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Formic acid cycle as partial alternative to Allam cycle less expensive and simpler

Mikhail Gotovsky*, Alexander Gotovsky, Vladimir Mikhailov, Sergei Kolpakov, Vitaly Lychakov, Yuri Sukhorukov

"Polzunov Institute", Atamanskaya Str., 3/6, St. Petersburg 193167, Russia

Corresponding Author Email: gotma@rambler.ru

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ABSTRACT

Allam proposed to realize problem of CO_2 emissions by using supercritical CO_2 cycle as working fluid with heating by carbon fuel burning in pure oxygen and then pumps CO_2 into underground volumes remaining after oil production.
Interest in the Allam cycle shows readiness for technological difficulties and high costs for combating CO_2 accumulation in atmosphere.
The formic acid cycle begins with the conversion of CO_2 from the atmosphere or from flue gases to an aqueous solution and the electrochemical reduction of CO_2 into formic acid.
Formic acid is a convenient and safe energy storage for fuel cells, since the electrochemical process is reversible. In the reverse process (oxidation), the released CO_2 can be immediately immobilized and further buried as a component of the building foam concrete. The formic acid cycle can serve as a "green" alternative to the dominant oil cycle of basic chemical production. It should be noted that even if the task of combating CO_2 emissions and global warming will be no longer relevant, the value of the formic acid cycle will be preserved, since it solves a broader spectrum of tasks for the ecologization of energy generation and organic chemistry.

1. INTRODUCTION

The optimization of the steam-power cycle of thermal and nuclear power stations by switching to the Brighton cycle with supercritical carbon dioxide (sCO_2) was actively engaged in 1960-1970. In the USSR, Professor P.D. Gokhshtein and his colleagues were engaged in similar works. The advantages of such a cycle were identified: high density of the working fluid throughout the cycle. Impressive were the compactness of such installations. The results of these studies were published in [1-2], and then generalized in monograph [3]. However, to realize the stated advantages of the cycle with carbon dioxide, technical capabilities were required that the USSR and the countries of the West did not possess. Therefore, these works were to some extent forgotten.

We have encountered these ideas in connection with the development of two major innovative areas, which now attract the attention of specialists.

The first of these is an attempt to use a steam cycle with sCO_2 with the preservation of supercritical parameters in the whole cycle. This is the so-called "split" cycle of Brighton with two compressors and recuperators, which is proposed for wide application for fast reactors of the fourth generation. Its use should allow simultaneously to improve economic characteristics of fast breeder reactors and substantially increase their safety. This approach can be especially useful for the current project "Breakthrough" in Russia, which involves the creation of a closed fuel cycle within the NPP with the lack of a system for transferring and storing SNF outside the power plant.

The second project is the implementation of schemes of conventional power plants, fuel, which use a cycle with sCO_2 as a working fluid at ultra-high temperatures and pressures. At the same time, along with electricity generation, carbon dioxide, which is formed as a result of fuel combustion must be pumped to great depths of the order of 1 km. The implementation of this project, especially its final phase, will require huge costs and, essentially, also time. Such a project could be considered relevant only on the basis of fashionable environmental alarm associated with greenhouse gases.

2. MODERN RETURN TO IDEAS OF ALTERNATIVE WORKING FLUIDS UTILIZATION AND IN ARTICULAR, SUPERCRITICAL CARBON DIOXIDE

The idea of developing plants with sCO_2 was put forward by RD Allam [4] in the framework of developing measures to combat "global warming". This idea has a very radical character and is associated with the use of sCO_2 as a working fluid. Working pressures can reach up to 700 atmospheres, and operating temperatures of 1200°C and above. The implementation of such a cycle will require a huge amount of engineering and material science work to develop such extremely high parameters for stationary power engineering, without guaranteeing an early positive result.

The core idea of this project is to reduce the carbon dioxide in the atmosphere by pumping liquefied CO_2 to a depth of about a kilometer. This cycle was called the cycle of Allam.

It should be noted that the introduction of a carbon dioxide supercritical cycle into nuclear power does not require such high parameters because of the absence of CO_2 generation.

