.2 |
| $C_6H_{12}O_6$T | 2802.04 | 205.03 | 29.37 |
| Cr | 0 | 0 | 5.74 |
| $CO_2$r | -393.51 | 0 | 213.66 |
| $H_2O$ | -241.81 | 0 | 188.74 |
| $CH_4$ | -74.85 | 0 | 186.27 |
| $CH_3COOH$ | -484.1 | -389.36 | 159.83 |

To estimate the effectiveness of processes, we need performing not only energy, but also the exergy analysis.

The mass, energy and exergy balance equations are presented here. The governing equations for mass conservation are

$$\Sigma M_{in} - \Sigma M_{out} = 0, \tag{38}$$

where $\Sigma M_{in}$ – the sum of all masses of components before the process; $\Sigma M_{out}$ – the sum of all final products.

The first law of thermodynamics gives the energy balance

$$Q - W = M_{out} - M_{in}, \tag{39}$$

where $Q$ – supplied heat [J]; $W$ – performed work [J].

The exergy balance equation [J]:

$$Ex_{in} - Ex_{out} = Ex_{dest}, \tag{40}$$

where $Ex_{in}$ – the total exergy before the process [J]; $Ex_{out}$ – the total exergy after the process [J]; $Ex_{dest}$ – the exergy destruction [J].
The total exergy rate of each component is calculated using the equation [J]

$$Ex = ex_{ph} - ex_{ch}, \tag{41}$$

where $ex_{ph}$ – the specific physical exergy; $ex_{ch}$ represents the specific chemical exergy. $ex_{ph}$ for the water, organic streams, and biogas streams are determined respectively using:

$$ex_{ph} = h_{\mathrm{t}} - h_0 - T\cdot(s_t - s_0); \tag{42}$$

$$ex_{ph} = C_p\,(T - T_0 - T_0\cdot\ln(T/T_0)); \tag{43}$$

$$Ex_{ph} = Cp\cdot(T - T_0 - T_0\cdot\ln(T/T_0) + RT_0\,\ln(p/p_0). \tag{44}$$

The specific chemical exergies of the organic streams are calculated using the model of Song et al [19]

$$Ex_{ch} = 369.439\ \mathrm{C} + 1075.633\ \mathrm{H} - 86.308\ \mathrm{O} + 4.14\ \mathrm{N} + 190.798\ \mathrm{S} - 21.1\ \mathrm{Ash}, \tag{45}$$

цhere C, H, O, N, S, and Ash determine the the organic content of the substances, which are carbon, hydrogen, oxygen, nitrogen, sulfur, and ash, respectively.

The exergy destruction for each state point is defined as [J]

$$Ex_{dest} = (1 - T_0/T)\cdot Q_i - W + M_{in}\cdot ex_{in} - M_{out}\cdot ex_{out}. \tag{46}$$

Energy and exergy the efficiency of biogas systems is carried out according to [20]

The maximum exergy efficiency of 35.52 % was attained at organic loading rates of 0.5 dm$^3$/day and hydraulic retention time of 15 days when food waste with fat concentration of 0.5 % was used. The exergy loss associated with irreversibility of AD, the biogas, liquid sludge and net waste heat accounted for 64.59 %, 23.19 %, 9.16 %, 2.96 % respectively.

**Conclusions.** The results allow assessing the potential of biogas production from various raw materials. The proposed methodology for calculating the output of biogas gives the opportunity to predict the biogas release. The proposed methodology of thermodynamic analysis of the anaerobic fermentation process and the exergy analysis showed that the exergy efficiency of the process is about 35.52 %.

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# МЕТОД ОЦІНЮВАННЯ ВИКОРИСТАННЯ ЕНЕРГІЇ БІОМАСИ ШЛЯХОМ ВИРОБНИЦТВА БІОГАЗУ

***Анотація.*** *На даний час близько 10% енергії, що виробляється у світі – це енергія біопалива, одержуваного в результаті ферментації рослинної біомаси. Біопаливо з біомаси отримало широкомасштабне використання: етанол із цукрової тростини в Бразилії, етанол із кукурудзи в США. Анаеробне бродіння це стійка технологія, що використовується при переробці відходів та виробництві енергії. Перші покоління біопалив виготовлені з сировини за технологією перетворення біоенергетичних культур.*

*Біопаливо другого покоління – це продукти на біологічній основі, що виробляються з використанням нехарчової сировини сільськогосподарського і лісового походження. Третє покоління біопалив вироблено з водної сировини.*

*Для оцінки виходу біогазу з біомаси необхідно виконати розрахунки процесів анаеробного бродіння. Широко відома модель Базуела дозволяє теоретично визначити кількість біометану із субстрату з органічних речовин. Модель поєднує хімічні, біохімічні і термодинамічні процеси, що відбуваються в біосистемі. Метод Базуела оцінює вихід продуктів анаеробного бродіння на основі теоретичної стехіометричної оцінки. Теоретичні біохімічні метанові потенціали (TBMP) розглядають всі органічні речовини як біорозкладні. Кількість біометану ($nCH_4$) є параметром, який залежить від елементарної композиції органічної матерії. Для визначення $nCH_4$ необхідні вимірювання і розрахунки, що базуються на елементному аналізі, а емпіричну формулу органічної речовини можна визначити за допомогою стехіометричного методу.*

*Більш високі значення отримані для зернових та лігніну - від 698.6 до 705.4 дм$^3$/кг, для деревини та соломи вихід біогазу становить від 476.5 до 514.2 дм$^3$/кг. Твердий осад стічних вод дає 570 дм$^3$/кг.*

*Біогаз, одержуваний у процесі анаеробного бродіння, не тільки є чистим джерелом енергії, але також сприяє зменшенню об'єму твердих відходів та зниженню викидів парникових газів. Це відбувається завдяки зменшенню утворення метану, який зазвичай виділяється під час розкладання органічних відходів у природних умовах. Анаеробне бродіння також може бути інтегроване в різні сільськогосподарські та промислові процеси, що дозволяє значно підвищити ефективність використання ресурсів.*

*Використання різних типів біопалива, як-от біодизель, біогаз та біоетанол, має важливе значення для переходу до більш стійкої енергетичної системи. Біодизель можна отримувати з різних видів рослинної олії та відходів харчової промисловості, що робить його перспективним замінником традиційного дизельного палива. Використання біоетанолу у транспортному секторі допомагає зменшити залежність від викопних палив та скоротити викиди шкідливих речовин.*

***Ключові слова:*** *біогаз, біометан, анаеробне бродіння, біотермодинаміка.*