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Effectiveness of Water-Amine Combined Process for CO_2 Extraction from Biogas

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***Abstract* – The EU countries are implementing biomethane production projects from biogas, supplying it to the natural gas distribution grid, or using it as motor fuel. It is also extremely relevant for Ukraine, supposing the problems with gas import due to Russian aggression. Biogas production from landfills, agriculture waste, and sewage is already implemented in Ukraine, so the next step must be biomethane production on an industrial scale and the selection of biogas separation technology is important. Using 11 years of industrial experience in biogas production from landfills, wide experience of the different methane-containing gases separations, and small companies' industrial possibilities, the most applicable separation technologies for Ukraine were selected: amine, water, and combined water amine carbon dioxide separation. These technologies had compared using computer simulation with real landfill biogas flow rate debt. Results of a software simulation of the most applicable water-amine absorption technology were verified using a laboratory setup. For carbon dioxide concentration in biogas at 32–42 % vol., the specific energy consumption when using water absorption is on average 2 times less compared to amine absorption, but at the same time, the loss of methane due to its solubility in water during water absorption amounted to 7.1–7.6 %, with practically no losses in amine absorption, and minor losses at 0.17–2.8 % in combined water-amine technology. The energy consumption of combined water-amine absorption is comparable to that of water absorption due to: a) reduction of heat losses for the regeneration process of saturated amine absorbent, as part of carbon dioxide has already been removed with water technology; b) using the methane excess to compensate power consumption of the biogas compressor during the preliminary water absorption of carbon dioxide and/or to compensate heat costs of the saturated amine absorbent regeneration**

***Keywords* – Absorption; amines; biogas; biomethane; carbon dioxide; landfills; water absorption.**

1. INTRODUCTION

Ukraine is a significant consumer of natural gas. It is mined in Ukraine, but the volume of mining does not cover its consumption and a large part of the demand is met through imports, Fig. 1. From 2014 to 2021, natural gas consumption decreased by 1.6 times with almost constant gas mining, so natural gas substitution with alternative sources is important.

At the same time the wastes management and the energy use of organic household waste is a key environmental concern across Europe with many countries, including Ukraine, witnessing the significant increase of the amount of municipal wastes especially organic ones produced and accumulated. Since Ukraine confirmed the European path of development in

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2014, having concluded the Association Agreement with the European Union, our wastes management system now needs to be modified to reflect the positive European experience in the field [1].

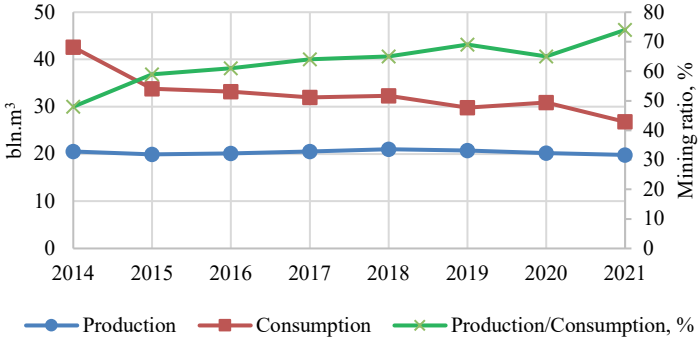

Fig. 1. Natural gas production and consumption in Ukraine from 2014 to 2021.

In 2012 the team of Gas Technology Department of Gas Institute of National Academy of Science of Ukraine put into operation the first biogas plant which produce electricity from landfills biogas. In future years similar plants was opened on other landfills. Also, agriculture and sewage biogas plants were implemented. But in all cases, biogas is used for heat or electricity production in the mining place, but in some cases, no electricity grids near a landfill or there is no heat needed so biogas is potentially not fully used.

Shifting biogas use from cogeneration to biomethane could reduce not only emissions from the agricultural sector, but also emissions from the energy and transportation sectors, which could significantly improve the climate [2].

The landfills biogas samples taken by us [3], have methane content is 50–70 %, carbon dioxide is 20–40 %, and nitrogen less than 7 %, so carbon dioxide extraction is enough to use that biomethane in local natural gas supply pipelines or CNG/LNG car filling.

At of the end of 2019, 49 biogas plants were installed in Ukraine, of which 28 operate at solid household waste landfills [4]. The total capacity of installations operating under the 'green' tariff was 86 MW, which is almost two times more than in 2018 (46 MW). According to the National Commission, which carries out state regulation in the spheres of energy and communal services, in 2020 there were 51 biogas plants with a total capacity of 96.7 MW [5], and as of October 2022, 64 installations were installed in Ukraine that produces energy from biogas and which operate under the 'green' tariff. The total electrical capacity of the installations is 130 MW [6].