The idea set out below regarding the development of environmentally "clean energy" is based on the following assumptions.

a). The doctrine of global warming under the influence of

technogenic greenhouse gases is essentially a hypothesis that is difficult to be considered as convincingly justified. Among its opponents are a number of specialists in the field of geophysics. This circumstance will be discussed in detail in Section 8 of this article.

b). In the modern history of science, waves of fashionable ecological alarm have already appeared on the basis of hypotheses that later turned out to be speculative (a typical example is the doctrine of expanding the ozone holes under the influence of technogenic freons).

c). Proceeding from (a) and (b), in the choice of technologies that reduce the concentration of greenhouse gases in the atmosphere, those that remain relevant even if the doctrine of "global warming" is disavowed are preferred.

Based on these assumptions, the authors propose a technological concept related to "green energy", which allows to reduce CO_2 emissions or to reduce the concentration of CO_2 in the atmosphere, while not requiring extreme costs and efforts. In other words: a concept that can be considered in the context of combating "global warming", but still relevant outside this context, simply as one of the energy and chemical technologies based on a renewable source of raw materials - atmospheric CO_2.

3. BRIEF DESCRIPTION OF THE APPROACHES TO BE USED

3.1 The raw material for the production of formic acid (HCOOH) in the proposed formate cycle is carbon dioxide extracted from fuel gases or from the atmosphere. The production of carbon dioxide from atmospheric air can be organized in a cyclic process of liquid chemisorption. As sorbent can be used, in particular

(1) An aqueous solution of potassium carbonate. Upon contact with air at ordinary temperatures and elevated pressures, the carbon dioxide passes into the solution to form potassium hydrogen carbonate. When the pressure is lowered, the decomposition of hydrocarbonate with the release of CO_2 occurs. The process of precipitation passes almost completely when the temperature is raised to 100°C.

(2) An aqueous solution of an amino alcohol (ethanolamine or methanolamine). At normal temperature and pressure, CO_2 is absorbed to form the hydrogencarbonate of the corresponding amino alcohol, and when heated to 60 °C, CO_2 is released. Both these processes have been thoroughly investigated.

Reversible sorption of CO_2 by specialized solid (granular) absorbers (including some types of zeolite) is also possible.

There are gas-membrane methods of separating CO_2 from other air components, but to date this promising technology has not been sufficiently developed for practical application.

The choice of a specific technology for reversible sorption of CO_2 from air is determined based on the technical and economic conditions of production, and does not affect the further stages of the formate cycle.

3.2 Electrochemical reaction (hydrogen source - water)

A wide range of possible electrode structures and catalysts for the reaction in an aqueous medium according to the electrochemical scheme

$$CO_2 + 2H (+) + 2e - > HCOOH \quad (1)$$

Or

$$CO_2 + H_2O + 2e - > HCOO (-) + OH (-) \quad (2)$$

Note: HCOO (-) - formate ion - dissociated formic acid. It was studied, in particular, the use of electricity received directly from solar panels. This is an ideally "green" method of absorbing CO_2 from the atmosphere.

3.3 Alternative start of the formate cycle. Direct catalytic hydrogenation of CO_2 by using an external hydrogen source and reaction

$$CO_2 + H_2 - > HCOOH \quad (3)$$

The most promising in terms of speed and degree of conversion is the reaction with a homogeneous catalyst with CO_2 in the supercritical state.

Note: a deeper electrochemical reduction of carbon dioxide was reported: to methanol (CH_3OH) and ethanol (C_2H_5OH). There is no data on the possibility of its large-tonnage (industrial) application. On the other hand, the electrochemical aqueous synthesis of CO_2 -> HCCOH has been investigated up to the possibility of industrial application

3.4 The practice of direct electrochemical production of formic acid when using solar batteries

Scientists from Priston University have developed a unique way of converting solar energy into biofuel. Transformation of carbon dioxide and water into formic acid was carried out with the help of special solar batteries. Studies of global warming caused by an increase in the level of greenhouse gas include several key aspects - the creation of alternative fuels, the collection and storage of gases, and their processing.

