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METHANE TRANSFORMATIONS IN BARRIER DISCHARGE

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A b s t r a c t. The work resumes the preliminary studies on the possibility of obtaining C_2 hydrocarbons from methane in a barrier discharge stabilised with a dielectric barrier.
The process of methane conversion was carried out in a flow-through plasma reactor made of quartz. The design of the reactor enabled to carry out the process at various temperatures and with various types of solid packing in the discharge gap. The kinetic characteristics of methane decomposition were determined without packing and with several packing materials: granular quartz, silica gel, iron deposited on silica gel, or $BaTiO_3$ ceramics.
It has been shown that the kind of packing can affect the methane transformations. Under the conditions applied, i.e. at temperatures below 300 ^{0}C, ethane was the main product of reactions where the initial mixture was methane + argon or methane + argon + carbon dioxide.

K e y w o r d s: dielectric-barrier discharges, methane conversion.

INTRODUCTION

The interest in conversion of methane, which is the main component of natural gas, arises from the will of its more efficient utilisation and from the fact that it is a greenhouse gas, which should not be released to the atmosphere. The real value of the natural gas accompanying crude oil is so small, as compared with the value of the oil itself, that it is usually burned near the bore hole (hence transformed into CO_2 which is also a greenhouse gas), or sometimes forced again into the oil deposit. Such procedures are usually due to the fact that most of the world oil and gas resources are very distant from the potential users and the cost of the gas transport exceeds by several times the cost of transport of crude oil. Therefore it seems advisable to convert methane, preferably at the site of its release, into compounds that are more attractive and/or easier to transport. Irrespective of the works on improvement of the traditional (chemical and high-temperature plasmatic) methods of methane conversion much research is being done on the application of low temperature plasma [1-7].

The aim of this work was to study the yield of the process of methane conversion into other hydrocarbons by means of the barrier (silent) discharge stabilised with a dielectric barrier. In general opinion the active particles such as electrons, ions, or free radicals produced in such a type of electric discharge in gas are carrying an energy sufficient for the transformation of a chemically stable methane molecule. On the other hand, contrary to the traditional processes using the high-temperature plasma and working at temperatures of the order of 10 kK, the low-temperature method enables to save considerable amounts of energy.

EXPERIMENTAL

1. APPARATUS

A diagram of the experimental setup is shown in Fig. 1. The main part of the experimental setup is a cylindrical quartz reactor (see Fig. 2) supplied with two concentric electrodes: a high voltage inner electrode and a grounded outer electrode. Electric power (18 kV, 50 Hz) is supplied to the reactor from a supply system. The design of the reactor enables to apply various process temperatures and various kinds of packing materials being introduced into the discharge gap. The width of the discharge gap is 3 mm.

The reactor is mounted in a tubular furnace that enables to maintain constant temperature in the reaction space. A system of control valves and flow meters enables to introduce to the reactor, from steel cylinders, CH_4, CO_2, Ar or mixtures of these gases of required composition and flow rate.

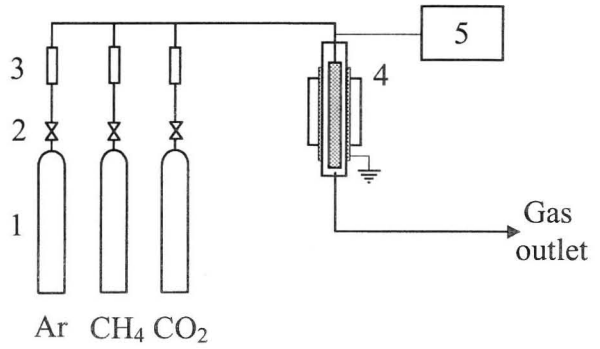

Fig. 1. Experimental setup: 1 - compressed gas cylinders, 2 – control valves, 3 – flow meters, 4 – reactor (electrically heated), 5 – high voltage power supply.

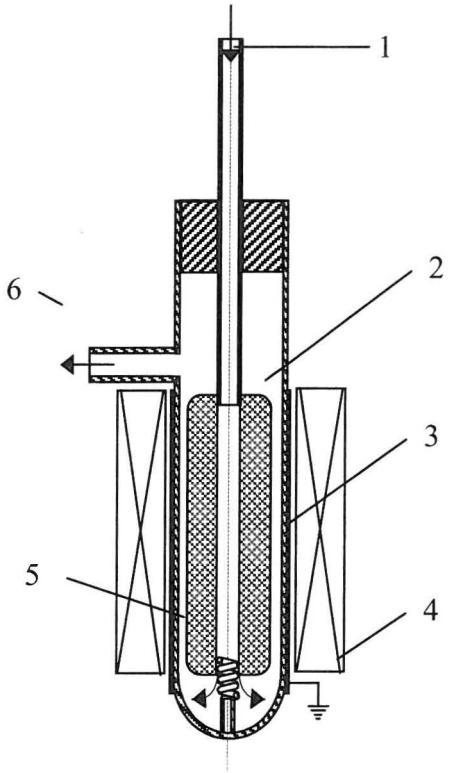

Fig. 2. Plasma reactor: 1 – connector pipe of the gas inlet, 2 – high voltage electrode, 3 – grounded electrode, 4 – electric furnace, 5 – discharge gap, 6 - connector pipe of the gas outlet.