The potential for biomethane production in Ukraine is estimated at about 8 billion m³/year, which is more than 50 % of the volume of natural gas imports (~14 billion m³/year) and more than 25 % of the total volume (~30 billion m³/year) of NG consumption [7].

In December 2020, at a joint meeting of the Bioenergy Association of Ukraine, the Ministry of Energy, the State Energy Efficiency Agency, Gas Transmission System Operator of Ukraine LCC, a draft Law of Ukraine 'On Amendments to the Law of Ukraine 'On Alternative Energy Sources' regarding the development of electricity production from biomethane' was developed. The draft law provides for the introduction of the biomethane market in Ukraine.

As of August 2022, the Regional Gas Company of Ukraine received 30 applications for connecting biomethane plants to the gas distribution network [8].

2. Analysis of Methods of Biogas Purification from Acidic Components for the Purpose of Biomethane Production

It is known that in the process of biogas production, the final phase of anaerobic bio destruction of waste is methanogenesis, i.e., synthesis of biogas. The methanogenic phase of anaerobic decomposition includes two stages: active and stable. In the active stage, the enzymatic decomposition of the acids formed in the acetogenic phase takes place, which is accompanied by a significant release of gases (methane, carbon dioxide, mercaptans, ammonia, etc.). The concentration of methane in biogas increases to 40–60 %. The maximum release of biogas occurs after two-year aging of the waste in the layer of the landfill and stabilization of the decomposition processes.

A stable stage of methanogenesis limits the overall rate of organic substances decomposition in the body of the landfill. A characteristic sign of the onset of this phase is the presence of more than 50 % methane in biogas [3]. If the conditions of solid waste storage are not violated, the process of anaerobic decomposition of waste is stabilized with an almost constant volume and composition of biogas.

At the temperature of the fermentation process of 30–40 °C, biogas is released in a water-saturated state and contains, along with methane and carbon dioxide, significant amounts of hydrogen sulfide (up to 3 %). In order to protect the gas treatment units from severe wear and tear and to meet the requirements of the following purification stages, water vapor, hydrogen sulfide, and carbon dioxide must be removed from the biogas. Moreover, if biogas is used in heating systems and internal combustion engines, pre-treatment and purification of biogas from harmful and ballast impurities is mandatory.

Currently, the most common technologies for biogas enrichment to biomethane are the following [9], [10]:

- Membrane method of purification;
- Method of short-cycle adsorption;
- Physical absorption;
- Chemisorption processes of CO_2 and H_2S extraction.

3. Modeling of Water and Amine Processes of Acidic Components Extraction from Biogas and Production of Biomethane

The Codex of the Gas Transportation System of Ukraine [11] establishes that the heat of combustion (lower) of natural gas supplied to the gas transportation system should not be lower than 32.66 MJ/m^3. According to NJSC ‘Naftogaz Ukraine’, the lower calorific value of natural gas on the territory of Ukraine varies between 33.4–34.5 MJ/m^3, i.e., higher (better for the consumer) than prescribed by the norm. The concentration of carbon dioxide and hydrogen sulfide in natural gas should be no more than 2 % (vol.) and 0.006 g/m^3, respectively.

When using natural gas as motor fuel in transport, according to the Interstate Standard for Internal Combustion Engines [12], the concentration of hydrogen sulfide should not exceed 0.02 g/m^3.

The most widespread technologies of biogas enrichment to biomethane in EU countries are water scrubber technology and amine absorption. Therefore, it is relevant to carry out evaluation comparative calculations of energy indicators of aqueous and amine processes of extraction of acidic components from biogas.

3.1. Modeling of the Water Absorption Processes

The project of biomethane production and its use in CNG stations is under consideration [13]. It is proposed to enrich 20 nm^3/h of biogas composition: CH_4 63 %, CO_2 34 % (vol.) to biomethane ($CH_4 \approx 90$ % and higher) using water scrubber technology.

The solubility of CO_2 and CH_4 in water is directly proportional to pressure. High operating pressure complicates the selection and manufacture of equipment and requires higher electricity costs for gas compression. Very low pressure leads to excessive water consumption and, as a result, to an increase in the size of the column. Thus, the optimal value of the working pressure was chosen at 1.0 MPa. To extract CO_2 from 20 nm^3/h of biogas, an absorbent – water in the amount of 4 m^3/h is fed into the absorber with a diameter of 0.15 m and a height of 3 m. The total energy costs, in this case, are 5.25 kW, and taking into account the supply to the gas filling station 8.25 kW.