It was these goals that the team, led by Andrew Bokarsli from the Laboratory of Chemistry at Princeton University, set for themselves. Scientists collaborated with engineers from the Liquid Light Inc Monmouth Junction start-up from New Jersey. The conversion of carbon dioxide and water into formic acid was carried out with the help of solar panels [5]. The process takes place inside special electrochemical cells, consisting of metal plates. The amount of energy received corresponds to the amount of carbon dioxide that enters the cells.

By stacking the three electrochemical cells together, scientists were able to achieve high energy efficiency - twice as much as energy efficiency in natural photosynthesis. A high result was recorded using special measuring devices. At present, formic acid is used in many fuel cells. For example, the salt formate contained in it is used in aircraft fuel, as it is less corrosive and safer for surrounding trails. Experts suggest that the active use of formic acid in the fuel industry may eventually supplant widely used fuels.

4. USE OF FORMIC ACID IN FUEL CELLS.

4.1 A few preliminary words about formic acid

Formic acid - 21st century petrol

This statement can be found now in literature often enough.Since formic acid occupies an important place in this article, we will devote a small preliminary section to it. Specialists in the field of energy have long called hydrogen the fuel of the future.

It can be used both directly as fuel, and to feed fuel cells. However, in any case the problem of hydrogen storage exists which is easily ignited and must be stored in special containers in a compressed form, and it takes a volume hundreds of times greater than gasoline. Scientists EPFL (Lausanne) and Institut fur Katalyse (Rostock) have fulfilled the storage of hydrogen in the form of formic acid and a reverse reaction. The various useful functions of using formic acid are discussed below.

Interesting method of obtaining fuel was developed by specialists from the University of Melbourne. They proposed a technology that makes it possible to efficiently produce hydrogen fuel from liquid formic acid. At the heart of the development is a molecular catalyst that releases only hydrogen and carbon dioxide from formic acid at a temperature of 70°C. Attempts to obtain fuel from formic acid have been made before, but all previous methods were economically inexpedient, since they assumed the use of high temperatures.

Hydrogenation of CO_2 to formic acid (H_CO_2H) is the subject of intensive research, since it allows direct production of chemical products from waste generated from the combustion of fossil fuels. Formic acid is an important product of the chemical industry, which is used in many fields - agriculture, food industry, leather industry. The possibility of applying formic acid as a material for hydrogen storage was considered. This allows you to successfully solve the problem of solar cars in the dark phase (when the car requires an electric battery, or a hydrogen battery - for a variant with fuel cells). It is assumed that cars with solar batteries can produce formic acid, from which hydrogen will be further released (in the dark phase) by catalytic reactions.

The possibility of using homogeneous catalysis to produce formic acid from CO_2 has been studied since the mid-1970s. The problem with this process is that one of its stages is an equilibrium reaction, and the equilibrium is shifted towards the starting materials. To displace equilibrium, it is necessary to remove formic acid from the reaction mixture, but for existing processes this is possible only by converting formic acid to salt or some other derivative. Thus, in order to obtain pure formic acid, an additional step is necessary - the destruction of this derivative, which is why it is impossible to organize a continuous process for the production of formic acid.

Researchers from the Walter Leitner group have developed a new concept that can be used to produce pure formic acid through a continuous process - the CO_2 hydrogenation stage and product isolation are integrated and conducted in a single apparatus. The effectiveness of the new process lies in the fact that the researchers proposed using a two-phase system in which supercritical CO_2 played the role of a mobile phase, and a liquid salt-ionic stationary phase. Both the catalyst and the base used to stabilize the acid are dissolved in the ionic liquid. The CO_2 stream enters the reactors at pressures and temperatures higher than the critical values (74 bar, 31 °C) and selectively removes formic acid from the reaction mixture. The dual role of CO_2 and the reagent and the phase for extraction has its advantages: the target product is continuously extracted and washed out of the reactor, which contributes to a shift in equilibrium.

Supercritical CO_2 does not dissolve either ionic liquids or catalyst with a base, so they do not contaminate the final product. The process can be carried out continuously - in the laboratory the stable operation of the pilot plant was observed for 200 hours.

