



<https://doi.org/10.15407/scine17.05.073>

**KAMENSKY, A. O.** (<https://orcid.org/0000-0001-7440-2860>),  
**OLSHEVSKY, O. P.** (<https://orcid.org/0000-0001-9689-5360>),  
**POCHYNOK, V. V.** (<https://orcid.org/0000-0002-7236-7130>),  
and **VIAZOVYK, V. M.** (<https://orcid.org/0000-0001-7113-9892>)  
Cherkasy State Technological University,  
460, Shevchenko Boulevard, Cherkasy, 18006, Ukraine,  
+380 472 51 3660, [htv@chdtu.edu.ua](mailto:htv@chdtu.edu.ua)

## ELECTROCATALYTIC PROCESSING OF CARBON DIOXIDE INTO METHANOL AND FORMALDEHYDE

**Introduction.** Since the middle of the XIX century there has been a steady increase in the amount of CO<sub>2</sub> in the atmosphere, which can lead to global warming due to the greenhouse effect. International climate change experts in 2018 indicated that with the current rate of CO<sub>2</sub> emissions in the next 10 years, the world will warm by 1,5°C, causing melting glaciers and rising sea levels.

**Problem Statement.** CO<sub>2</sub> can be used to produce a large number of organic compounds. The formation of these compounds in large quantities depends on the method of CO<sub>2</sub> processing. Before them include such methods as biological, thermal conversion, photochemical, plasma. Most of these methods use catalysts. One of the plasma methods is the electrocatalytic method using a barrier discharge.

**Purpose.** Determination of the basic physicochemical laws of the process of electrocatalytic conversion of CO<sub>2</sub> into organic compounds, namely into methanol and formaldehyde using two arresters — a source of nonthermal plasma.

**Materials and Methods.** Studies on the electron-catalytic conversion of CO<sub>2</sub> to methanol and formaldehyde were performed in a laboratory installation, which included two sources of low-temperature plasma arresters, one of which contains a heterogeneous catalyst. Water vapor was used as a source of hydrogen.

**Results.** Two samples of catalysts at different temperatures of the reaction zone and barrier discharge voltages were studied. The dependences of methanol and formaldehyde formation at different modes of operation of installation were obtained. The dependences of energy consumption in the production of methanol and formaldehyde from CO<sub>2</sub> are obtained.

**Conclusions.** The use of the electrocatalytic method allows the processing of CO<sub>2</sub> into various organic compounds, which can then be further used either as a raw material for various chemical processes, or as a fuel. This processing allows to reduce emissions into the environment and increase the range of products of the chemical industry.

**Key words:** carbon dioxide, electrocatalytic method, barrier discharge, formaldehyde, methanol.

Citation: Kamensky, A. O., Olshevsky, O. P., Pochynok, V. V., and Viazovyk, V. M. Electrocatalytic Processing of Carbon Dioxide into Methanol and Formaldehyde. *Sci. innov.* 2021. V. 17, no. 5. P. 73–82. <https://doi.org/10.15407/scine17.05.073>

The history of civilization is closely linked to the combustion of fuel, from the use of fire to advanced electricity and heat systems. The main chemical element of solid fossil fuels involved in the combustion process is carbon. The combustion of fossil fuels, such as coal, gas and oil, and many others (wood, straw) leads to the formation of carbon dioxide ( $\text{CO}_2$ ) as a result of integral reaction of carbon with oxygen.

Carbon dioxide in the Earth's atmosphere is a small component of the modern Earth's atmosphere, the concentration of carbon dioxide in dry air is 0.02–0.04% (250–450 ppm). Since the middle of the 19<sup>th</sup> century, there has been a steady increase in the amount of this gas in the atmosphere. As of the beginning of July 2019, its concentration in the air was about 410 ppm [1], while at the end of July 2020, it reached about 415 ppm and continues to show upward dynamics. In Ukraine that ranks 27<sup>th</sup> out of 213 in terms of  $\text{CO}_2$  emissions, produced about 225 million tons at the end of July 2020 [2]. The three leaders are China (10,065 million tons), the United States (5,416 million tons), and India (2,654 million tons). In total, in 2108, more than 36,573 million tons of  $\text{CO}_2$  were released into the atmosphere as a result of human activities [2].

Emissions of such large amounts of  $\text{CO}_2$  may cause global warming as a result of the greenhouse effect. In the special report on global warming of the Intergovernmental Panel on Climate Change (IPCC) in Incheon, Republic of Korea, on October 6, 2018, it is stated that with the current emission rates between 2030 and 2050, the world will get warmer by 1.5 °C, which will lead to significant climate changes. The Secretary-General of the World Meteorological Organization, Professor Petteri Taalasa, has pointed out that the mean global temperature is already more than 1 °C higher than in the pre-industrial era. Arctic sea ice is declining and sea levels are rising. We suffer from more extreme weather conditions. Increasing the temperature for each fraction of a degree is important [3].

The main sources of carbon dioxide emissions are the production, transportation, processing, and consumption of fossil fuels (86%), tropical deforestation and other biomass combustion (12%), as well as other sources (2%), such as cement production and carbon monoxide oxidation.

