Electrophysical Methods of Hydrocarbon Gases Conversion

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Abstract – In the paper the review of investigation results on light hydrocarbon gas processing (methane, propane – butane mixture, ethane and others) carried out at the gas-discharge installations is presented. The review is done for the last 15–20 years in different scientific groups. The comparison of different electrophysical installations according to the energy imputs value for initial hydrocarbon gas conversion and efficiency is carried out. The perspectives of equilibrium and non-equilibrium plasmochemical processes application in the high volume chemical process of hydrocarbon gas processing are analyzed. In the paper the alternative methods of conversion such as partial methane oxidation in the non-equilibrium conditions, hydrocarbon gas conversion at the condensation and others are considered.

Introduction

The wide use of nonrenewable fields of liquid hydrocarbon raw stock to obtain fuel causes fields' depletion and the rise of refinement process price. Due to this, last years the development investigations on new fuel synthesis methods for internal-combustion engine out of gas hydrocarbon raw stock – associated gas, methane and others are actively carried out. Moreover, the hydrocarbon gases are very valuable raw stock fro chemical industry.

One of the present problems that has to be solved under the modern technologies development in large capacity production of chemical industry, metallurgy and other production branches is the equipment productivity increase with the simultaneous energy consumption decrease.

In chemical production the productivity increase is achieved mainly due to the technological process temperature increase as any chemical or metallurgical process in the context of classical kinetics is exponentially accelerates according to the Arrenius law [1]. But the reaction zone and reagent heating up to the high temperature requires the exponential increase of energy carrier consumption that is why new ways of traditional production productivity increase are necessary.

2. Traditional Ways of Hydrocarbon Gas Conversion

The synthesis-gas is used for majority of technological processes of compound hydrocarbon synthesis (synthetic fuel, methanol and others). The main ways of synthesis gas generation require high energy imputs which determine the final product cost value. For example, according to different evaluations depending on the concrete conditions the synthesis-gas cost in the methanol and ammonia production is from 50% up to 80% [2].

Now three methods of synthesis-gas generation out of methane are used: steam conversion, hydrocarbon conversion and partial methane oxidation. The first two methods require high energy imputs – 200–250 kJ for 1 mole (22.4 liters) of methane ignoring the imputs for raw stock and reaction zone heating up to 600–1500 °C [2]. The energy source is the combustion reaction (complete oxidation) in the conversion furnace. To get the required energy in the methane conversion technology up to 80% of raw stock is combusted. At the partial methane oxidation the additional energy imputs are not necessary as the oxidation reaction goes with energy liberation. At the present moment the investigations on the incomplete (partial) methane oxidation in the mixture with oxygen or air under the increased temperature are carried out [2] with the application of power installations [3], microwave discharge plasma [4], continuous electron beams [5]. At the reaction passing of partial methane oxidation the energy liberates and the synthesis-gas generation can be carried out without power supply line. But at the external action absence the partial methane oxidation process goes under the temperature higher than 450 °C and the pressure higher than 7.5 MPa [2]. Such conditions creation requires high energy imputs (for heating and pressure increase) and complete energy balance still will be negative. Moreover if the oxygen content in mixture is more than 10% the reaction velocity of partial oxidation will sharply decrease. And this limits the conversion degree of raw stock for one reaction zone pass.

To decrease the temperature and pressure which require for the methane partial oxidation reaction is possible at the external reaction mixture firing with the help of spark or precombusion chamber. This is used in the power installations [3]. The power installation use (similar to chamber of internal-combustion engine) allows to decrease the working temperature of the process down to 370 °C. But the reaction chamber volume does not exceed several liters what limits the installation productivity. Moreover, the problem of gas and reaction zone heating up to high temperature stays unsolved.

3. Gas Discharge Application for Hydrocarbon Gas Conversion in Equilibrium Conditions

The superposition of reaction zone and gas discharge one allows to increase the temperature greatly in the reaction zone what provides the local reagent heating up to high temperatures without reaction walls heating. The given conditions are easy to realize at the gas reagent mixture excitation by continuous electron beam, in the arc barrier discharge, in high-frequency plasmatron and microwave plasmatron. But in the given case the same problems as in the common thermal initiation of chemical process appear: high energy imputs, non-productive energy use for heating of reaction side-products (especially at low conversion level), the problem of useful products stabilization (quenching).

