Обосновано применение электрических теплоаккумулирующих нагревателей вместо тепловых систем, работающих на биогазе. Рассмотрена методика расчета системы регулирования температурного режима электроаккумулирующей тепловой установки.

Биогазовые установки, ферментация, теплоаккумулирующие электронагреватели, количество теплоты.

Application of electric heaters heat accumulators instead of heating systems that run on biogas. The method of calculating system for regulating temperature of electric heat storage thermal installation.

Biogas plants, fermentation, heat accumulating heaters, amount of heat.

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APPLICATION OF THE HALLOYSITE-BASED SORBENT FOR AGRICULTURAL BIOGAS PURIFICATION AND ELONGATION OF THE INTERNAL COMBUSTION ENGINE LIFE

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Preliminary research results on sulphur, nitrogen and silicon compounds sorption from biogas produced in a representative small agricultural biogas plant are presented. Applicability of mineral sorbent prepared by the authors based on natural halloysite from Dunino deposit (Poland) was tested. Prototype plant designed for investigation on effectiveness of the S, N and Si compounds removal from biogas was demonstrated. Influence of crude biogas combustion on selected elements of internal combustion engine and exhaust silencer was studied. Chemical composition of deposit formed in internal combustion engine was identified, as well.

Agricultural biogas, halloysite sorbent, sulphur, nitrogen, silicon, impurities removal.

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Preliminary research results on sulphur, nitrogen and silicon compounds sorption from biogas manufactured in a representative small agricultural biogas plant are presented. Practical applicability of mineral sorbent prepared from natural halloysite from *Dunino* deposit (Poland) was verified. Prototype plant designed for investigation on the S, N and Si compounds removal effectiveness was demonstrated. Corrosive effects from crude biogas combustion on selected elements of internal combustion engine and exhaust silencer were discussed. Chemical composition of deposit formed was also identified.

Biogas as a biomass derived product, especially from biochemical conversion of plant or animal wastes, waste-water treatment plants and municipal landfill areas is regarded as one of the most profitably energy carriers. Its main component is methane – gas of greenhouse effect's potential ca. 72-time higher than of CO_2. For natural environment especially important is preventing of spontaneous methane fermentation. Instead, controlled biogas production and its energy recovery – even by incineration – is a better option. Chemical composition of biogas from agricultural biogas plant significally differs from landfill gas, biogas from municipal waste-water treatment plant or mine gas. Considering heterogeneity of biogas sources, depending even on the season, one can observe significant variation in impurity concentrations and in its general composition (Table 1). Also impurity removal efficiency can be different, depending on a given final application of biogas. Different types of impurities must be removed from biogas for fuel cells while different for gas turbines, gas network and for internal combustion engines. It should be also emphasized, that contents of individual impurities in different applications is a subject of strict regulations and norms.

Many research centers focus on elaboration and improvement of efficient methods of sulphur components removal from biogas [1–7]. Depending on biogas source one is able to identify different S compounds like: hydrogen sulphide - H_2S, sulphides - R_2S, disulphides – RSSR, dimethyl sulphide - CH_3SCH_3, methane thiol - CH_3SH, dimethyl disulphide - CH_3SSCH_3, carbon disulphide - CS_2, methyltiophene – C_5H_7S, ethyltiophene – C_6H_9S, alkyl disulphides C_3 – C_{10} : $C_3H_8S_2$ – $C_{10}H_{22}S_2$, alkyltrisulphide C_6 - $C_6H_{14}S_3$ or carbon oxysulphide – COS.

Another environmentally important problem, indirectly affecting chemical composition of biogas, is common use of Si-organic compounds. The most often detected Si-organic compounds in biogas are: trimethylsilanol, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane. Presence of these compounds, individually or in various combinations, of different concentrations, is confirmed analytically in biogas independently of its origin. Various, more or less efficient technologies of these compounds removal were developed in many research centers worldwide [8–11].

The most commonly identified nitrogen compounds in biogas are mainly ammonia, aliphatic amines, aromatic amines and organic nitrogen components with N in a form of heteroatom.