Therefore, it is necessary to create and to develop a global low-carbon economy based on low-carbon energy sources that have minimal greenhouse gas emissions and emissions into the biosphere. One of the distinctive features of this economy is the creation and mass introduction into the industry of technologies for the utilization of  $\text{CO}_2$  that is formed in the course of the production of thermal energy, in metallurgy, and in other industries. One of the most promising areas is the conversion of  $\text{CO}_2$  into fuel or other organic compounds, i.e. conversion of emitted  $\text{CO}_2$  from waste into raw materials. This solves not only the problem of climate change, but also the problem of dependence on fossil fuels.

Fig. 1 shows compounds that may be obtained from  $\text{CO}_2$ .

Various methods can be used to obtain various  $\text{CO}_2$  compounds:

- ♦ normal thermal conversion of  $\text{CO}_2$ . It is divided into  $\text{CO}_2$  cleavage and  $\text{CO}_2$  conversion in combination with a co-reagent,  $\text{CH}_4$ ,  $\text{H}_2$  or  $\text{H}_2\text{O}$ . The first method is realizable thermodynamically and energetically only at very high temperature. At a temperature below 2000 K, the equilibrium production of CO and  $\text{O}_2$  is less than 1%, whereas at 3000–3500 K, it reaches 45–80%. Therefore, it is little used.

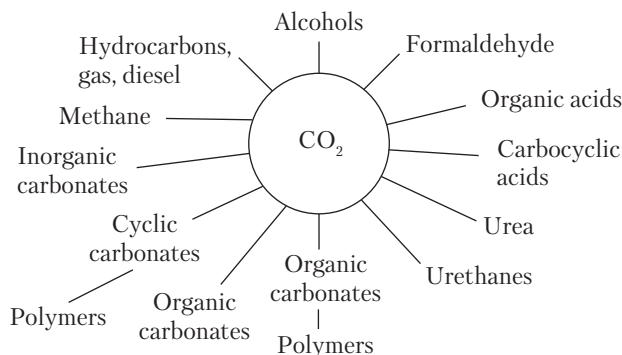
The second method allows obtaining various organic compounds. The most common are the processes of  $\text{CO}_2$  conversion in the presence of either  $\text{CH}_4$  or  $\text{H}_2$ . The process in the presence of methane (dry reforming) is a conventional reforming  $\text{CO}_2$  into synthesis gas (a mix of  $\text{H}_2$  and CO and  $\text{H}_2\text{O}$ ) The combination of carbon dioxide and hydrogen (hydrogenation) can be used to produce alcohols. Selective hydrogenation of  $\text{CO}_2$  into methanol is a process that currently used on an in-

dustrial scale. Most catalysts for hydrogenation of  $\text{CO}_2$  contain Cu and Zn as main components together with various modifiers (Zr, Ga, Si, Al, B, Cr, Ce, V, Ti, etc.). However, these processes take place at a temperature around 513–430 K and a pressure higher than 3 MPa [3];

- ◆  $\text{CO} + \text{H}_2\text{O}$ : artificial photosynthesis. This is an attempt to reproduce the natural process of photosynthesis. Under the influence of electromagnetic radiation of the visible spectrum, water and carbon dioxide are converted into molecular oxygen and glucose. Sometimes, the artificial photosynthesis includes the separation of water into hydrogen and oxygen under the influence of solar energy. This process requires as high temperature as in the case of cleavage of pure  $\text{CO}_2$ , but has a slightly lower energy efficiency. The highest energy efficiency (40%) is achieved at 3300 K, with 60% conversion. At a higher temperature, the energy efficiency decreases to 25% at 5000 K, for complete conversion;
- ◆ Solar thermochemical conversion. This is a method of using solar energy for thermochemical conversion. This method does not require additional energy sources and does not have a negative impact on the environment. There are the two forms of direct conversion of solar energy: thermal conversion may be used after the absorption of sunlight in the form of thermal energy, and the quantum conversion is the direct absorption of light.

The main advantage of  $\text{CO}_2$  solar thermochemical conversion, obviously, is the direct use of solar energy. The solar technologies that are currently commercially used for large-scale electricity generation may be associated with high-temperature thermochemical reactors that have the capacity to achieve a high efficiency of converting solar energy into fuel and, consequently, the capacity for large-scale solar production at competitive costs.