The software simulation system GasCondOil (GCO) was used to model the process of water absorption of CO_2 [14]–[17]. Testing of the methods for calculating phase balances of the main components of biogas with H_2O, i.e., CO_2–H_2O and CH_4–H_2O systems, laid down in GCO, is shown in Table 1. The results of calculations of solubility of CH_4 and CO_2 in H_2O based on GCO and their comparison with data [18] show their almost complete coincidence.

TABLE 1. RESULTS OF CALCULATIONS OF THE SOLUBILITY OF CH_4 AND CO_2 IN H_2O

Temperature, °C	**Solubility of CH_4 and CO_2 in H_2O, g/kg_H_2O**			
	Data [18]		**GCO**	
	CH_4	**CO_2**	**CH_4**	**CO_2**
0	0.04	3.3	0.045	3.1
20	0.023	1.7	0.024	1.6
40	0.016	0.95	0.016	0.97

The technological scheme of CO_2 water absorption from biogas, biomethane production, and its supply to the CNG station is presented in Fig. 2.

Biogas (flow 1) in the amount of 20 nm^3/h with a concentration of CH_4– 63 %, CO_2– 34 % at P = 0.1 MPa and T = 30 °C is compressed in the CO-1 compressor to 1.0 MPa, cooled in the recuperative heat exchanger HE-1 by water flow 18 and enters the absorber A-1. The absorber is irrigated with water flow 22 at T = 25 °C. In the absorber column, the CO_2 concentration in biogas decreases to ~2 % (vol.). Residual water is removed from purified biogas – biomethane (flow 9), then biomethane (flow 16) is compressed in the CO-2 compressor to 20 MPa, cooled in the HE-2 recuperative heat exchanger by water flow 15 and directed (flow 3) to the consumer CNG station. The CO_2-saturated aqueous solution (stream 4) is throttled to a pressure of 0.1 MPa and then enters the S-1 separator, where the gas phase (stream 5) and water (stream 12) are separated from it. Flow 12 is divided into three flows, two of which enter the recuperative heat exchangers HE-1 and HE-2, and then they are mixed in the mixer Mix and the flow 23-2-22 is fed to the upper part of the absorber A-1 by pump P-1.

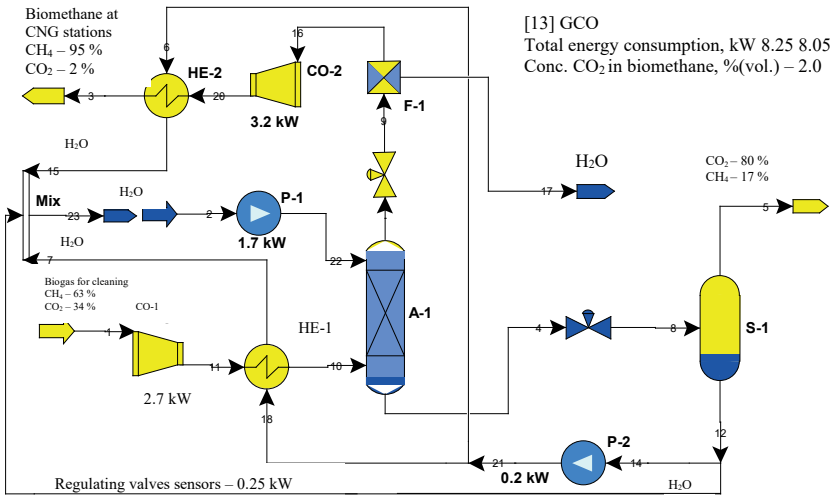

Fig. 2. The technological scheme of CO_2 water absorption from biogas. A-1 – absorber; S-1 – separator; CO-1, CO-2 – compressors; HE-1, HE-2 – recuperative heat exchangers; F-1 – filter; Mix – mixer; P-1, P-2 – pumps.

The estimated total energy consumption, taking into account the control valves and sensors, was 8.05 kW, which differs from the data of the water scrubber project by 8.25 kW by 2.5 %.

3.2. Modeling of the Amine Absorption Process

It is known that up to 80 % of the capital investment for an amine CO_2 absorption plant from biogas is related to the amount of circulating amine solution, which determines the size of the absorber, desorber, heat exchange equipment, etc. 70 % of the operating costs consist of energy costs for the regeneration of the saturated amine solution, i.e., they are largely dependent on the efficiency of the absorbents used and the optimal parameters of the absorption/desorption processes, such as pressure, temperature, and the extent of CO_2 extraction from the saturated absorbent during its regeneration in the desorber.

Amine absorption processes of biogas purification use ethanol amine sorbents. Most often, CO_2 absorption processes are used with aqueous solutions of monoethanolamine (MEA), the strongest base among ethanolamines. The process of absorption of carbon dioxide is accompanied by the release of heat, and the process of regeneration of the absorbent solution is accompanied by the absorption of heat.