Even in case of the use of all the energy liberated in the gas discharge for chemical reaction going the installation with high power consumption is required to obtain the necessary products of significant volumes. For example, at the methane conversion 19 kJ of the input energy is required for 1 liter of gas (under normal conditions) to form the methene radicals (first conversion act) in the following reaction:

$$CH_4 + 425 \text{ kJ/mole} \rightarrow CH_3{}^* + H. \qquad (1)$$
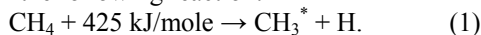
At the installation with methane conversion productivity of $100 \, m^3$/hour the power consumptions of electrophysical installation will exceed 500 kW even under the condition of 100% operating effectiveness and unproductive losses absence.

4. Pulse Discharge Application

The next step for energy imputs decrease for chemical process realization is the use of non-equilibrium processes which are characterized by the significant energy content increase at the inner degree of molecule freedom in comparison with thermodynamically equilibrium state [6]. In this case the gas temperature does not exceed 300–400 K what except for energy imputs decrease (for gas and reactor heating) makes easier the problem solution of chemical process product quenching (stabilization). The more effective way of chemical transformation initiation is the non-equilibrium excess energy stock creation at the oscillatory degrees of molecule freedom [6]. Figure 1 shows the dependence of CO_2 molecule decomposition effectiveness on the specific energy consumption at the oscillatory degrees of molecule freedom [7].

The decomposition effectiveness was calculated as the relation of energy spent for the initial CO_2 molecules decomposition (composition of CO_2 molecule decomposition energy and decomposed molecule quantity) and the energy at the oscillatory molecule degrees. As it is seen from Fig. 1 at the energy of molecule oscillatory degrees of about 1 eV all this energy is spent for its decomposition.

But even if all the molecule excitation energy is used for their decomposition and for further useful product generation the energy imputs for technological
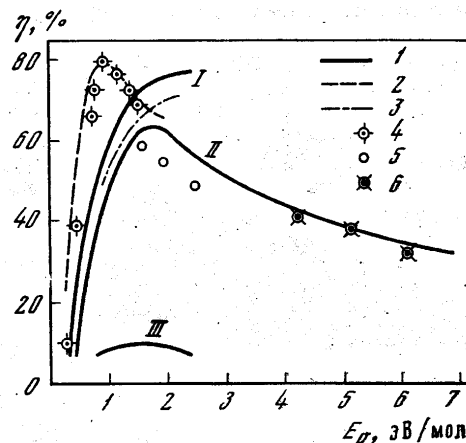

Fig. 1. Dependence of CO_2 decomposition effectiveness on the specific energy consumption [7]. *1* – computation in one-temperature approach; *2* – computation in two-temperature approach; *3* – numerical computation of complete efficiency in one-temperature approach; *4* – experiments with microwave discharge; *5, 6* – high-frequency discharge

process realization are significant and can not be less than process enthalpy (1). Moreover the pulsed gas discharge goes under the condition of higher non-equilibrium degree when the temperature of electron gas subsystem is much higher than forward gas temperature. This allows to use the advantages of molecular oscillatory excitation but prevent from using the heat energy extracted at the following stages of chemical synthesis (for example, energy of exothermic reactions of high-molecular compound synthesis out of synthesis-gas) to initiate the initial raw decomposition.

5. Investigation Results Review on Light Hydrocarbon Gas Conversion

We carried out the experiment analysis made during last 15–20 years at the gas-discharge installations in different scientific groups. The process of methane and propane-butane mixture conversion in the barrier discharge, arc discharge, high-frequency discharge and microwave discharge was the most investigated. The different electrophysical installation comparison is made according to energy imputs value for the initial hydrocarbon gas conversion, to output and process selectivity.

The part of the analysis results is presented in the Table 1. In case of molecular oxygen or oxygen-containing compositions (water, CO, CO_2) absence in the initial mixture the electrophysical installation energy imputs for one methane molecular conversion exceed 20 eV (2 MJ/mole). The main products of methane conversion in the gas discharge at the oxygen absence are ethane and ethylene. At the oxygen or oxygen-containing addition the energy imputs decreases down to 8–20 eV/molecule. It is obvious that gas-discharge electrophysical installations where the electric discharge is the only energy source of hydrocarbon gas conversion process can be used only for small volume synthesis or at the stage of hydrocarbon raw stock preparation.