The reaction of oxidation of formic acid in the fuel electrochemical cell:

$$HCOOH - 2e \rightarrow CO_2 + 2H (+) \quad (4)$$

The process is sufficiently well studied for different scales, temperatures and different designs of electrodes (including the type of membrane and the type of catalyst).Virtually the power supply elements were built from several watts (for electronic devices) to 25 kW (for an electric bus). Of particular interest are fuel cells, which can act as charging electric batteries when the voltage is applied (implementing process 3.1.).

Note: when formic acid is used in fuel cells, CO_2 absorbed in the synthesis is released. The ecological balance for CO_2 is zero.

After a number of new works in this area, a number of vehicle projects were developed based on the use of such fuel cells. Below is an example of such a project with comments.

For example, a group of students from the Eindhoven Technical University in the Netherlands developed the world's first bus that operates on formic acid. According to the inventors, this is a much cheaper and more practical solution than the use of other alternative fuels. Thus, students want to develop a transport network without harmful emissions, helping in the fight against climate change Formic acid was first derived from red forest ants (why it got its name) in the XVII century. Also in nature it is in some plants, for example, nettles and needles, and in the caustic secretions of bees. Usually it is obtained chemically by producing acetic acid as a by-product. Formic acid is already used in many areas: the chemical industry (as a solvent), food (as a preservative), beekeeping (for fighting parasites) and medicine (as an external pain killer).

The fuel that uses the new bus, the inventing students called hydrozine (not to be confused with hydrazine). It is a liquid that can be transported easily and relatively safely. Stations with formic acid will look and be used as the most common refills. The only difference is that the fuel in them is much cleaner. The bus will not emit any harmful gases - just water and CO_2.

Figure 1. Project of bus used formic acid as the fuel

Fuel is created inside the device, which Dutch students are now trying to patent. There, Hydrozine decomposes into hydrogen and carbon dioxide with the help of a catalyst. Then, hydrogen is added to the fuel cell, with which it will react to generate electricity, which feeds the engine [6].

The bus has an electric drive system developed by VDL. The tank is designed for 300 liters, so researchers say that the bus will be able to travel up to 200 kilometers. It is expected

that by the end of year the vehicle will already be actively used.

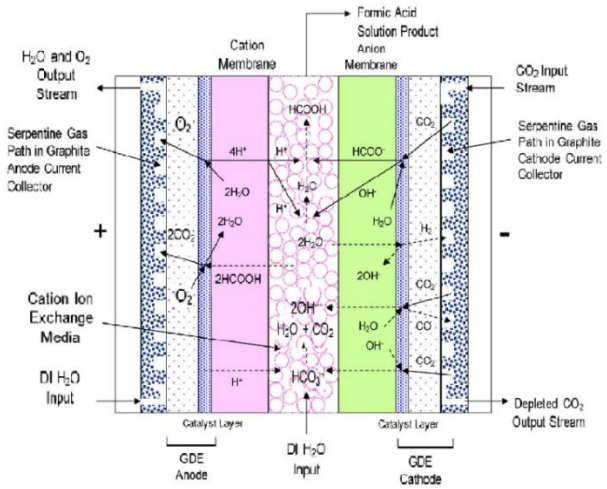

Figure 2. Qualitative scheme of fuel cell produce formic acid

5. THE USE OF FORMIC ASID IN ORGANIC SYNTESIS

It is interesting to construct a wide range of production of organic substances from formic acid, obtained by the binding of atmospheric CO_2. In this case, CO_2 is fixed in industrial products.

With a significant number of options for chemical processing of formic acid, it will be rational to consider the simplest versions available.

5.1 Processing through decomposition to carbon monoxide (CO)

This is a fairly simple process of dehydration. Carbon monoxide is a large-tonnage intermediate for organic synthesis. But it is quite toxic, gaseous under normal conditions, therefore, is problematic in storage and transportation.

5.2 Processing by hydrogenation to formaldehyde (CH_2O) and methanol (CH_3OH)

Both products are large-capacity for chemical production Formaldehyde, in particular, is used for the preparation of polymer-polyformaldehyde, and phenol-formaldehyde resins. Methanol is used to produce biodiesel from technical vegetable oil.

