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PROSPECTS FOR DEVELOPMENT OF FUEL CELLS

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The article is devoted to the solution of a complex of problems that arise in small and medium-scale treatment complexes, gas production plants and small and medium-capacity power plants associated with the processing of crude methane and the possibility of reducing the greenhouse effect.

The economic feasibility of the development of fuel cells (FC) on raw biomethane was demonstrated by the authors in previous publications.

The specificity of the solution of problems is focused on small and medium-scale treatment complexes, gas production plants and small and medium power plants.

The aim of the study is to show the possibility of solving a multicomponent task of developing fuel cells, including the experimental determination of the actual use of sodium formate as a reducing agent for the production of electricity in a fuel cell (FC).

Results are the following: the possibility of solving the issues of reducing greenhouse gas emissions into the atmosphere during processing of waste products of human vital activity is proved. A method for converting methane and carbon dioxide emissions into useful products is shown.

***Key words*: s**ynthesis gas, fuel cell, fuel element, electricity generation

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Introduction. In recent years, fuel cells are not being used and there are many reasons for this: the cost of all types of fuel cells is extremely high – at least 1000 euro/100 W, the high cost of «dry» hydrogen with purification class 99.95 %. Usually this fact is not in the focus of attention of the majority of «not-well-informed» and they notice only high efficiency coefficient, low operation cost, and long working time before appearance of any failures. Despite the guaranteed long time of operation (5-10 years), a high payback period remains. The operation of fuel cells, taking into account the cost of accident elimination in comparison with nuclear power plants, is already low in many countries. Even a relatively small (ordinary) accident at a hydroelectric power plant (for example, a dam break) excludes a low cost of electricity.

The article is devoted to the solution of a complex of problems that arise in small and medium-scale treatment complexes, gas production plants and small and medium-capacity power plants being used for processing of crude methane and the possibility of reducing the greenhouse effect.

Research methods. Various methods were used in the research process: mathematical modeling, mathematical statistics, methods of analysis of organic chemistry, and methods for analyzing electrochemistry – the method of oxidative conversion of methane to synthesis gas $CO + H_2$; a method of using a fuel cell on sodium formate and an industrial method for the production of formic acid.

Methane and carbon dioxide are two by-products that intensify the greenhouse effect and increase the cost of electricity.

At the same time, simultaneously with electricity generation, it is possible to process crude methane in a fuel cell.

Emissions of the largest mass of methane occur during the extraction of coal, oil and natural gas. More than 40 % is directly related to human activities: the utilization of agricultural waste and sewage, the burning of plant residues in the fields and biomass. At the same time, the number of agricultural emissions remains at the same level, emissions from fossil fuel production are significantly increasing. Especially it concerns coal mining in China [13].

Mandatory rules should be introduced to reduce emissions, if it will become evident that fossil fuels are becoming a major problem.

Methane is a powerful gas with a greenhouse effect. After 100 years, the impact of methane on the climate will be 25 times greater than the effect of carbon dioxide, and in 20 years the methane will create a greenhouse effect 72 times greater than carbon dioxide creates now. Therefore, it is very important to limit methane emissions and improve its processing.

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Unlike methane, carbon dioxide is stored in the atmosphere for a long period of time. However, a reduction in the number of explosive gases will provide an opportunity to move aside the catastrophe of global warming. Many initiatives have been put forward, including global ones, to reduce hazardous emissions. Efforts are being made to limit carbon dioxide emissions. There are some concerns that methane can be used as an excuse to avoid problems with carbon dioxide.

Methane is also present in all sources of fossil fuels, so it must be disposed of or evaporated. It's an explosive substance. To calculate the amount of methane emitted into the atmosphere, one can use data on the presence of oil and gas wells in Canada and satellite images of gas flares in the world.

Interpolation of data on the rest of the world gives conservative estimates.

There are good and fairly cheap technologies that can be used to reduce emissions of fossil methane, but we need to have international agreements to use them. On the eve of the Climate Summit in Copenhagen (2009), several projects were submitted for consideration in the Chinese coal mines. But the projects were not realized, as the market, which was used to sell the technology of this production, was reduced.

Methane is one of the so-called greenhouse gases that contribute to the global warming of the Earth's climate. The contribution of methane to the greenhouse effect may be overestimated, since the calculation models do not take into account the height of the gas in located the atmosphere when calculating its warming effect. This issue was studied at the Max Planck Institute in Germany [20].

The most important among the greenhouse gases is carbon dioxide. Despite the fact that methane is present in significantly lower concentrations than carbon dioxide, it is estimated by experts to affect the global warming. This is due to its «heating effect», which is 10 times higher than carbon dioxide. Over the past 10 years, the methane concentration in the atmosphere has increased more than two times.