1. Chemical composition of biogas produced from different types of biomass raw material

Component	Biogas 1	Biogas 2	Biogas 3	Biogas 4
CH_4 [%]	50 - 60	60 - 75	60 - 75	68
CO_2 [%]	34 - 38	19 - 33	19 - 33	26
N_2 [%]	0 - 5	0 - 1	0 - 1	-
O_2 [%]	0 - 1	<0.5	<0.5	-
H_2O [%], 40°C	2 - 5	2 - 5	2 - 5	2 - 5
H_2S [mg/m^3]	100 - 900	1000 - 4000	3000 - 10000	100
NH_3 [mg/m^3]	150	100	50 - 100	400
Aromatics [mg/m^3]	0 - 200	90	0 - 100	50 - 150
Cl- or F-organics [mg/m^3]	100 - 800	150 - 250	140	250

Biogas 1 – biogas from organic fraction of kitchen wastes
Biogas 2 – biogas from municipal waste-water treatment plant
Biogas 3 – agricultural biogas
Biogas 4 – biogas from agricultural and food industry wastes

Similar problems are reported in case of energetics and coal mine industry, where impurities accompanying coal bed methane, depending on geological conditions, involve: C, S, N, Si, P and the halogen group compounds.

Presentation of the Research. To possibly reduce concentration of S, N and Si compounds the halloysite-based mineral sorbent was prepared. Halloysite $Al_2Si_2O_5(OH)_4$ is a unique aluminosilicate of two-layer structure (Fig. 1), included to kaolin group. Because of structural nanotubes of dozen nanometers diameter and several micrometer length, halloysite found itself very useful in nanotechnology zapplications, not only as a filler, but also as a carrier of special substances. Specific surface area of raw, unmodified halloysite from *Dunino* deposit (Poland) which was used in research is ca. 60 m^2/g. Halloysite is a negatively charged, porous mineral (Fig. 2), which sorption and ion-exchange properties are dependent on particles structure and polarization degree, as well as on their pore diameters. Inside interlayer space small amount of water can be found, forming monomolecular layer between the packages (Fig. 1).

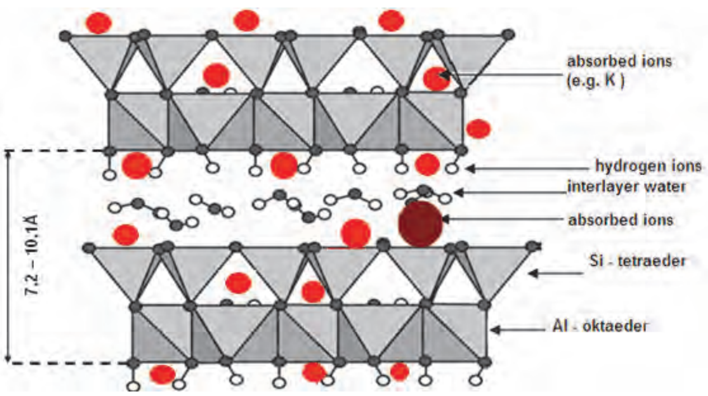

Fig. 1. Scheme of halloysite structure demonstrating potential possibility of binding ions locations [12]

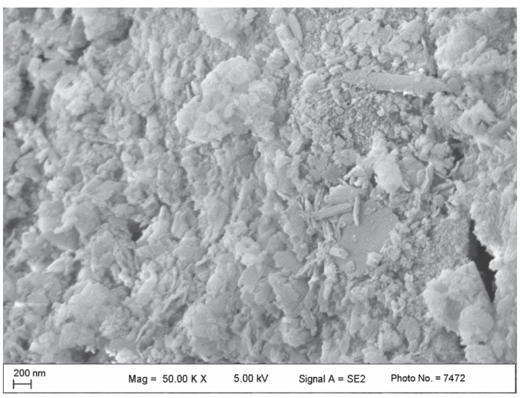

Fig. 2. Raw halloysite structure - loosely dispersed nanotubes and plates (SEM)

Working sorbent, denoted as HA1S, was specially prepared in physicochemical processes (acid activation + high temperature calcination) on raw halloysite, tailored to the specific adsorbates (S, N, Si compounds) properties. In such modified sorbent presence of all three pore types: micropores (<2 nm), mesopores (2– 50 nm) and macropores (>50 nm) was identified (porosimetric method). Agricultural biogas for the tests was provided from anaerobic fermentation plant on site. Its chemical composition is presented in Table 2.

2. Chemical composition of the raw agricultural biogas from the plant tested

Component	Concentration
CH_4 [%]	54 - 56
CO_2 [%]	38 - 44
N_2 [%]	1 -3
O_2 [%]	0 - 1
H_2O [%], 40°C	2 - 5
H_2S [mg/m^3]	1840
NH_3 [mg/m^3]	2400
Aromatics [mg/m^3]	90
Cl- or F-organics [mg/m^3]	120
S compounds [mg/m^3]	before:1840, after 5
Si compounds [mg/m^3]	before: 42, after 0.1

Research focused on evaluation of sorption properties – efficiency and selectivity towards S, N and Si compounds. Special attention aimed at:

- construction of research stand for agricultural biogas purification (Fig. 3),
- deposition on elements of engine's combustion chamber constructed for biogas fuel,
- deposition on exhaust gases silencer,
- pollution of the engine oil,
- pollution of combustion gases.