2. PROCEDURES

The process of methane conversion was studied at temperatures up to 300°C using mixtures of methane with argon or methane with carbon dioxide and argon of various flow rates as the reaction mixtures. In some experiments the discharge gap was filled with a solid material of granulation Φ = 1-2 mm. The materials tested were: quartz, silica gel, silica gel coated with a layer of Fe (3% by wt.) deposited by impregnation, and $BaTiO_3$ ceramics.

The following procedure was applied:

- Gas mixture of appropriate composition and flow rate was let to flow through the reactor.

- Electrical heating of the reactor was switched on to obtain the required process temperature.
- After the required reactor temperature had been attained, high voltage (18 kV) was applied to the reactor.
- The composition of the gas mixture flowing out of the reactor was determined by means of a gas chromatograph Agilent 6890N fitted with a thermoconductometric detector and column packed with Carbopack B or, alternatively, gas chromatograph Chrompack CP 9002 fitted with a flame ionisation detector and column packed with Poropack Q.
- The results of the chromatographic analyses were used for determining the kinetic characteristics and the material balance of the process.

RESULTS AND DISCUSSION

Figure 3 shows the relationship between the overall methane conversion x_{CH4} versus the percentage of methane in the starting mixtures with argon.

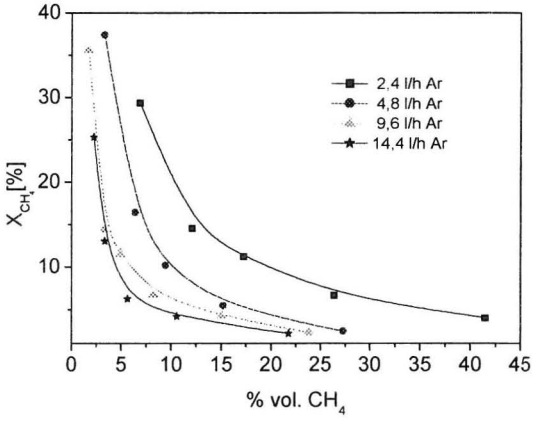

Fig. 3. Effect of methane content in the starting mixtures with argon on overall methane conversion without packing. The individual curves correspond to different argon flow rates. (reactor temperature ca. 45 ^{0}C).

As can be seen on the graphs in Fig. 3, the overall methane conversion decreases with increasing CH_4 concentration and increasing gas flow rate. Figure 4, based on the same experimental data, shows the relation between overall methane conversion and residence time t of reagents in the reactor.

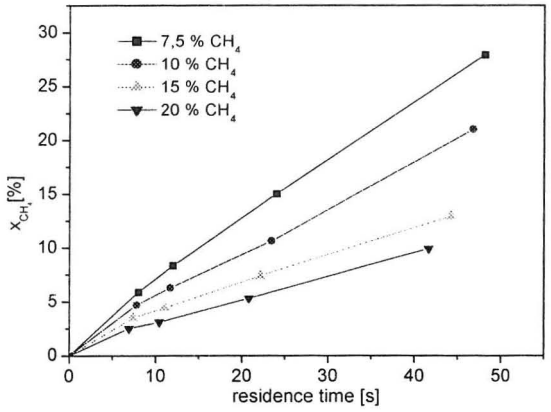

Fig. 4. Effect of residence time and methane concentration in starting mixtures with argon on the overall methane conversion without packing; temperature ca. 45°C.

The effect of flow rate of the methane mixture with argon (CH_4 : Ar = 1 : 2) and of the reactor temperature on overall methane conversion is shown in Fig. 5.

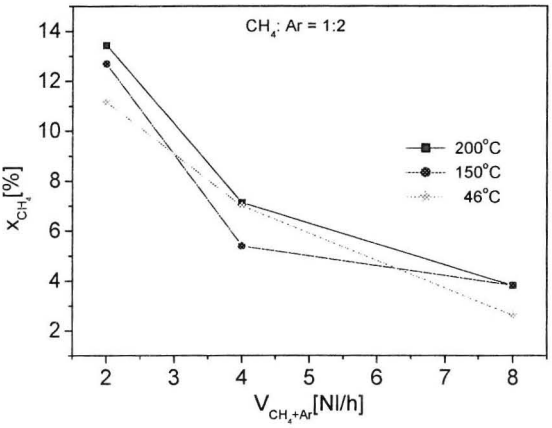

Fig. 5. Effect of flow rate V_{CH4+Ar} of methane mixture with argon (CH_4 : Ar = 1 : 2) and temperature on the overall methane conversion.