The absorbing properties of MEA increase with decreasing temperature and increasing pressure. With an increase in temperature and a decrease in pressure, the equilibrium of chemical reactions shifts to the left. This is the basis for the regeneration of the MEA solution saturated with acid gases during absorption. When a saturated solution is heated, chemical compounds decompose and acid gases are desorbed from the solution.

In the MEA process of gas purification from CO_2, side reactions occur, which lead to an irreversible change in the composition of the absorbent (oxidation and thermal decomposition), a decrease in the absorption capacity, as well as serious corrosion of the equipment. Therefore, the recommended degree of saturation of the absorbent with carbon dioxide is limited to 0.30–0.35 mol CO_2/mol MEA at the usual concentration of it in a solution with water of 15–20 % by mass.

In recent decades, a more effective absorbent based on methyldiethanolamine (MDEA) has been used, which has the advantage of MDEA compared to MEA:

- The partial pressure is lower and the boiling temperature is significantly higher, which reduces absorbent losses during its regeneration;
- The heat of reaction with CO_2 is 1.43 times less, which leads to a decrease in the heat load of the desorber boiler and allows deeper regeneration of the sorbent;
- The corrosion activity is lower and therefore a more concentrated solution (up to 50 % by weight) and a higher degree of carbonation (0.55–0.6 mol CO_2/mol MDEA) is used, which allows to reduce the amount of circulating absorbent;
- Significantly reduced thermochemical degradation of the absorbent and, as a result, there are practically no deposits on the internal surfaces of the equipment, which increases the efficiency of heat exchange and reduces energy costs;
- Low toxicity and significantly lower degree of biodegradability of the absorbing solution;
- Reduced foaming.

However, MDEA, like a tertiary amine, does not have a mobile H+ atom in the amine group (N), so the direct carbonate-type reaction (as in the case of MEA) is slow. This deficiency is compensated by the introduction of activating additives such as piperazine, ethylenediamine, monoethanolamine, diethanolamine, and others.

Methyldiethanolamine with the addition of piperazine (PZ) has a lower desorption energy compared to MEA, which allows saving up to 10 % of the energy for solution regeneration, while evaporation losses for MDEA and PZ are significantly lower than for MEA [19], [20]. Aminomethylpropanol (AMP) is a promising solvent for CO_2 removal due to its absorption properties: absorption rate, selectivity, and resistance to decomposition. [21]. Studies have shown that AMP effectively affects the solubility of CO_2 in MDEA solution, the rate of absorption increases with increasing concentration of AMP in MDEA aqueous solution [22]. The authors [23] suggest using a mixture of MDEA/MEA with a concentration of each component of 20 % (by weight) as an absorbent.

Activated additives have, as a rule, higher values of saturated vapor pressures than MDEA and are volatile components, which can lead to instability of the absorbent composition. It is obvious that while preserving the activating properties of these additives, their concentrations in MDEA solutions should be minimized.

At the Gas Institute, using computer modeling, technological schemes for amine extraction of CO_2 and H_2S from biogas were developed. An effective absorbent MDEAmod is proposed – an aqueous solution of methyldiethanolamine (40 % MDEA) and monoethanolamine (10 % MEA), the use of which reduces the load of the desorber reboiler by 1.5–2.5 times compared to the use of traditional aqueous solutions of MEA [24]–[26]. The optimal parameters of amine absorption/desorption processes were determined: the temperature of the absorbent at the absorber input is 45 °C at a pressure of 0.26–0.28 MPa, the pressure in the desorber is 0.16–0.18 MPa, the degree of carbon dioxide extraction in the desorber is taken as $\varepsilon \leq 0.7$ [27], [28].

In Fig. 3 the basic technological scheme of amine purification of biogas, production of biomethane, and gaseous carbon dioxide is presented. Process modeling was carried out using the *HYSYS* software.

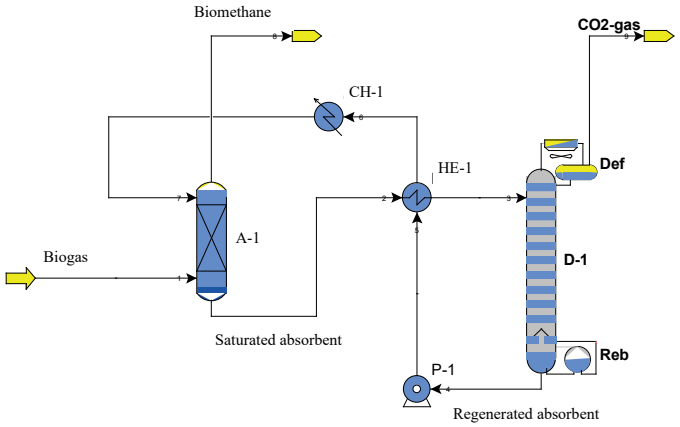

Fig. 3. Schematic technological scheme of amine purification of biogas. A-1 – absorber; D-1 – desorber; Def – dephlegmator; Reb – boiler; HE-1 – recuperative heat exchanger; CH-1 – heat exchanger (cooler); P-1 – pump.