Although significant advances have been made in  $\text{CO}_2$  solar thermochemical conversion technologies with the use of metal oxides, the lack of fun-



**Fig. 1.** Compounds that may be obtained from  $\text{CO}_2$  [4]

damental studies of the behavior of metal oxides in the high-temperature conditions in these cycles complicates the development of materials. The main problems related to oxygen transfer, surface chemistry, structural changes in comparison with redox reactions, methods of material synthesis, the influence of thermochemical cyclic effects on material have to be solved;

- ◆ Photochemical conversion. Photochemical conversion differs from solar thermochemistry as the former uses photon energy in chemical reactions, whereas the latter uses absorbed thermal energy to overcome activation barriers and affects chemical equilibrium. Although many studies of photochemical conversion suggest the use of sunlight as a source of a certain spectrum of light, such as ultraviolet radiation. The efficiency of the process is influenced by several factors, such as catalyst dosage, reagent ratio, reaction temperature, time, system pressure, pH, light intensity, and wavelength. Like in the case of the electrochemical method, a wide range of reduction products, including carbon monoxide, formic acid, formaldehyde, methanol, methane, ethylene, ethane and ethanol can be obtained. However, nevertheless, the existing methods are insufficient today, and additional efforts are needed to increase the efficiency of converting solar energy into fuel. The existing photocatalytic reactors are often inefficient, which limits their practical application. This technology requires developing photocatalysts that are sen-

sitive to visible light and play an important role in CO<sub>2</sub> processing;

- ◆ Non-chemical conversion. This alternative way of producing biofuels is the conversion of solar energy into chemical energy (natural photosynthesis). Biological conversion of CO<sub>2</sub> for the production of chemicals or fuels is an attractive way. However, the use of first-generation biofuels has caused much controversy, mainly because of their competition with agriculture for the use of arable land for food production, which affects world food markets and food security.

The use of microalgae may satisfy the conditions for technically and economically viable biofuel production. In particular, viable biofuel production shall be competitive or cheaper than petroleum fuel, require little or no additional land use, minimal water use, and shall lead to improving air quality.

It should be emphasized, however, that a significant disadvantage of all biochemical methods is the large share of cultivation costs. Among other things, the collection of algal biomass has the largest share in energy consumption, and there are currently no standard collection methods. Thus, currently algae biomass is not suitable for cultivation exclusively for bioenergy applications, it shall be integrated with the production of other value-added products, such as pharmaceuticals, cosmetics, and food.

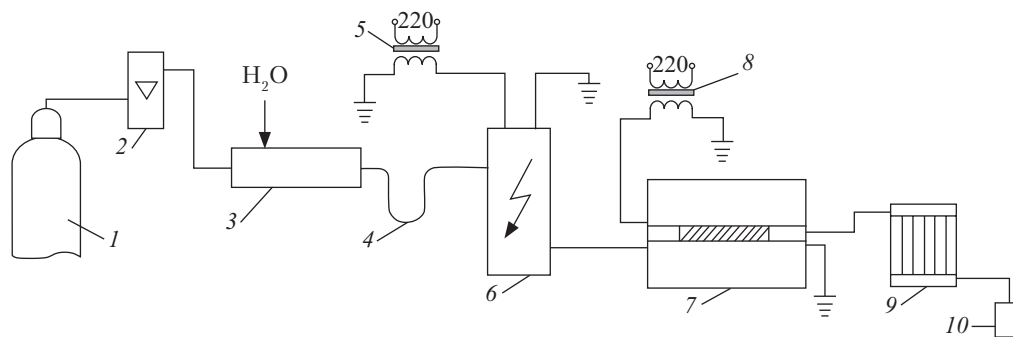
- ◆ Electrochemical conversion. This is a method in which electrical energy is supplied to create a potential between the two electrodes of the cell, which allows converting CO<sub>2</sub> into chemical compounds. Electrochemical reduction of CO<sub>2</sub> may take place in two-, four-, six- and more electron pathways due to reduction in gas and liquid phases at different cell and electrode configurations. This method has some problems, such as high overvoltage; low solubility of CO<sub>2</sub> in aqueous solutions; formation of mixes that require expensive separation; growth and catalytic deactivation of electrodes by impurities, transition products, and by-products; instability of the electrode material; kinetic barriers

leading to a low efficiency; and electrode / reactor design and system unadjusted for practical use. And the biggest problem is the low performance of electrocatalysts because of low activity, low selectivity and, most importantly, instability.

- ◆ Plasma technology for CO<sub>2</sub> conversion. This is a method that uses different types of plasma. Among the largest plasma sources used for CO<sub>2</sub> conversion there are the dielectric barrier discharge (also called “quiet” because of the “slow” electrons), microwave and sliding arc, glow, corona, spark, and pulse discharges. Both high-temperature plasma (temperature range from 4000 K to 20,000 K) and low-temperature plasma may be used.

High-temperature plasma has numerous advantages over the conventional technologies due to its properties, including high temperature, high intensity of non-ionizing radiation, and high energy density. The heat source is directional, with sharp limits and steep temperature gradients that may be controlled regardless of chemical composition. On the other hand, the nature of this plasma makes it unsuitable for efficient CO<sub>2</sub> conversion. As a result, the maximum energy efficiency is limited to 47% in contrast to low-temperature plasma, where the efficiency in laboratory tests reaches 90%.

Low-temperature plasma is created by applying a potential difference between two parallel electrodes that are inserted into a reactor filled with gas (or they form the reactor walls). This potential difference creates an electric field that causes a so-called gas breakdown, i.e. gas “dissociates” (to some extent) into positive ions and electrons. When these electrons collide with gas molecules, it can lead to ionization, excitation, and dissociation. This makes the plasma self-sustaining. Excitation collisions create excited molecules that dissociate to the ground state (or other lower level), thus emitting light, which is one of the characteristic features of plasma. Finally, dissociative collisions create radicals that may easily form new compounds, and this underlies the application of non-thermal plasma gas conversion.