The graphs presented in Fig. 5 show that the increase of reactor temperature to 200 ^{0}C results in only a small increase of methane conversion degree, of the order of 1-2 %.

Figure 6 shows a histogram of the overall methane conversion obtained in the reactor without packing and with several packing materials.

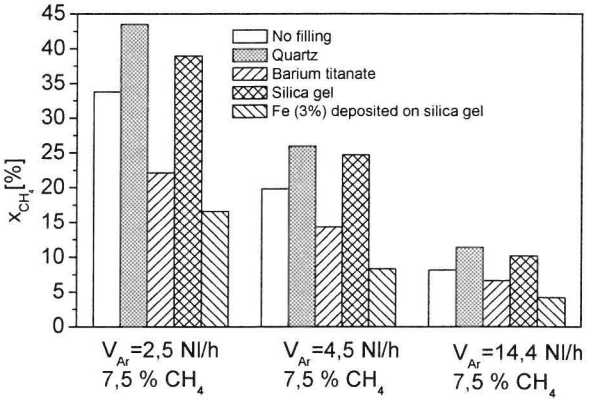

Fig. 6. Effect of packing materials and of flow rate of methane + argon mixture (7.5 % CH_4) on methane conversion. No electrical heating applied.

Granular quartz-glass and silica gel packing exhibited a favourable effect on the methane conversion. In the case of barium titanate and of Fe deposited on silica gel the degree of methane conversion was lower than that obtained without packing. The observed sequence of C_2H_6 concentrations in the product gas mixture was similar to that of the overall methane conversion obtained with various packing materials (see Table 1).

Table 1. Overall methane conversion and the methane conversion to ethane as determined for various packing materials. No electric heating applied; V_{Ar} = 2.5 Nl/h, 7.5% CH_4

Packing	*Overall CH_4 conversion [%]*	*CH_4 conversion to C_2H_6 [%]*
No filling	*33.8*	*8.4*
Quartz	*43.5*	*9.2*
Barium titanate	*22.1*	-
Silica gel	*38.9*	*9.2*
Fe deposited on silica gel	*16.6*	*2.85*

The effect of CO_2 addition to the starting gas mixture on the methane conversion and on the composition of the product gas mixture was studied using a filling of Fe deposited on silica gel. It seemed interesting to check if iron can have a catalytic effect, like that observed in the Fischer-Tropsch reactions. For the sake of comparison a series of experiments was performed under identical conditions

with no dielectric filling in the reactor. Figures 7 and 8 show the results of experiments performed with an empty and a filled reactor, respectively.

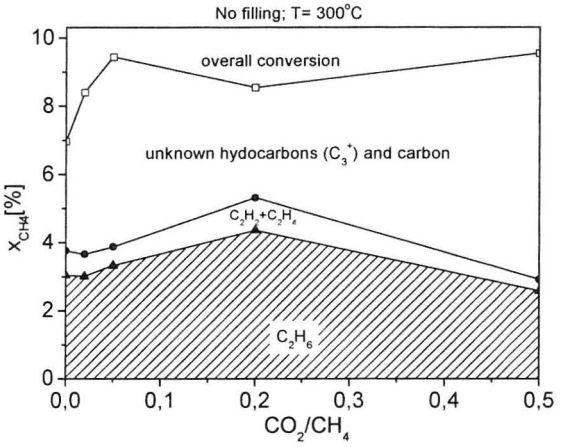

Fig. 7. Effect of the CO_2/CH_4 ratio in mixtures with argon on the overall methane conversion (- □ -) and the methane conversion to C_2H_6 (- ▲ -) and to C_2 hydrocarbons (- ● -). The fields between the curves represent the shares of the individual products. No filling; T = 300°C; V_{Ar} = 12.7 Nl/h; V_{CH4} = 1.2 Nl/h.