Biogas (flow 1) at P = 0.26 MPa and T = 40 °C enters absorber A-1. The absorber is irrigated with an aqueous solution of the chemosorbent at T = 45 °C (flow 7). In the absorber column, the concentration of carbon dioxide in the biogas decreases to ~2 % (vol.). Purified biogas (stream 8) is sent to the consumer. The saturated chemosorbent solution (flow 2) enters the recuperative heat exchanger HE-1, in which it is heated to a temperature of ~100 °C by the hot return flow 5 of the regenerated sorbent solution, which comes from the desorber D-1. The heated saturated sorbent solution (flow 3) enters the upper part of the D-1 desorber, where the absorbed carbon dioxide is vaporized to the required concentration. The regeneration process is carried out at the boiling temperature of the chemosorbent of 114–118 °C. The steam-gas mixture that leaves the upper part of the desorber is cooled in the condenser to 25–30 °C, while water vapor condenses and enters the desorber as irrigation (phlegm) in its upper part, and the gas leaves the condenser (stream 9) and contains, in mainly carbon dioxide (~98 % vol.). The regenerated chemosorbent solution (stream 4) is fed by the H-1 pump to the HE-1 recuperative heat exchanger (stream 5), then to the CH-1 cooler (stream 6). After the CH-1 cooler, it enters (flow 7) in the upper part of the absorber A-1.

3.3. Combined Water-Amine CO_2 Absorption from Biogas

As noted, water and amine absorption are fairly common technologies for obtaining biomethane from biogas in EU countries. Calculation comparisons of aqueous and amine absorption processes of CO_2 extraction from biogas are given in publications [29]–[31].

In work [32], it is proposed to use a combined water-amine method for cleaning biogas from CO_2, in which the preliminary extraction of CO_2 from biogas occurs with the help of water absorption at a pressure close to atmospheric or increased to 0.2–0.3 MPa. For the final purification of biogas to biomethane, amine absorption is used.

Obviously, it is relevant to carry out comparative calculations of water, amine, and combined water-amine absorption processes for a wide range of CO_2 concentrations in biogas.

Fig. 4 shows a two-stage technological scheme of water purification of 250 nm^3/h of biogas from CO_2 using two options. When using variant A (Var A), the obtained aeration gas is mixed with the input biogas in order to increase the yield of methane in the purified gas. According to variant B (Var B), degassing gas (aeration gas) with a relatively high concentration of CH_4 (≥30 %) it can be used as fuel gas. Below is a brief description of the technological process of preliminary purification of biogas from CO_2.

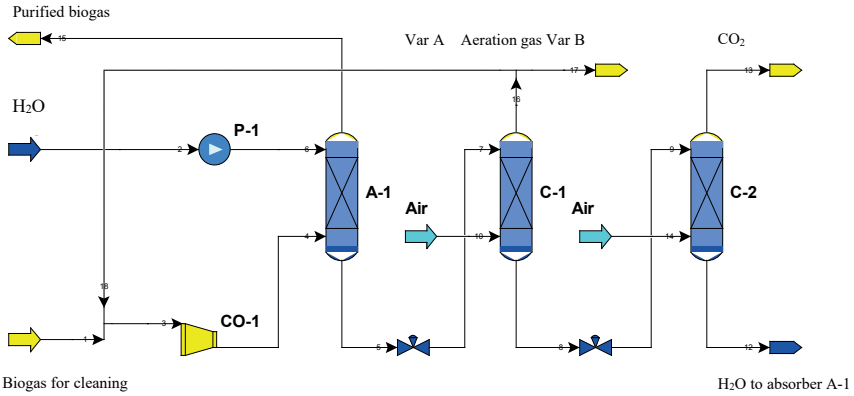

Fig. 4. Schematic of two-stage technological scheme of water absorption purification of biogas from carbon dioxide. A-1 – absorber; C-1, C-2– evaporation column; CO-1 – biogas compressor; P-1 – water pump.