Table 1

#	Discharge type	Initial mixture	Main products	Conversion degree	Energy imputs eV/molecule	Paper authors
1	Barrier discharge	CH_4 + Ar (7.5% CH_4)	C_2H_6 + H_2	40%	51.5	[8]
2	Barrier discharge	$CH_4 : H_2O = 1 : 2$	Saturated Hydrocarbons $C_2 - C_4$, $C_2H_6 - 65\%$.	14%	14.8	[9]
3	Non-self-maintained volume discharge (evaluation)	$CH_4 : H_2O = 1 : 2$	Saturated Hydrocarbons $C_2 - C_4$, $C_2H_6 - 65\%$.	20%	6.9	[9]
4	Barrier discharge	CH_4	C_2H_6, $C_3 - C_5$ and liquid	25%	400	[10]
5	Crown discharge	CH_4	C_2H_2, C_2H_4, C_2H_6	25%	200	[10]
6	Spark discharge	CH_4	$C_2H_2 - 85\%$	20%	12–36	[10]
7	Methane pyrolysis in plasma	CH_4	$C_2H_2 - 80\%$	90%	9	[11]
8	Methane electrical cracking	CH_4	$C_2H_2 - 50\%$	70%	14	[11]
9	Thermal oxidative methane pyrolysis	CH_4	$C_2H_2 - 30\%$	90%	4	[11]
10	Steam conversion	CH_4 + H_2O	CO + $3H_2$		2.1	[6]
11	CO_2 conversion	CH_4 + CO_2	$2CO$ + $2H_2$		2.6	[6]

6. Perspective Directions of Gas Conversion at the Electrophysical Installations

The carried out paper review and experimental investigations on hydrocarbon raw stock conversion showed that electrophysical installations at the high raw volume processing are very effectively used for initiation of processes which go with energy liberation. The following processes should be emphasized among them:

– Partial methane oxidation in the non-equilibrium conditions.

– Hydrocarbon gas conversion at the condensation.

– Synthesis of high-molecular compounds which do not contain oxygen.

7. Partial Methane Oxidation Initiated by Pulsed Electron Beam

The chain chemical processes investigation executed in 1930–1940 showed [12] that the hydrocarbon oxidation process as a rule has a chain character. Under the optimal conditions (in the ignition peninsula) for complete initial gas conversion the energy of exothermal reaction of chain process is enough and the external energy sources are not required. Particularly, to oxidize methane in the mixture with oxygen and air at the pressure of 0.1 MPa and room temperature the optimal ignition conditions correspond to the lean mixtures (5–15% of methane in the mixture with air) and the chain process is completed by the full methane oxidation to CO_2 and H_2O.

The investigations of chain oxidation processes, particularly, hydrogen oxidation showed that the chain process is easily controlled by external action and can be developed out of the common area of self-ignition [13–16].

The carried out kinetics investigations of hydrogen oxidation reaction in the area of low pressure (30–250 Torr) [17] showed that the pulsed electron beam influence on the hydrogen-oxygen mixture leads to the ignition induction time shortening to 2–5 ms. The pulsed electron beam application for $2H_2 + O_2$ mixture ignition initiation allows to significantly widen the ignition area to the area of low temperatures and increase the reaction velocity due to the induction time decrease. The pulsed electron beam in contrast to laser radiation allows to provide more uniform gas mixture excitation. This is very important for selective plasmochemical processes organization in large reactors. At the initiation of hydrogen oxidation by pulsed electron beam the oscillatory character of the chain oxidation process was found [17] what indicates the radical (no thermal) chain development, i.e. the cold flames mode.

The principal advantages of partial methane oxidation in non-equilibrium conditions are:

– Low power imputs.

At the chain development character of partial methane oxidation process the energy imputs of electrophysical installation contain the insignificant value of total energy which is used for conversion.

– High efficiency.

The reactor volume is not limited by the accelerator power and can be more than 10 liters for the accelerator with power of not more than 1 kW. The chain process duration does not exceed 10 ms, what allows to carry out the oxidation process with the frequency up to 100 Hz. Then the installation output can be up to $3.6 \cdot 10^3$ m^3/hour of the initial gas mixture.