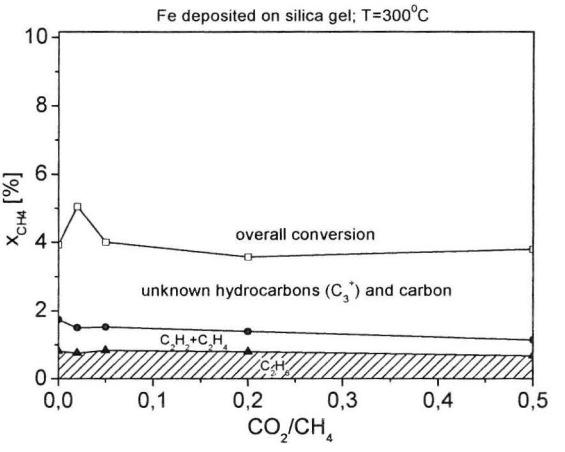

Fig. 8. Effect of the CO_2/CH_4 ratio in mixtures with argon on the overall methane conversion (- □ -) and the methane conversion to C_2H_6 (- ▲ -) and to C_2 hydrocarbons (- ● -). The fields between the curves represent the shares of the individual products. The reactor filled with silica gel grains coated with Fe (3% by wt.); T = 300 °C; V_{Ar} = 12.7 Nl/h; V_{CH4} = 1.2 Nl/h.

The data presented in Figs. 7 and 8 show that an addition of carbon dioxide to the mixtures of methane with argon results in a change of methane conversion and a change in composition of the product mixture. The extent of these changes depends on both the amount of CO_2 added and the presence or absence of the packing in the reactor. In the absence of packing the increase of CO_2 content results in an increase of the overall methane conversion from 7% to about 9% (at a ratio of $CO_2/CH_4 = 0.05$) and then it remains practically constant. The highest content of C_2 hydrocarbons in the product gas mixture is observed at the ratio of $CO_2/CH_4 = 0.2$. Further increase of CO_2 concentration in the reaction mixture reduces the amount of C_2 hydrocarbons produced, with simultaneous increase of the share of unidentified products.

In the case when the reactor is filled with the packing - iron deposited on silica gel - and the starting gas mixture contains no CO_2, the degree of methane conversion is about 4%. When CO_2 is added, the degree of methane conversion first increases, then it decreases to almost a constant value of about 4%. The maximum value of methane conversion is about 5% as observed at the ratio of $CO_2/CH_4 = 0.02$. This ratio is also featured by the highest contents of C_2 hydrocarbons in the gas product mixture. However, it should be pointed out, that the content of C_2 hydrocarbons observed does not exceed the values obtained without packing. It may be concluded that the packing of iron on silica carrier is not active catalyst for methane conversion and because of electrical conductivity of iron this kind of packing may influence the conditions and feature of the barrier discharge.

CONCLUSIONS

- The degree of methane conversion in the barrier discharge depends on the composition of the reaction mixture, its flow rate, and presence of packing in the discharge gap. In the mixtures containing argon the overall methane conversion decreases with increasing concentration of CH_4 and with increasing flow rate of the reaction mixture.
- Various types of dielectric filling differ in their effect on the degree of methane conversion.
- Under the reaction conditions applied ($T \leq 300^{\circ}C$) no clear effect of temperature on the methane conversion was observed.
- Addition of carbon dioxide to mixtures of methane with argon results in changes of both the overall methane conversion and composition of the product mixture. The nature of the changes depends on the presence of packing in the discharge gap.

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REFERENCES

1. **Czernichowski A.**, Pure & Appl. Chem., 66 (1994) 1301-1310.
2. **Czernichowski A., Nassar H., Ranaivosoloarimanana A., Fridman A. A., Simek M., Musiol K., Pawelec E., Dittrichowa L.**, Acta Phys. Polonica A, 89 (1996) 595-603.
3. **Mustaf-Yardmici O., Fridman A. A., Saveliev A. V., Kennedy L. A.**, 14th International Symposium on Plasma Chemistry, Praha, Czech Republic, 1999, pp. 997-1002.
4. **Liu C.-J., Mallinson R., Lobban L.**, Applied Catalysis A: General 178 (1999) 17-27.
5. **Okumoto M., Mizuno A.**, Catalysis Today 71 (2001) 211-217.
6. **Zhang X., Dai B., Zhu A., Gong W., Liu Ch.**, Catalysis Today 72 (2002) 223-227.
7. **Jiang T., Li Y., Liu C.-J., Xu G.-H., Eliasson B., Xue B.**, Catalysis Today 72 (2002) 229-235.

PRZEMIANY METANU W WYŁADOWANIU BARIEROWYM

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S t r e s z c z e n i e. Celem pracy były wstępne badania nad możliwością otrzymania węglowodorów C_2 z metanu w wyładowaniach barierowych. Proces konwersji metanu prowadzono w przepływowym reaktorze kwarcowym bez wypełnienia lub z wypełnieniem stałym (granulowany kwarc, silica żel, żelazo osadzone na silica żelu oraz ceramika $BaTiO_3$) w szczelinie wyładowczej. Stwierdzono, że rodzaj wypełnienia wpływa na przemianę metanu i w temperaturze poniżej 300 ^{0}C podstawowym produktem był etan.

S ł o w a k l u c z o w e : wyładowania barierowe, konwersja metanu.