**Fig. 2.** Laboratory plant for electron catalytic processing of  $\text{CO}_2$  into methanol and formaldehyde: 1 – cylinder with  $\text{CO}_2$ ; 2 – rotameter; 3 – humidifier; 4 – condensate drain; 5 – power supply source 1; 6 – gas discharger 1; 7 – tubular furnace with catalyst and gas discharger 2; 8 – power supply source 2; 9 – refrigerator; 10 – sampler

In this research, we will focus on the discharge of dielectric barrier or barrier discharge.

Barrier discharge is a discharge that occurs in a gas under the action of high voltage applied to the electrodes, when at least one of the electrodes is covered with a dielectric. The presence of a dielectric reduces the rate of electron exit from the surface of the electrode (by overcoming the dielectric resistance), weakens kinetic energy of electrons impacting gas molecules exposed to discharge, and prevents the formation of an avalanche of electrons that lead to breakdown and transformation of barrier discharge into arc. Thus, there is a uniform bulk distribution of the discharge, which differs favorably from all other types of low-temperature plasma.

This type of discharge is characterized, on the one hand, by a relatively high average energy of electrons released in short-lived, low-intensity sparks – micro-discharges [5, 6] and, on the other hand, by a low gas temperature, in most cases 10–20 degrees above ambient temperature. At the same time, these micro-discharges are formed by energy electrons, as they have a fairly high temperature of electrons (1–5 eV), which enables activating inert molecules (e.g.  $\text{CO}_2$ ) and leads to the formation of a cascade of reaction compounds (free radicals, excited atoms, ions, and molecules). All this allows a large number of chemical reactions to run at a low temperature.

Catalysts can be combined with barrier discharge plasma to generate a hybrid plasma catalytic

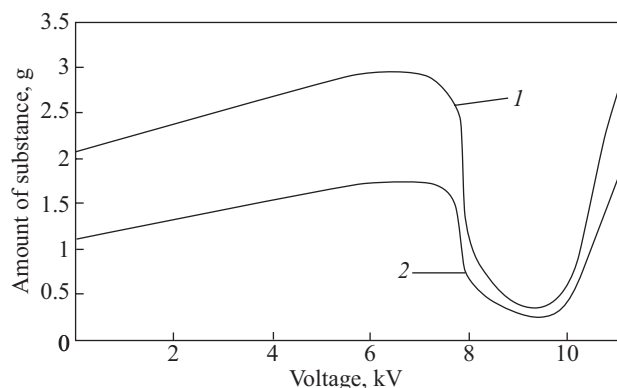
process, thereby increasing the degree of  $\text{CO}_2$  conversion, yield, and selectivity of the target product and energy efficiency of the process.

Plasma catalysis is a new field of plasma application at the intersection of various disciplines, including physical chemistry, materials science, nanotechnology, catalysis, plasma physics, and plasma chemistry. In other words, its purpose is to enhance plasma reactions by adding a catalyst to the reaction cycle and vice versa. Theoretically, plasma and catalysis combine the best of both directions. The inert molecules are activated by plasma under mild conditions, and subsequently the activated particles are selectively recombined on the surface of the catalyst to obtain the desired conversion products for selective production of the desired liquid products.

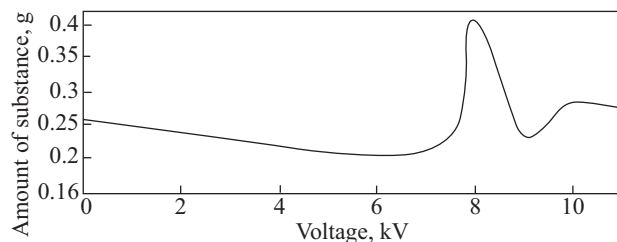
Therefore, the purpose of this research is to determine the basic physicochemical laws of the process of electron-catalytic conversion of  $\text{CO}_2$  into organic compounds, namely into methanol and formaldehyde, with the use of two dischargers as a source of low-temperature plasma. Water vapor is used as a source of hydrogen.

The electron-catalytic conversion of carbon dioxide into methanol and formaldehyde have been studied with the use of plant (Fig. 2) that consists of a gaseous mix pre-treatment unit, a system of dischargers as sources of barrier discharge, and a refrigerator.