The investigation of the above-mentioned task is related to the solution of the problem of methane usage, which is connected with the processing of agricultural waste and waste products of human life. The field specific data were given in [1]. What do we have? Virtually all sewage treatment plants (Sweden, Canada) have long been equipped with devices for obtaining crude methane of average proportion: 65 % of CH_4, 35 % of H_2O and CO_2. The majority of these facilities (gas manufacturing plants) produce synthetic biomethane (about 95-97 % methane). In many cases agricultural cooperatives are engaged in this type of activity but it becomes their non-core business. Synthetic biomethane (methane produced by high purification and drying) is being used for production of liquid fuel – fuel for motor vehicles. The cost of such fuel is almost two times higher than the cost of conventional fuel [1, 9, 14, 17, 18]. The main energy costs allocated for drying processes. What kind of consumer, despite the public belief about the importance of the environment, can afford to buy such fuel? This is possible only for state vehicles, existing on subsidies and not paying taxes. Reality is much worse. There is a well-known case: in the commune, not far from Stockholm, there are two reactors at the treatment facilities with a capacity of 1600 m^3 per day, but they use only one – with a capacity of 800 m^3. Approximately 200 m^3 are simply flared just to be used and at the same time a tax is paid for the production of carbon dioxide. Residual methane is burned to produce heat. This is quite an ordinary situation and not only in Sweden. Frequently, synthetic biomethane is also being just burned – it is not easy to sell expensive products. These information is available in open access publications.

What can be done now, without waiting for another scientific and technological revolution? The answer is to use raw methane to generate electricity [1]. The most suitable way of processing crude methane is by conversion in the reformer unit [4].

Carbon dioxide conversion of methane to synthesis gas. Is one of the most important chemical reactions, suitable for industrial production of hydrogen and which gives rise to the synthesis of hydrocarbons (liquid fuel) and other technologically valuable products.

There are three methods of oxidative processes for reforming methane to synthesis gas $CO + H_2$:

• steam reforming

$$CH_4 + H_2O \rightleftarrows CO + 3H_2,$$

$$\Delta H = +206 \text{ kJ/mol}; \quad (1)$$

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• partial air oxidization

$$CH_4 + 1/2O_2 \rightleftarrows CO + 2H_2,$$

$$\Delta H = -35.6 \text{ kJ/mol}; \quad (2)$$

• carbon-dioxide reforming

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2,$$

$$\Delta H = +247 \text{ kJ/mol}. \quad (3)$$

In industry, only the steam reforming method is currently used (1). The reaction is carried out with a Ni-supported catalyst and a high temperature (700-900 °C). As for the reaction (2), on its basis the Shell company developed the technological process in the non-catalytic version at very high temperatures (1100-1300 °C), that is implemented at a small plant in Malaysia. Unfortunately, according to the latest information, this plant is not working now because of the accident. Reaction (3) is still under investigation at the level of laboratory and pilot tests.

As follows from equations (1)-(3), the quantitative composition of the resulting synthesis gas in these reactions is different: in reaction (1), a synthesis gas has a composition CO: H2 = 1:3, in reaction (2) we obtain a 1:2 composition, in the reaction (3) – a 1:1 mixture. The need for synthesis gas of a given composition is determined by its subsequent industrial appliaction. So, synthesis of methanol requires a synthesis gas of 1:2:

$$CO + 2H_2 \rightleftarrows CH_3OH.$$

So, with the help of a reformer unit we get carbon monoxide CO and hydrogen H_2 from methane [2, 10-12, 15]. Currently, no progress is being made in this area, and carbon monoxide, when produced in the reformer unit, is still being used in engines, if not burned, and with extremely low efficiency coefficient.

As for application of fuel cells (FC), a hydrogen atom fuel cell is a sufficiently developed method. Hydrogen technology has existed for almost 200 years and does not offer any progressive solutions, with the exception of some engineering solutions and small innovations.

A lot of gases and liquids can be used in fuel cells, if there are some carriers like anions and cations. This has already been known for a long time. The choice of components for the fuel cells significantly reduces the requirements for temperature, corrosion resistance, etc.

There is a way to avoid a lot of both environmental and energy problems using a fuel cell on sodium formate.

As early as 1856 Marcellin Berthelot synthesized formate from carbon monoxide.

In 1856 Berthelot conducted a series of experiments on the synthesis of formic acid. When carbon monoxide is passed through a solid heated sodium hydroxide, a formic acid salt forms – sodium formate:

$$NaOH + CO \longrightarrow H-C(=O)-ONa.$$

It is possible to displace formic acid from its salt by the action of a solution of a stronger sulfuric acid:

$$2H-C(=O)-ONa + H_2SO_4 \longrightarrow 2H-C(=O)-OH + Na_2SO_4.$$

Until now, this process is the main industrial method of producing formic acid. The interaction of carbon monoxide with solid sodium hydroxide occurs at a pressure of 600-800 kPa and a temperature of 120-150 °C.