5.3 Processing by symmetrization with CO2 to oxalic acid (HOOCCOOH)

Formic acid can be converted to oxalic by incomplete electrochemical oxidation, and this process is sufficiently well studied. More promising, however, is the process of symmetrizing formic acid with carbon dioxide to oxalic acid.

$$HCOOH + CO_2 = HOOC\text{-}COOH \quad (5)$$

The advantage of this process is the additional absorption of carbon dioxide from the atmosphere or from industrial flue gases. The process has not been studied in sufficient detail, but there are a number of data on equilibrium in such a three-component reaction system. The technological use of the process of symmetrization of formic acid and carbon dioxide to oxalic acid looks promising enough to justify the feasibility of research. Oxalic acid itself is a large-tonnage chemical product. In addition, it can be electrochemically reduced:

to glyoxylic acid: CHOCOOH - is used as an intermediate in organic synthesis (in particular - in the synthesis of complexons).

to glycolic acid: CH_2 (OH) COOH - used as an intermediate in organic synthesis, and as an independent product.

A separate topic, which goes beyond the scope of this article, are the processes of converting formic acid into more complex organic compounds. In particular, a process is described in which the electrochemically obtained formic acid (1.1.) Is processed into a number of different more complex organic compounds by the method of biotechnology. However, there is no data on the possibility of large-scale (industrial) application.

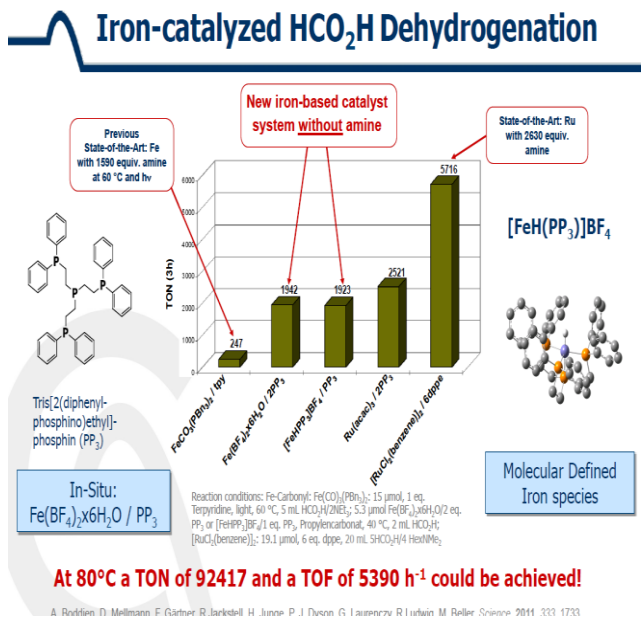

Figure 3. Iron-catalyzed HCO_2H dehydrogenation

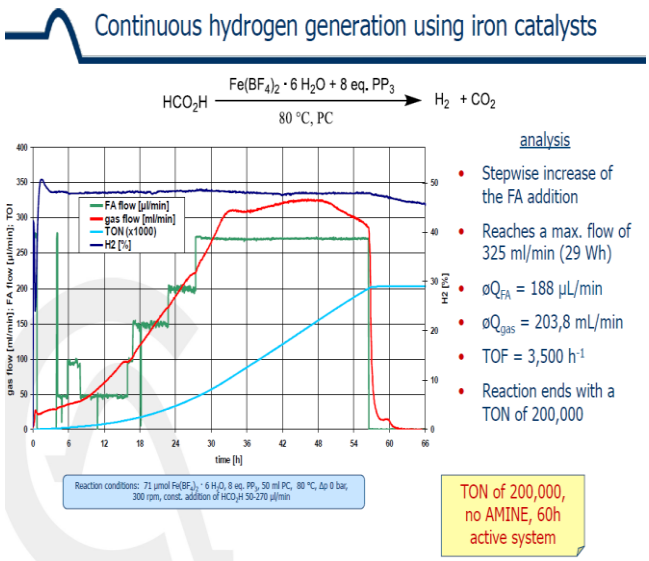

Figure 4. Continuous hydrogen generation with iron-catalysts

6. USE OF FORMIC ACID FOR THE BINDING OF HEAVY METAL WASTE

The peculiarity of formic acid (and its salts - formates) and oxalic acid (and its salts - oxalates) is that formates are generally very soluble in water, and oxalates are practically insoluble. Thus, it is possible to dissolve toxic heavy metal oxides in formic acid and transform them into a harmless insoluble precipitate by incomplete oxidation (for example electrochemical oxidation) of formate in solution to insoluble