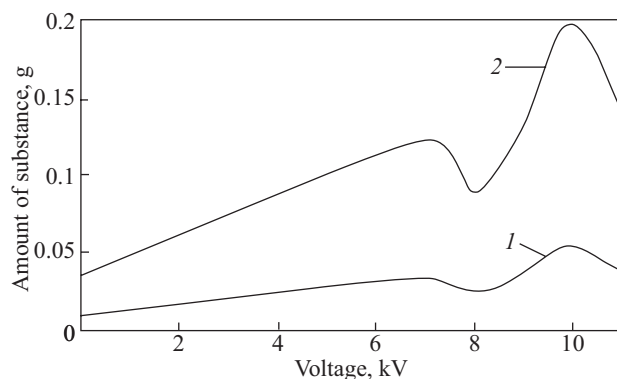
Gaseous  $\text{CO}_2$  from the cylinder with a flow rate of  $1 \text{ dm}^3/\text{min}$  is fed to the humidifier, where at a



**Fig. 3.** Dependence of carbon dioxide conversion into organic compounds on catalyst KT1, at 250 °C: 1 – formaldehyde; 2 – methanol



**Fig. 4.** The dependence of carbon dioxide conversion into methanol on catalyst KT1, at 350 °C (formaldehyde is not formed)

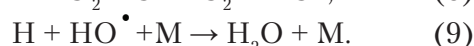
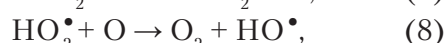
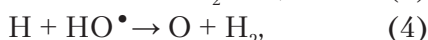
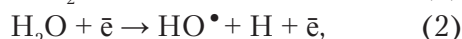


**Fig. 5.** The dependence of carbon dioxide conversion into organic compounds on catalyst KT2, at 250 °C: 1 – formaldehyde; 2 – methanol

temperature of 70 °C it is saturated with water vapor. Humidified carbon dioxide is supplied to the primary discharger, where carbon dioxide is activated and water vapor dissociates with the formation of hydrogen and oxygen-containing radicals HO and HO<sub>2</sub>, which play a significant role

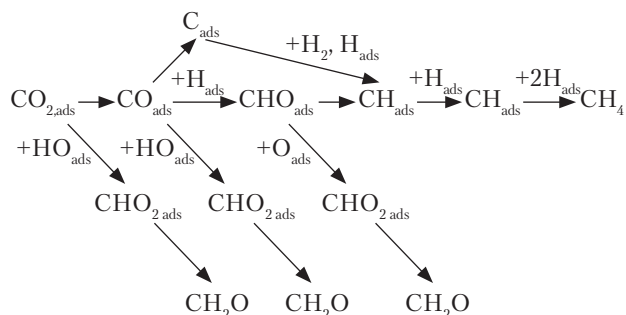
in the conversion of carbon dioxide. *Siemens* ozonator made of quartz glass at a wall thickness of 2 mm is used as a discharger. Voltage in the discharger is 10 kV. The time of stay of the gas mix in the discharge zone is 0.3 s.

The chemistry of the process in the primary discharger may be represented by the following reactions [7]



The gas mix containing CO, hydrogen, atomic oxygen, and oxygen-containing radicals HO and HO<sub>2</sub> after the primary discharger is fed to the secondary discharger that is located in a tubular furnace and kept at a temperature of 250–450 °C. The secondary discharger is a quartz tube with a wall thickness of 2 mm, which houses high-voltage and ground electrodes. The catalyst is located between these electrodes.

The chemistry of the process in the secondary discharger may be represented by the example of formaldehyde, with the use of the following scheme:



The gas containing organic compounds in addition to the previously mentioned substances, namely formaldehyde and methanol, is fed to the refrigerator and to the sampler (a glass of Drexel with 50 cm<sup>3</sup> of distilled water).



The water-absorbed methanol and formaldehyde are analyzed on a UV-5800PC spectrophotometer in a scanning mode with a step of 0.5 nm.

Simultaneously with the experiment, the total electricity consumption for both dischargers is measured.

This research presents the results of the study of two catalysts samples. Let us denote them by KT1 and KT2.

These catalysts have the following composition:

KT1: ZnO – 41%, CuO – 43.7%, Al<sub>2</sub>O<sub>3</sub> – 8.3% (industrial catalyst SHIFTMAX 217).

KT2: Cr – 18%, Ni – 10%, Ti – 1%, Fe – 71%.

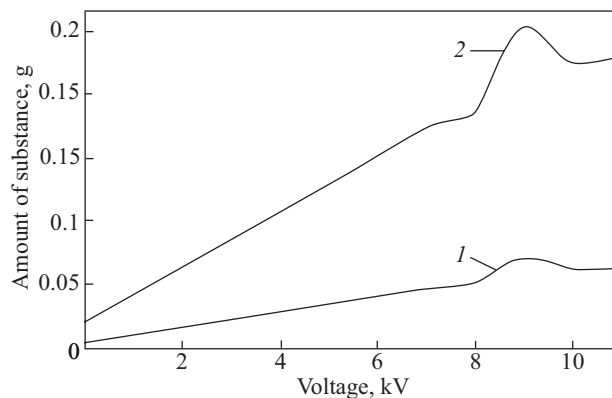
The study is carried out at a temperature of the primary discharger about 20 °C, a voltage of 10 kV; on the secondary discharger, the temperature varies within the range of 250–350 °C, the voltage ranges from 7 to 11 kV. The research results are presented in Figs 3–6.

As can be seen from Figs. 3–6, the formation of formaldehyde and methanol is influenced by various conditions. They include temperature and voltage at the secondary discharger and the catalyst composition.