Biogas enters absorber A-1 at a pressure of 0.26 MPa. Absorbent – fresh water, is supplied to the absorber in the counter flow of the gas. In this process, carbon dioxide dissolves in water, and enriched methane gas leaves the absorber for further amine purification at a pressure of 0.26 MPa. Water saturated with CO_2 leaves the absorber and enters the C-1 evaporation column, where it is blown with air under a pressure of 0.12–0.15 MPa, while the dissolved methane is almost completely removed from H_2O. The aeration gas leaving column C-1 can be mixed with the biogas flow feed to absorber A-1 (Var A) or used as fuel gas (Var B). In column C-2 at close to atmospheric pressure the aqueous solution in the countercurrent is blown by aeration air, while CO_2 is almost completely removed from the absorbent H_2O, which then enters the absorber A-1 again.

Modeling of absorption water processes was carried out using the *GasCondOil* program.

4. Results of Comparative Calculations of Water, Amine and Combined Water-Amine Absorption Processes

The results of the simulation of CO_2 absorption/desorption processes with 250 nm^3/h of biogas of different compositions are presented in Table 2. The CO_2 concentration in biogas varied from 32 to 42 % (vol.). Such concentrations of CO_2 are the most common for biogas, in particular, biogas from solid household waste landfills (~30–40 %).

Table 2. Results of Simulation of Water, Amine, and Water-Amine 2 Absorption from 250 nm^3/h of Biogas

Indicators	**CH_4/CO_2 concentration in biogas, % (vol.)**		
	55/42	**60/37**	**65/32**
CH_4 content in biogas, nm^3	137.5	150	162.5
Water P_{abs} = 1.0 MPa (Var B)			
CH_4 content in biomethane, nm^3	127	139	151
CH_4concentr. in degassing gas, % (vol.)	10.7	12.9	15.6
Energy consumption, kWh	47.7	47.7	47.7
Energy consumption, kWh/nm^3_CH_4	0.38	0.34	0.32
CH_4 losses, %	7.6	7.3	7.1

Amine P_{abs} = 0.26 MPa			
CH_4 content in biomethane, nm^3	137.5	150	162.5
Energy consumption, kWh	119	110	101
Energy consumption, kWh/nm^3_CH_4	0.86	0.73	0.62
CH_4 losses, %	–	–	–
Water-Amine P_{abs} = 0.26 MPa (Var A)			
CH_4 content in biomethane, nm^3	137.3	149.7	162
Energy consumption, kWh	72.8	76.3	79.5
Energy consumption, kWh/nm^3_CH_4	0.53	0.51	0.48
CH_4 losses, %	0.15	0.2	0.3
Water-Amine P_{abs} = 0.26 MPa (Var B) *			
CH_4content in biomethane, nm^3	133.7	146.5	159.2
CH_4concentr. in degassing gas, % (vol.)	33.7	33.9	35.6
Energy consumption, kWh	57.8	62.5	67.5
Energy consumption, kWh/nm^3_CH_4	0.43	0.43	0.42
CH_4 losses, %	2.8	2.3	2.0
Water-Amine P_{abs} = 0.26 MPa (Var B) **			
CH_4 content in biomethane, nm^3	133.7	146.5	159.2
CH_4concentr. in degassing gas, % (vol.)	33.7	33.9	35.6
Energy consumption, kWh	36	42	48.5
Energy consumption, kWh/nm^3_CH_4	0.27	0.29	0.3
CH_4 losses, %	2.8	2.3	2.0

* Combined water-amine CO_2 absorption from biogas using the potential energy of degassing gas (CH_4>30 %) to compensate for power consumption of the biogas compressor during preliminary water absorption.
** Combined water-amine CO_2 absorption from biogas using the potential energy of degassing gas (CH_4>30 %) to compensate for heat costs for regeneration of saturated amine absorbent

The specific energy consumption of the water process compared to amine absorption is lower, on average, by ~2.0 times, but the total losses of CH_4 during water absorption amounted to 7.1–7.6 % with practically zero losses of CH_4 when using amine technology. It should also be noted that during the water absorption of CO_2 at P = 1.0 MPa, the methane contained at the outlet of the evaporation column A-2 due to its low concentration (10.7–15.6 %) can be used as fuel only with the help of an auxiliary combustion system, therefore it is considered as losses.

According to the Var A scheme (Fig. 4), where the degassing gas of the A-2 evaporation column is mixed with biogas in order to increase the potential content of CH4 in the obtained biomethane and fed to the input of the KO-1 compressor, the combined water-amine absorption has an excess of energy costs by ~50 % compared to water, and methane losses are insignificant and amount to 0.14–0.24 %.