7. USE OF FORMIC ACID AS A HYDROGEN STORAGE BATTERY

Reversibility of the chemical hydrogenation of CO_2 to formic acid (and, the possibility of reverse dehydrogenation) allows the use of the CO_2 <->HCOOH system as hydrogen battery. There are research works on carrying out both reactions (direct and reverse) in one reaction-catalytic system reaction.

$$HCOOH = CO_2 + H_2 \quad (6)$$

Proceeds with the use of modern catalysts under relatively mild conditions. That allows to place a container with formic acid (as a hydrogen accumulator) and a compact catalytic

For the storage of formic acid, special cylinders are not required, and the mass fraction of hydrogen in formic acid is 4.34%, - more than 3%, at which the hydrogen accumulator is considered technically and economically acceptable.

Even more impressive results are presented in [8], where the efficiency of the process reached 95%. In this case, iron was also used as the catalyst.

8. USE OF THE PROPOSED DIRECTION FOR THE BINDING OF CO_2 IN CONJUNCTION WITH THE DISPOSAL OF CERTAIN TYPES OF NON-RECYCULAR INDUSTRIAL WASTE

Formic acid synthesized by electrochemical method from atmospheric CO_2 in aqueous solution can be used as an energy carrier for a fuel cell, not in the form of HCOOH itself, but in the form of a salt (formate) of a metal.

In particular, iron or other metal formates obtained by washing secondary metal (large-capacity scrap) from corrosion layers (oxide or hydroxide of metal) can be used. When oxidizing formate in the fuel cell, in this case the reaction occurs:

$$HCOO\ (-) - 2e + H_2O = CO_3\ (2-) + 3H\ (+) \quad (7)$$

Formates of transition and alkaline earth metals are soluble in water. The carbonate-ion formed by the oxidation of formate carbonate CO_3 (2-) forms carbonate-insoluble carbonates with the same metals. Those after the fuel (formic acid, formate) is processed in the fuel cell, the oxidation product, i.e. CO_2, does not return to the atmosphere, but settles in the reaction vessel and can be separated as a solid phase.

Carbonates of iron and other metals are practically non-toxic, fairly stable, and can be added to any non-acidic building mixes (concrete, sintering solution for ceramics, etc.) - in this case, CO_2 is fixed for an indefinite time in the building material. In addition, it is possible to use the property of transition metal carbonates to decompose with the release of CO_2 at a temperature of about 500 ° C. Those. It is possible to use carbonates as foaming agents in the production of foam ceramics. In this case, the gaseous CO_2 remains fixed in the foam (deaf pores) of the foam ceramic product. Thus, it is possible to use formic acid in two ways depending on the state of energy supply problems and the reduction of CO_2 emissions, if the urgency of this task is maintained.

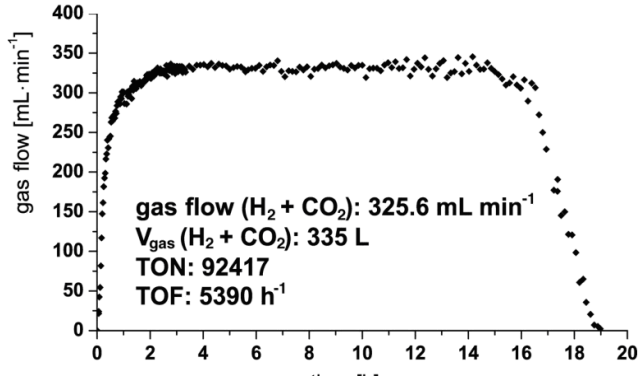

Figure 5. Main results of work [8]

9. SOME CONSIDERATIONS REGARDING THE DEGREEE OF PERSUASIVENESS OF THE DORTRINE OF GLOBAL WARMING FROM THE IMPACT OF TECHNOGENIC GREENHOUSE GASES

The processes of climate change are extremely complex, not yet fully investigated, depend on a number of factors, and have a complex periodicity with several amplitude-frequency characteristics. On intervals of the order of centuries these processes are subject to significant fluctuations. Climate monitoring is conducted during a historically short period, in which it is statistically difficult to separate systemic and random changes. The last remark is due to the fact that experts in climatology and earth physics are reasonably saying that the warming period will soon end. Below we give two quotes of famous experts in climatology.