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It is known that the main component of the cost of chemical processes is energy. If cheap electric energy can be obtained on the hydrogen fuel cell, then it is also possible to produce cheap formic acid, sodium formate, and methanol. Electricity is the most costly product. In the presence of treatment plants, reformers units and fuel cells, the cost of energy will be minimal.

If we have an inexpensive technology to produce sodium formate or formic acid, these products can be sold without increasing the amount of greenhouse gases.

here is another positive aspect of using the sodium formate.

There was developed a fuel cell to produce electricity from a noncombustible substance, that is sodium formate. Experiments have shown that such a fuel cell can work without the use of precious metals, and therefore it is cheaper to use it in production process. During operation of this fuel element there are no emissions of carbonic gas, nitric oxide and other toxic substances. The energy carrier is non-toxic and biodegradable [5]. The fuel element «burns out» the formate.

The purpose of the study is the experimental determination of the actual use of sodium formate as a reducing agent for the production of electricity in a fuel cell.

Sodium formate is a biological substance of natural origin. In a fuel cell, it is oxidized to carbon dioxide, it is not flammable or explosive. Such a «fuel» does not require special security measures, they are reduced to zero, unlike hydrogen, it has a high density. Anion sodium formate is a sufficiently reactive reducing agent, it is oxidized at the electrode. As a result, here is its charge on graphite

$$HC(O)O^- = HC(O)O^* + e^-;$$
$$HC(O)O^* = OC^*OH;$$
$$OC^*OH + H_2O = OC(OH)_2 + H^*;$$
$$H^* + C = H^*\ldots C;$$
$$H^*\ldots C = H^+ + C + e^-.$$

Thus, the formate donates two electrons.

Graphite does not have a pronounced catalytic activity, but the process proceeds with sufficient speed.

The oxygen dissolved in the electrolyte is reduced on graphite in the reaction between water and alkaline medium:

$$O_2 + C = O_2\ldots C;\ O_2\ldots C + 2e^- = O_2^{2-} + C;$$
$$O_2^{2-} + H_2O = 2OH^- + O;$$
$$O + C = O\ldots C;$$
$$O_2\ldots C + 2e^- = O_2^{2-} + C;$$
$$O_2^{2-} + H_2O = 2OH^+.$$

The hydroxide ions transfer the anion charge to the membrane:

$$2OH^- + R - S(O)_2^- H^+ = H_2O + R - S(O)_2^-.$$

But there is an additional opposite potential, at the same time, hydrated protons pass through the membrane unhindered. The latter circumstance reduces the theoretical value of EMF. The oxygen dissolved in the electrolyte is reduced on graphite by reaction in an acid medium:

$$O_2 + C = O_2\ldots C;$$
$$O_2\ldots C + 2e^- = O_2^{2-} + C;$$
$$O_2^{2-} + 2H^+ = 2H_2O + O;$$
$$O + C = O\ldots C;$$
$$O\ldots C + 2e^- = O_2^{2-} + C;$$
$$O_2^{2-} + 2H^+ = 2H_2O.$$

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Discussion of the results. The activity of sodium formate as a reducing agent in the oxidation process with various oxidants: oxygen from air and hydrogen peroxide is high. Even at low concentrations of the oxidizing agent has a stable effect. This means that the electro-catalytic activity of the graphite electrode was sufficient for the continuous operation of the fuel cell for a long time (see tables). The time of each experiment is 50 minutes.

Results of the experiment performed for a fuel cell with a membrane

Electrolyte	EMF, mV	*U*, mV (load 2 kOhm)	*I*, mA
Air oxygen (15 mg/l) – medium NaOH (1 mol/l)	81	70	34
Oxygen in water (15 mg/l)	135	100	50
H_2O_2 20 % in volume	330	302	149
Oxygen (15 mg/l), $NaHCO_3$, solution 1 mol/l	208	80	41
Oxygen (15 mg/l), H_2SO_4, solution 1 mol/l	381	–	150
Oxygen (15 mg/l), H_2SO_4, solution 0.2 mol/l	636	–	–
Oxygen (15 mg/l), H_2SO_4, solution 0.1 mol/l	465	405	205

During the experiment, the voltage was fairly stable. A relatively low value of EMF is associated with a high membrane resistance. As the cation exchange membrane was used Tofion (Germany), sulfonated fluoropolymer. The charge carriers are a hydrated hydrogen cation. This helps to achieve a significant effect and concentration of the acid. The best concentration corresponds to 0.2 mol/l sulfuric acid. As the concentration of acid increases, the ionic strength of the solution increases, respectively, as a result of swelling, the conductivity of the membrane changes. Therefore, when the acid concentration exceeds mol/liter, the EMF decreases again.