When using Var B (Fig. 4) in the aeration gas-degassing gas of column A-2, the concentration of CH_4 is, on average, about 30–35 %, and this gas can be used as a fuel for the production of both electricity and heat and, in a significant measure, to compensate for the energy costs of the biogas compressor during the preliminary water absorption of CO_2 or the heat costs for the regeneration of the saturated amine solution. Thus, when compensating the compressor power when compressing biogas to 0.26 MPa, the specific energy consumption amounted to an average of 0.42 kWh/nm^3_CH_4, which is 1.2 times higher than the energy consumption of traditional water absorption at P = 1.0 MPa. For the option of compensation of heat and energy consumption of the reboiler of the amine desorber, the specific energy consumption was, on average, 0.29 kWh/nm^3_CH_4, which is 20 % less than the water technology.

Methane losses for both variants of the water-amine process with compensation of energy consumption are the same and range 2–2.8 %.

Fig. 5 illustrates the specific energy consumption in the production of biomethane from 250 nm^3/h of biogas of different compositions using water, amine, and water-amine absorption processes. It can be seen that with a decrease in CO_2 concentration in biogas there is a sharp decrease in specific energy consumption in the amine process, while water and water-amine absorption has an almost insignificant decrease in energy consumption for all biogas compositions.

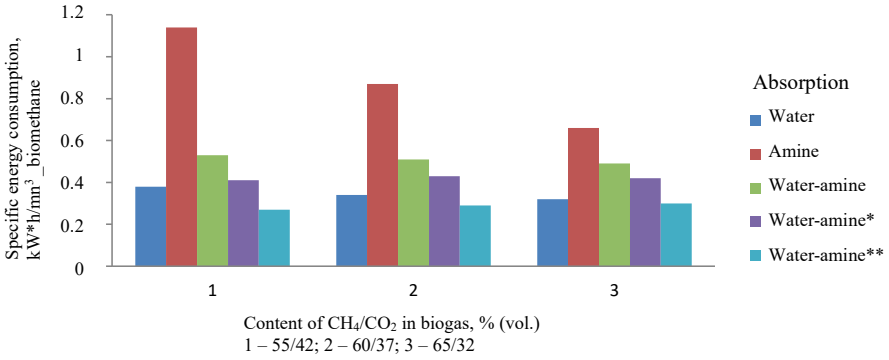

Fig. 5. Specific energy consumption in the production of biomethane from 250 nm^3/h of biogas of different compositions using water, amine, water-amine, and combined water-amine absorption using the potential energy of degassing gas (CH_4>30 %) to compensate for the power consumption of biogas compressor during preliminary water absorption (*) and heat costs for regeneration saturated amine absorbent (**).

In Fig. 6 losses of methane (%, vol.) in the obtained biomethane in the considered processes are shown. The most significant losses occur during water absorption, which is associated with increased solubility of CH_4 in H_2O. The content of CH_4 in biomethane when applying the technology of amine and water-amine absorption practically corresponds to its potential content in biogas.

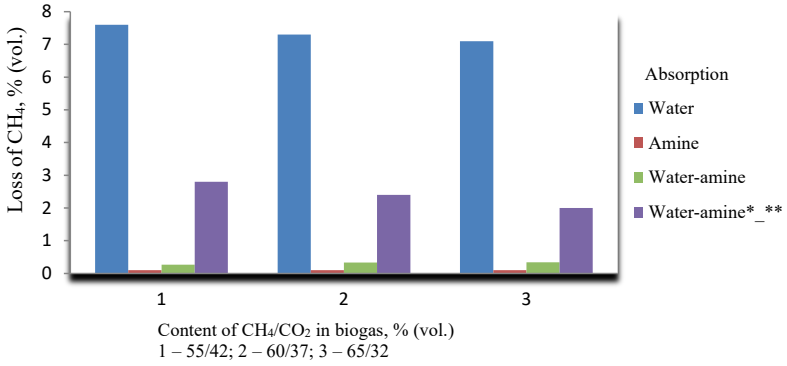

Fig. 6. CH_4 losses during the production of biomethane from 250 nm^3/h of biogas of different compositions using water, amine, water-amine, and combined water-amine absorption (*_**) using potential degassing gas energy (CH_4>30 %).

Energy consumption when using amine absorption of CO_2 from biogas is ~2 times higher compared to water absorption, but the yield of biomethane is 7.1–7.6 % higher due to the absence of methane losses, as in the case of its dissolution in H_2O. This biomethane difference

can be used to compensate for the energy costs of regenerating the circulating amine absorbent. The energetics of combined water-amine absorption is commensurate with the energy consumption when using water absorption due to:

- Significant reduction in the work of biogas compression during the initial water absorption of CO_2 from biogas;
- Reduction of heat costs for the regeneration of saturated amine solution, since part of CO_2 has already been previously removed from biogas;
- Use of aeration gas (CH_4>30 %) to compensate for the power consumption of the biogas compressor during the preliminary water absorption of CO_2 and/or to compensate for the heat load of the amine desorber reboiler.