– High uniformity of process initiation conditions.

The carried out investigations showed that pulsed electron beam is absorbed in gas with the formation of secondary electron cascade which fills out the significant volume. The uniformity of chemical process allows to provide high selectivity.

– Possibility of high degree methane conversion generation.

At the partial methane oxidation initiated by pulsed electron beam the process going is possible in the cold flames mode (similar to hydrogen oxidation under the electron beam influence). In this mode the inhibitory oxygen action to the partial methane oxidation reaction can be low and the process will pass at the stoichiometric correlation for the following reaction

$$CH_4 + 1/2O_2 = CO + 2H_2 \text{ or } 2CH_4 + O_2 + 3.76N_2 =$$
$$= 2CO + 4H_2 + 3.76N_2.$$
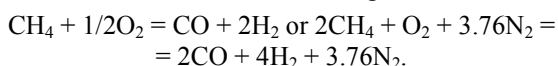
8. Hydrocarbon Gas Conversion at the Condensation

It is known that at the gas compositions condensation the energy of phase transfer is liberated. At the creation of special conditions this energy can be used for gas composition conversion.

The ion presence in the gas which contains the volatile liquid vapor greatly accelerates the condensation process of the latter. The ion-induced condensation as a frequent case of heterogenic condensation plays a significant role in different atmospheric and technological processes and that is why it is the object of investigation of many scientific groups. Usually to create the ions the isotope sources of radioactive radiation are used. The appeared positive and negative ions in gases become the motes for steam molecules and in gas the aerosol particles of nanometer size are formed. For stable existence of non-charged particles the supersaturation degree must increase at their radius decrease that is why the small-size non-charged particles can exist stable only in the rather supersaturated steam. The charged particles exist in the unsaturated steam.

The effects connected to the heterogenic condensation of steam molecules at ions including the aerosol formation can appear in different electric discharges. In the paper [18] the measurement results of mass aerosol concentration formed in gas hydrocarbons at the electron beam action. From the presented in this paper data it is seen that the aerosol formation was in strongly saturated steam of gas hydrocarbon radiolysis products. In the papers [19, 20] it is shown that at the interconnection of pulsed crown discharge plasma with unsaturated steam of different organic compositions (linear C_5–C_8, styrene, xylole) the formation of aerosol particles take place at low partial steam pressures – not more than 1% from the saturation pressure.

The possible conversion degree of hydrocarbon gases at the condensation is estimated. Suppose, that all the energy of phase gas-liquid transfer at the molecule condensation of methane and propane-butane mixture is spent for initial gas molecule decomposition. The calculation of conversion degree is presented in the Table 2. Similar to the calculations in the part 3 the conversion degree calculation is made according to the energy of methane bond opening in the reaction (1).

Let's calculate the possible hydrocarbon gas conversion degree under the condition of the polymerization process going at the condensation. The organic compositions polymerization at the aerosol formation was experimentally found at the styrene condensation process investigation in the plasma of pulsed crown discharge [19, 20].

At the methane condensation and its subsequent polymerization to octane in the following reaction:

$$8 \cdot CH_4 \rightarrow C_8H_{18} + 7 \cdot H_2 + 390 \text{ kJ/mole}$$
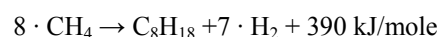
the energy liberated at the polymerization is 49 kJ for 1 methane mole. Suppose that all this energy is also spent for methane decomposition to methyl radicals in the reaction (6). In this case the possible conversion degree increases up to 13.2%. The calculation of different hydrocarbon gas conversion degree at the condensation and different liquid hydrocarbons formation are given in Table 2.

9. Synthesis of High-molecular Compositions Containing No Oxygen

The intensive methane conversion investigation with the use of catalyses showed the possibility of high-molecular compositions synthesis without oxygen out of methane and oxygen mixture [2]. The most investigated process is the ethylene synthesis out of methane and oxygen mixture according to the following reaction:

$$2CH_4 + O_2 = C_2H_4 + 2H_2O.$$
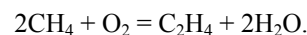
This reaction goes at the temperature above 700 °C in the catalyses presence. The oxygen takes part in the conversion process but is fixed to water in the synthesis process.