Measurements on efficiency of agricultural biogas purification were done using various sorption beds composed of halloysite, 40 cm height. Research stand integrated with small-scale agricultural biogas plant is presented in Fig. 3.

During combustion of crude biogas corrosion of concrete elements was observed. Acid sulphur and nitrogen oxides strongly destroyed concrete construction of exhaust gases silencer (Fig. 4). Contrary, combustion of correctly purified biogas is not connected with formation of significant amounts of deposit inside the engine. The internal combustion engine after 30,000 h of continuous work as an agricultural biogas plant's element is presented in Fig. 5.

Chemical analysis of deposits in combustion chamber of the engine fed with mine gas (coal bed methane) of chemical composition similar to agricultural biogas is presented in Table 3.

Effects of direct use of crude biogas is presented in Fig. 6.

Fig. 3. Research stand in a small-scale agricultural biogas plant

Fig. 4. Destructed elements of concrete exhaust gases silencer – corrosion effect of acid gases from the engine

Fig. 5. Application of purified biogas as the fuel – no destruction and corrosion effects are visible

Fig. 6. Effects of direct use of crude biogas (no purification)

As it results from the table, deposit contains relatively small amount of carbon, however large contents of Si and Al are observed. It should be noted, that deposits can also involve some products of complex chemical reactions of raw agricultural biogas compounds with lubricating oils improvers and other commercial additives like soot dispersants, viscosity modificators, emulsifiers, antioxidants, anticorrosion additives, detergents and others.

3. Chemical analysis of deposits formed in combustion chamber fed with mine gas (coal bed methane) of chemical composition similar to agricultural biogas

Element	Test 1 [%]	Test 2 [%]	Test 3 [%]
Carbon	3.454	1.567	4.115
Oxygen	53.609	50.266	51.071
Silicon	17.353	22.225	20.48
Aluminium	17.765	18.304	17.627
Iron	1.428	2.375	0.388
Potassium	3.617	4.1	3.218
Magnesium	0.441	0.442	0.388
Titanium	1.857	0.717	0.931
S + Na	rest	rest	rest

Conclusions. Purification of crude agricultural biogas is important part of the technology. Appropriate biogas cleaning results in no deposits formed on movable and stationary elements of the engine. In the specific engine work conditions sulphur compounds are the most often chemically transformed into $CaSO_4$ while silicon compounds into SiO_2. Both products are responsible for engine corrosion effects.

Sorption efficiency of S, N and Si compounds depends mainly on preliminary physicochemical activation of halloysite. Future work should involve more thorough insight into physicochemical mechanisms of S, N and Si compounds sorption on halloysite. Research results can be also applied in energetic and coal mining industries directly.

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Наведено результати практичних досліджень щодо концентрації сірки, азоту і кремнію сорбції з біогазу, який був отриманий в малій сільськогосподарської біогазовій установці. У ході дослідження протестовано застосування мінерального сорбенту, отриманого авторами на основі натурального галлуазіту від Dunino депозиту (Польща). Також наведено результати використання заводського прототипу для дослідження ефективності видалення з біогазу S, N і Si з'єднань. Вивчено вплив згоряння сирої біогазової маси на окремі елементи двигуна внутрішнього згорання. Хімічний склад, утворений в двигуні внутрішнього згоряння оцінений як відмінний.

Сільськогосподарський біогаз, галлузіат сорбенту, сірка, азот, кремній, видалення домішок.

Представлены результаты практических исследований по концентрации серы, азота и кремния сорбции из биогаза, который был получен в малой сельскохозяйственной биогазовой установке. В ходе исследования протестировано применение минерального сорбента, полученного авторами на основе натурального галлуазита от Dunino депозита (Польша). Также приведены результаты использования заводского прототипа для исследования эффективности удаления из биогаза S, N и Si соединений. Изучено влияние сгорания сырой биогазовой массы на отдельные элементы двигателя внутреннего сгорания и глушителя. Химический состав, образованный в двигателе внутреннего сгорания оценен как отличный.

Сельскохозяйственный биогаз, галлузиат сорбента, сера, азот, кремний, удаление примесей.