"In fact, we now live at the peak of a relatively small local warming, after which a new phase of cooling will begin (if it has not already started). The main regulator of the temperature of the earth's atmosphere is the radiant energy of the Sun, connected with the distance between the Earth and the Sun. The distance varies periodically with time. A few years ago it was minimal, which led to a warming, and now it starts to increase. In 10-15 years, not global warming awaits us, but on the contrary - global cooling. [10]:

"And every time it was warming that preceded the increase in the concentration of CO_2 in the air. The theory of the greenhouse effect assumes the reverse sequence. Cosmic factors lead to serious climate changes. The temperature changes the fluctuations in solar activity, as well as changes in the slope of the earth's axis, the period of revolution of our planet. Such fluctuations in the past, as we know, led to the onset of glacial periods" [11].

The history of the planet includes periods of hundreds of millions of years, during which the concentration of carbon dioxide was an order of magnitude higher than now. So, in the Cambrian period, it was about 20 times higher than today. Then, during the Paleozoic era, it was roughly equal to modern

or even lower. After that, in the Mesozoic era, it was about 10 times higher than the modern one. In this case, neither in the Cambrian period. Neither in the Mesozoic period, there was an irreversible greenhouse CO_2 effect with the heating of the planet by analogy with the greenhouse processes on the planet Venus (closer to the Sun). The reasons for the lack of such warming up for the Earth has a well-known calculation-physical explanation:

"A direct calculation shows that the greenhouse effect caused by carbon dioxide plays a very limited role in the heating of the earth's surface. The amount of carbon dioxide in the earth's atmosphere is 500 times less than water vapor, and the windows of non-transmission of these gases in the infrared part of the radiation overlap. In addition, the greenhouse effect of carbon dioxide is masked by the screening effect of cloudiness in both directions of radiation propagation. " [12].

The doctrine of global warming under the influence of technogenic greenhouse gases does not contain clear answers to these comments - at least for now. Given this situation, work that is inextricably linked to especial on this doctrine should perhaps be treated with reasonable caution.

10. CONCLUSIONS

When implementing synthesis processes 3.1 and / or 3.2 - the production of formic acid from atmospheric carbon dioxide (or from the carbon dioxide emissions of industrial or energy enterprises) has prospects as a separate ecological branch of industrial organic chemistry - the so-called. «Green technologies».

Formate technologies (based on a renewable resource - atmospheric CO_2) and positively affecting the fight against the so-called. "Greenhouse gases" and "global warming" can partially replace the oil and gas technologies that dominate modern industrial organic chemistry. The paper also gives some results of the study the use of different versions of catalysts for increasing the efficiency of hydrogenation (reduction) and dehydrogenation (oxidation) processes in fuel cells.

Here it is also necessary to note the following. The scale of the practical use of the ideas presented is closely related to the dynamics of the transition to new energy generation schemes. In particular, this applies to mobile power plants (mobile electric generators on fuel cells). Energy consumption in the schemes in question occurs without increasing the amount of CO_2 in the atmosphere, and the combined waste management scheme provides additional absorption of CO_2.

The presented experimental results obtained by researchers from Germany, Switzerland and Netherlands show a real practical prospect of using the approach proposed in the paper.

One can assume that the proposed parallel development of energy cycles based on the use of formic acid and thermal power plants based on the Allam cycle will allow achieving a more successful solution of environmental problems. The presence of two simultaneously implemented substantially alternative conception on different power objects can ensure maximum approach to the optimal structure of energy production and consumption.

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NOMENCLATURE

FA	Formic Acid
sCO_2	Supercritical Carbon Dioxide
EPFL	Ecole Politechnique Federale de Lausanne
TON	Turnover Number
TOF	Frequency of Turnover, h^{-1}
Time	Hours, h
Time	Minutes, Min
Gas flow rate	mL. min^{-1}
V	Volume L, m^3
SNF	Spent Nuclear Fuel