Studies have shown that the presence of a reformer unit, crude methane, carbon dioxide, water and electricity without special difficulties makes it possible to manufacture products needed in various fields. Including those that can be applied in solving our problems.

The economical way of obtaining formic acid by oxidation of formaldehyde. In a number of reactions, product concentrations and reagents in the process are calculated for different time periods. The operation is modeled as the production of formic acid (HCOOH) by oxidation of formaldehyde (HCHO). During oxidation, a side reaction occurs in which formaldehyde reacts with itself to form methyl formate ($HCOOCH_3$):

$$HCHO(g) + 1/2\,O_2(g) \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} HCOH(g), \quad \Delta H_f = -279\ \text{kJ/mol}^{-1}; \tag{4}$$

$$2HCHO(g) \underset{k_{22}}{\overset{k_{21}}{\rightleftarrows}} HCOOCH_3(g), \quad \Delta H_f = -226.9\,\text{kJ/mol}^{-1}. \tag{5}$$

Let us denote the equation (4) as the desired reaction, (5) – undesirable side reaction, where formaldehyde reacts with itself and forms methyl formate ($HCOOCH_3$). Both reactions occur in the gas phase, and are assumed to be elementary, and a titanium vanadium oxide catalyst is used in the process.

To obtain a relatively high amount of formic acid, a long period of time is required.

Method for the production of formic acid by oxidation of methane on a catalyst. This method is well known, well developed and simple:

$$2CH_4 + 3O_2 \xrightarrow{t,\,\text{cat}} 2HCOOH + 2H_2O.$$

Production of formate by the interaction of carbon monoxide CO with alkali:

$$CO + NaOH \xrightarrow{120\text{–}130\,^\circ\text{C},\ 0.6\text{-}0.8\ \text{MPa}} HCOONa;$$

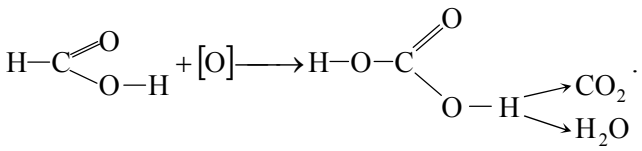
$$HCOONa + HCl \longrightarrow HCOOH + NaCl.$$

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The most advantageous method (from the point of view of economic costs – a non-waste process) for the production of formic acid is the preparation of formic acid ether (with subsequent acid hydrolysis) from carbon monoxide and the limiting monohydric alcohol [8]:

$$CO + ROH \xrightarrow{80\ ^\circ C,\ P=3\ MPa,\ RONa} HCOOR;$$

$$HCOOR + H_2O \xrightarrow{H^+} HCOOH + ROH;$$



One of the attempts to use formic acid – an alternative to storage batteries and hydrogen tanks – was an electric car [16, 19, 21].

Some of these processes can be used in fuel elements (*FuelCellstack*). A tonal method for the production of formic acid is the combination of hydrogen and carbon dioxide molecules. In this case, it is possible that formic acid is the fuel of the future.

However, the heat of formic acid combustion process is small, the calculation by the Mendeleyev formula gives 5.74 MJ/kg, according to Hess 5.62 MJ/kg, in the Korolchenko Handbook [3] – 4.58 MJ/kg. This amount is not enough for a modern car, although environmental requirements are high.

Let us mention some solutions that can be useful in the production of electricity with the help of fuel cells [7].

The main advantage of this development is the generation of electricity during the production of chemical goods and in the process of processing various wastes, with the associated production of chemical products, a technical effect is achieved, that is a reduction in the cost of electricity, which means that in the process of wastewater treatment, new valuable chemical products are obtained.

The systems of treatment facilities in almost any city use about 30 % of all electricity produced only for wastewater treatment, which should always be considered.

The proposed installation [7] refers to the field of energy and devices for generating electricity, designed for use in objects in an explosive and flammable environment. Electricity is generated from wastewater and supplied to the fuel cell, or the associated gas is used.

The existing fuel cells use hydrogen, methanol and other easily flammable, explosive and toxic substances as fuel. For the safe operation of such devices, their careful sealing, complex and expensive fuel and oxidizer supply devices are required. Electrodes in fuel cells are made of precious metals: platinum, palladium. Therefore, they are expensive and difficult to manufacture. Existing fuel cells are poorly adapted to work in an explosive atmosphere, since they contain an explosive atmosphere and complex electrical and mechanical devices.

Thus, it is obvious that the task of creating a fuel cell that allows to receive electricity from a non-combustible energy carrier using cheap electrodes can be solved.

Conclusions

Based on the carried-out research, the following conclusions can be drawn:

• the reduction of energy costs is possible due to the use of fuel cells for the utilization of greenhouse gases (methane and carbon dioxide);

• the possibility of processing human waste products and converting them into useful products was proved;

• after carrying out steam-carbon reforming using carbon dioxide, sodium formate is produced to generate electricity.

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