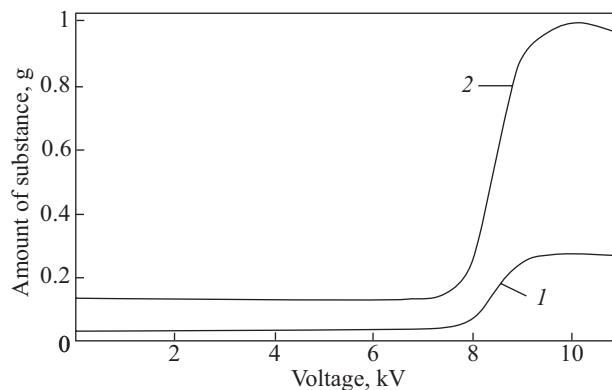
Let us consider the influence of each factor on the formation of formaldehyde and methanol from carbon dioxide.

**The catalyst composition.** The catalyst composition significantly affects the formation of formaldehyde and methanol, regardless of the raw material from which they are synthesized – whether a mix of CO<sub>2</sub> and hydrogen (used worldwide, both in classical thermal technologies and in more advanced ones mentioned earlier) or the mix used in the described studies (CO<sub>2</sub> and water vapor). Therefore, one of the tasks for increasing the yield of formaldehyde and methanol is the selection of the catalyst composition. In [8–10], the generalized results of studying the best catalysts mentioned in the scholarly research literature have been considered.

Let us consider KT1. According to the literature, most catalysts contain copper oxide for the synthesis of methanol from CO<sub>2</sub>. Therefore, a copper-containing catalyst is used. Addition of ZnO and



**Fig. 6.** The dependence of carbon dioxide conversion into organic compounds on catalyst KT2, at 300 °C: 1 – formaldehyde; 2 – methanol



**Fig. 7.** The dependence of carbon dioxide conversion into organic compounds on catalyst KT2, at 350 °C: 1 – formaldehyde; 2 – methanol

Al<sub>2</sub>O<sub>3</sub> to copper oxide increases the yield of methanol and improves the overall properties of the catalyst. Since methanol is a preliminary product of the formation of formaldehyde, an increase in the formation of methanol leads to growing yield of formaldehyde, under appropriate conditions.

In the studies, SHIFTMAX 217 catalyst in a laboratory plant gives a fairly high yield of methanol at a relatively low temperature (250 °C) with a low CO<sub>2</sub> productivity, up to 3 g methanol. At the same temperature, the yield of formaldehyde is quite high. The yield may increase by extending the time of reaction mix stay on the catalyst.

However, research has shown that the catalyst that has worked for some time in the secondary discharger starts changing its color from black to

black-red. The appearance of red color indicates the reduction of copper oxide in the presence of hydrogen formed by reactions (2), (3), (5) under the action of a directed flow of electrons to copper. The appearance of copper reduces the formation of the target products and requires replacement of the catalyst. Therefore, attempts to use catalysts that do not contain copper oxide have been made.

KT2 catalyst is used for the electron catalytic intensification of the combustion process of gaseous fuel and the formation of formaldehyde and methanol in the electron catalytic incomplete oxidation of methane [11–13]. Quite high indicators of the studied processes have been reached with the use of this catalyst.

Figs. 5–6 show that the yield of formaldehyde and methanol on catalyst KT2 is less than that on catalyst KT1 and does not exceed 1 g for methanol and 0.25 g for formaldehyde. This catalyst has worked much longer and there have been no changes in it. In addition, on this catalyst, it is possible to synthesize formaldehyde and methanol at different temperature, which allows controlling the yield of formaldehyde and methanol.

*Process temperature.* The temperature in the second discharger ranges within 250–350 °C. While analyzing the yield of formaldehyde and methanol, we have seen that the formation of methanol increases as the temperature grows. Thus, the formation of methanol on catalyst KT2 increases from 0.2 g (at a temperature of 250 °C) up to 1 g (at 350 °C), while on catalyst KT1, as already

mentioned, the simultaneous synthesis of formaldehyde and methanol occurs only at a temperature of 250 °C. At higher temperature, the yield of methanol decreases, and formaldehyde is not synthesized.

At a temperature above 350 °C, neither formaldehyde nor methanol is formed.

*Voltage in the secondary discharger.* The effect of stress on the formation of formaldehyde and methanol is quite controversial. Figs. 3–4 show that in the case of catalyst KT1, the highest (maximum) yield at a temperature of 250 °C is observed at a voltage of about 7 kV. An increase in the temperature shifts this maximum to 8 kV. The second maximum wave is observed at a voltage of more than 10 kV. However, at a voltage higher than 10 kV, quartz requires thicker walls of the discharger, which increases the energy costs of maintaining the plasma.

KT2 catalyst has other maxima of formaldehyde and methanol formation. This catalyst is characterized by maxima of the formation of substances at a voltage of 9–10 kV, depending on the process temperature. There is no second maximum.