5. EXPERIMENTAL PRODUCTION OF BIOMETHANE

For the practical study of the separation of biogas into CH_4 and CO_2, a project of a laboratory installation using the amine process of CO_2 absorption was developed in the Gas Technology department of the Gas Institute of the National Academy of Sciences of Ukraine. The installation scheme includes an absorbent regeneration system, which allows heating the saturated absorbent to the temperature at which intensive release of carbon dioxide from the saturated absorbent begins. During these experiments, the process of CO_2 absorption and absorbent regeneration was studied.

To control the process, a special controller of technological processes was developed, which allows monitoring of all temperatures, consumption of the amine solution, and control pump.

During the testing of the laboratory installation for CO_2 extraction from biogas, it was planned to use amine absorbents MDEAmod and 20 % MEA. But since it is currently impossible to officially purchase methyldiethanolamine in Ukraine, testing was carried out using 20 % monoethanolamine. Several samples of the biogas composition were taken from the Kamianets-Podilskyi landfill and the average composition of biogas was obtained with the content of 62 % CH_4 and 36 % CO_2.

Comparative indicators of the calculations and those obtained at the laboratory installation are given in the Table 3.

TABLE 3. COMPARATIVE CALCULATED AND LABORATORY INDICATORS OF THE AMINE CO_2 EXTRACTION FROM BIOGAS

Absorption/desorption indicators	**Biogas G = 1.0 nm³/h. Content, % (vol.): CH_4 – 62; CO_2 – 36**		
Absorbent – 20 %MEA	**Pressure in the absorber P_{abs}, MPa**		
	0.12	**0.16**	**0.2**
	exp/calc	**exp/calc**	**exp/calc**
Absorbent consumption, kg/h	18/19	15/15	14/13
The temperature of regenerated absorbent at the entrance to absorber, °C	39/39	52/55	53/55
The temperature of saturated absorbent at the outlet of the absorber, °C	47/52	76/71	76/73
The temperature of the saturated absorbent at the entrance to the desorber, °C	83/83	92/92	98/98
The temperature of the regenerated absorbent at the outlet from the desorber, °C	97/100	113/112	117/118

Concentration in biomethane, % (vol.)*: CH_4 CO_2	95.5/95.4 3.3/4.3	93.8/95.7 5.5/4.0	92.6/95.2 6.6/4.6
Thermal load of the reboiler desorber, kW	1.5	2.0	2.0

* Concentrations of components in biomethane are given taking into account drying to the temperature of the dew point according to humidity –8 °C (at P = 3.92 MPa).

The maximum deviation of calculated from the experimentally obtained concentration of CH_4 in biomethane at the pressure in the absorber P_{abs} = 0.12–0.2 MPa is 2.8 %. The content of CO_2 in the obtained biomethane at the laboratory installation is within the range of 3.3–6.6 % (vol.), which exceeds the maximum permissible 2 %, therefore, further work is planned to improve the laboratory installation.

The use of $MDEA_{mod}$ absorbent, as noted in the article, reduces the desorber reboiler load by 1.5–2.5 times compared to the use of traditional aqueous MEA solutions, so will significantly reduce the energy consumption for regeneration of saturated absorbent.

6. CONCLUSIONS

Using computer simulation, energy costs in the production of biomethane from biogas for the most common amine and water processes for extracting carbon dioxide from biogas are analyzed. The comparative analysis included a combined water-amine absorption method for purifying biogas from CO_2.

In the production of biomethane from biogas, energy consumption when using water absorption of CO_2 is in ~2 times lower compared to amine absorption, but the loss of biomethane due to its solubility in H_2O is 7–8 %. With amine absorption, there are practically no losses of biomethane, and this amount of biomethane can be used to compensate the energy costs for the regeneration of a saturated amine absorbent.

When using combined water-amine absorption, the energy costs for the production of biomethane are commensurate with the energy costs for water absorption due to a significant reduction in the work of biogas compression during preliminary water purification and a decrease in heat costs for the regeneration of saturated amine absorbent, since part of the CO_2 has already been removed from biogas. At the same time, CH_4 losses are, on average, in ~3 times lower than when using water absorption.

Comparison of the calculated indicators and those obtained on a laboratory installation shows that the maximum deviation of the calculated from the experimentally obtained concentration of CH_4 in biomethane at a pressure in the absorber P_{abs} = 0.12–0.2 MPa is 2.8 %.

The results of the above calculations and studies can be used to model the processes of extracting carbon dioxide from biogas and obtaining biomethane – an analogue of natural gas.

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