Such different dependences may be explained by the electrical conductivity of the catalyst. Since catalyst KT2 consists of a mix of metals and therefore has a fairly high electrical conductivity that allows it to show higher catalytic properties at a lower voltage. KT1 catalyst consists of metal oxides, some of which are even dielectrics. This reduces the electrical conductivity of the catalyst and, consequently, leads to a decrease in its catalytic activity.

The high electrical conductivity of catalyst KT2 also introduces additional requirements for the design features of the dischargers, namely for the design of the electrodes. These electrodes shall have a dielectric layer on both sets to prevent short circuits and to extend the service life of the equipment, while this is not necessary in the case of KT1 catalyst.

As mentioned earlier, in addition to the yield of the compounds under study, the total electricity consumption for both dischargers has been deter-

**Table. Total Energy Consumption for Both Dischargers, W/dm<sup>3</sup> CO<sub>2</sub>**

Temperature, °C	7	8	9	10	11
Catalyst KT1					
250	3.05	3.15	3.26	3.31	3.37
350	2.71	2.79	2.87	2.9	3.26
Catalyst KT2					
250	1.09	1.11	1.27	1.42	—
300	1.11	1.17	1.42	1.48	—
350	1.48	1.54	1.61	1.7	—



mined. The results of these measurements are presented in Table 1. For catalyst KT2, measurements at 11 kV are not performed.

As can be seen from Table 1, catalyst KT1 has a higher energy consumption than catalyst KT2. This is one more confirmation of the effect of electrical conductivity on the properties of the catalyst. However, having compared the energy costs for the formation of compounds, one can see that in the case of catalyst KT1, at higher power consumption, the yield of compounds is also higher, which reduces the cost of electricity per unit mass of compounds formed as compared with catalyst KT2 that has lower power consumption.

The current state of the environment no longer allows us to treat it thoughtlessly. A large amount of different substances is released into the environment. Carbon dioxide is one of them. Its emissions into the air have reached such critical values that many researchers start to take it seriously and to develop a variety of technologies for not only reducing the emissions into the air, but also for recycling those that have been discharged into the air. These are both the biological methods and the catalyst-based methods. The catalytic methods include both the classical thermal methods

that have been used for a long time and the new advanced methods with the use of plasma and a variety of radiation.

One such method is the electron catalytic processing of CO<sub>2</sub> into organic compounds such as formaldehyde and methanol. This research presents one of the options of this method, with the use of two dischargers as barrier discharge source. Water vapor is used as a source of hydrogen.

The test results of the two catalysts have been presented: KT1: ZnO—41%, CuO—43.7%, Al<sub>2</sub>O<sub>3</sub>—8.3% (industrial catalyst SHIFTMAX 217); KT2: Cr—18%, Ni—10%, Ti—1%, Fe—71%.

Catalyst KT1 has a higher yield of formaldehyde and methanol and a low energy consumption per unit mass of compounds. However, because of the reduction of copper oxide to copper under the action of hydrogen that is formed in the discharge zone, it cannot be used for a long time and needs frequent replacement.

Catalyst KT2 has a lower yield of formaldehyde and methanol and a higher energy consumption per unit mass of compounds. However, it may be used for a longer time and therefore can be the basis for further development of catalysts in the catalytic conversion of CO<sub>2</sub> into organic compounds.

## REFERENCES

1. CO<sub>2</sub>, Earth is live!! Daily CO<sub>2</sub>, URL: <https://www.co2.earth/daily-co2> (Last accessed: 28.07.2020).
2. Global Carbon Atlas. CO<sub>2</sub> Emissions. URL: <http://www.globalcarbonatlas.org/ru/CO2-emissions> (Last accessed: 28.07.2020).
3. Masson-Delmotte, V., Zhai, P., Pörtner, H.-O., Roberts, D., Skea, J., ..., Waterfield, T., Press release: Special Report on Global Warming of 1.5 °C. *Incheon, Republic of Korea: Intergovernmental Panel on Climate Change (IPCC). 7 October 2018*. Retrieved 7 October 2018. 32 p. URL: [https://www.ipcc.ch/site/assets/uploads/2018/10/SR15\\_SPM\\_version\\_stand\\_alone\\_LR.pdf](https://www.ipcc.ch/site/assets/uploads/2018/10/SR15_SPM_version_stand_alone_LR.pdf) (Last accessed: 28.07.2020)
4. Payal, B. (2014). Joshi Carbon dioxide utilization: a comprehensive review. *Int. J. Chem. Sci.*, 12(4), 1208–1220.
5. Samoilovich, V. G., Gibalov, V. I., Kozlov, K. V. (1989). *Physical chemistry of a barrier discharge*. Moscow [in Russian]
6. Ulrich Kogelschatz. (2003). Dielectric-barrier Discharges: Their History, Discharge Physics, and Industrial Applications. *Plasma Chemistry and Plasma Processing*, 23(1), 1–46. <https://doi.org/10.1023/A:1022470901385>
7. Ma, X., Li, S., Ronda-Lloret, M., Chaudhary, R., Lin, L., ..., Hessel, V. (2019). Plasma Assisted Catalytic Conversion of CO<sub>2</sub> and H<sub>2</sub>O Over Ni/Al<sub>2</sub>O<sub>3</sub> in DBD Reactor. *Plasma Chemistry and Plasma Processing*, 39(1), 109–124. <https://doi.org/10.1007/s11090-018-9931-1>
8. Hasliza Bahruji, Michael J. Bowker, Graham J. Hutchings, Nikolaos Dimitratos, Peter P. Wells, ..., Georgi M. Lalev. (2016). Pd/ZnO catalysts for direct CO<sub>2</sub> to methanol. *Journal of catalysis*, 343, 133–146.
9. Mun-Sing Fan, Ahmad Zuhairi Abdullah Subhash. (2009). Catalytic technology for carbon dioxide reforming of methane to synthesis gas. *ChemCatChem.*, 1, 192–208. <https://doi.org/10.1002/cctc.200900025>.
10. Mehrnoush Khavarian, Siang-Piao Chai, Abdul Rahman Mohamed. (2013). Carbon dioxide over carbon-based nanocatalyst. *Journal of nanoscience and nanotechnology*, 13, 4825–4837. <https://doi.org/10.1166/jnn.2013.7569>.

11. Stolyarenko, G. S., Viazovyk, V. M., Vodyanik, O. V., Frolov, K. I. (2010). Electrocatalytic intensification of gaseous fuel combustion. *Bulletin of the National Technical University of Kharkiv Polytechnic Institute*, 13, 112–120 [in Ukrainian].
12. Stolyarenko, H., Martsynyshyn, U., Viazovik, V., Vodianik, O., Honchar, S. (2008). The alternative burning of hydrocarbon. *Contributed Papers International Workshop "Nonequilibrium Processes In Combustion And Plasma Based Technologies"*, 84–89.
13. Viazovyk, V. (2017). Direct oxidation of methane to formaldehyde. *Current research in the modern world. Collection of scientific works*, 11(31), 10, 5–11 [in Ukrainian].

Received 08.10.2020

Revised 18.02.2021

Accepted 09.04.2021

А.О. Каменський (<https://orcid.org/0000-0001-7440-2860>),  
О.П. Ольшевський (<https://orcid.org/0000-0001-9689-5360>),  
В.В. Починюк (<https://orcid.org/0000-0002-7236-7130>),  
В.М. Вязовик (<https://orcid.org/0000-0001-7113-9892>)  
Черкаський державний технологічний університет,  
бульв. Шевченка, 460, Черкаси, 18006, Україна,  
+380 472 51 3660, htv@chdtu.edu.ua

#### ЕЛЕКТРОННО-КАТАЛІТИЧНА ПЕРЕРОБКА ВУГЛЕКИСЛОГО ГАЗУ В МЕТАНОЛ ТА ФОРМАЛЬДЕГІД

**Вступ.** Починаючи з середини ХІХ століття спостерігається стійке зростання кількості  $\text{CO}_2$  в атмосфері, яке може призвести до глобального потепління, спричиненого парниковим ефектом. Міжнародні експерти зі зміни клімату в 2018 році зазначали, що при поточних темпах викидів  $\text{CO}_2$  в найближчі 10 років у світі температура підвищиться на  $1,5^\circ\text{C}$ , що призведе до танення льодовиків і підвищення рівня моря.

**Проблематика.** Оксид карбону може бути використано для отримання значної кількості органічних сполук, утворення яких залежить від методу його переробки. До останніх належать такі методи як біологічні, термічна конверсія, фотохімічні, плазмові. Більшість з них потребують застосування каталізаторів. Одним із плазмових методів є електронно-каталітичний метод з використанням бар'єрного розряду.

**Мета.** Визначення основних фізико-хімічних закономірностей процесу електронно-каталітичного перетворення  $\text{CO}_2$  в органічні сполуки, а саме в метанол та формальдегід, з використанням двох розрядників — джерела низькотемпературної плазми.

**Матеріали й методи.** Дослідження електронно-каталітичного перетворення  $\text{CO}_2$  в метанол та формальдегід здійснювали на лабораторній установці, до складу якої входили два джерела низькотемпературної плазми — розрядників, в одному з яких знаходиться гетерогенний каталізатор. Як джерело водню використовувалися пари води.

**Результати.** Досліджено два зразки каталізаторів за різних температур реакційної зони і напруг бар'єрного розряду. Отримано залежності утворення метанолу та формальдегіду при різних режимах роботи установки. Визначено залежності енергетичних витрат при отриманні метанолу та формальдегіду з  $\text{CO}_2$ .

**Висновки.** Використання електронно-каталітичного методу дозволяє переробляти  $\text{CO}_2$  в різноманітні органічні сполуки, які в подальшому можуть бути використані як сировина для різноманітних хімічних процесів або як паливо. Ця переробка дозволяє зменшити викиди  $\text{CO}_2$  в навколишнє середовище та підвищити асортимент продукції хімічної промисловості.

*Ключові слова:* діоксид вуглецю, електроннокаталітичний метод, бар'єрний розряд, формальдегід, метанол.