The works on tetrachlormethane decomposition in the mixture with oxygen under the pulsed electron beam influence were carried out. The works on

Table 2

Initial gas	Final product	Conversion degree	
		at condensation	at condensation and polymerization
Methane CH_4	Heptane C_7H_{16}	1.9%	12.6%
Methane CH_4	Octane C_8H_{18}	1.9%	13.2%
Ethane C_2H_6		1.4%	
Propane C_3H_8	Heptane C_7H_{16}	3.5%	9.7%
Propane C_3H_8	Octane C_8H_{18}	3.5%	10.4%
Butane C_4H_{10}	Heptane C_7H_{16}	4.9%	8.2%
Butane C_4H_{10}	Octane C_8H_{18}		10%

plasmochemical tetrachlormethane decomposition process were carried out at the specialized high-current pulsed electron accelerator [21]. The accelerator was developed for investigations execution on non-equilibrium plasmochemical processes initiation. The accelerator parameters are the following: electron energy is 400–500 keV, pulse duration at the half-height is 50 ns, pulse energy is up to 200 J, frequency is 5 Hz.

The investigations under the influence of pulsed electron beam on the gas-phase mixture of $CCl_4 + H_2 + O_2$ are carried out. The electron beam was injected from the butt-end to the closed reactor which represents a glass cylinder with inner diameter of 14 cm and volume of 6.16 liters. The pulsed electron beam initiated the hydrogen ignition reaction which was accompanied by the significant energy liberation. For 66 Torr $O_2 + 132$ Torr $H_2 + 4$ ml CCl_4 mixture the complete tetrachlormethane decomposition was done for one pulse of electron beam. At the electron beam energy of 100 J per pulse the energy imputs of electron beam for tetrachlormethane decomposition were 2.6 kJ/mole and taking into consideration the electron accelerator efficiency (35–40%) [21] did not exceed 6.4 kJ/mole.

The experimental investigations showed that at the tetrachlormethane decomposition in the chain plasmochemical process initiated by pulsed electron beam the nanodispersed carbon is formed. Fig. 2 shows the powder picture obtained at the transmission electron microscope.
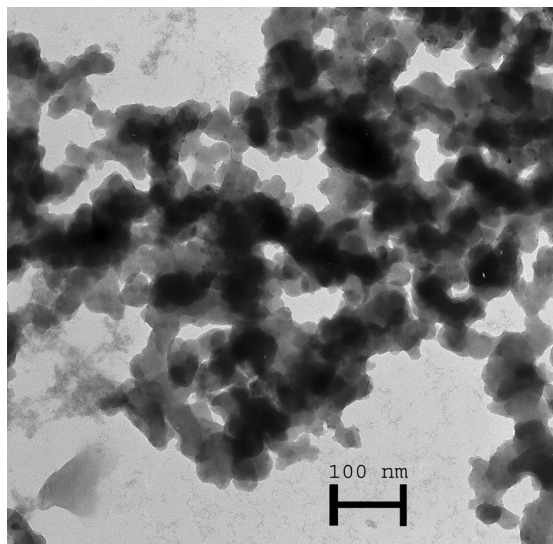

Fig. 2. Picture of superdispersed carbon obtained at the transmission electron microscope

The geometric size of synthesized nanosize carbon is within the limits from 7 to 50 nm (average 17.8 nm).

For the tetrachlormethane, hydrogen and oxygen mixture the calculation at the computer was carried out with the use of automatic thermodynamic calculation system "TERRA". The calculations were carried out for the temperature interval of 300–10000 K and pressure interval of initial mixture 0.01–0.1 MPa were exe-

cuted. The calculations were made for the mixture in the following mole relations: C:Cl:H:O –12:140:4:18. The part of the presented calculation s are presented in Fig. 3.

It is important to note that in non-equilibrium conditions of tetrachlormethane conversion in the mixture with oxygen (under the influence of pulsed electron beam) the exothermic reaction of oxygen and hydrogen takes place with water formation. The oxygen did not interconnect with carbon formed at the terachlormethane decomposition. The atomic carbon forms the nanosize particles in the reactor volume not at the walls what indicates the volumetric process character.
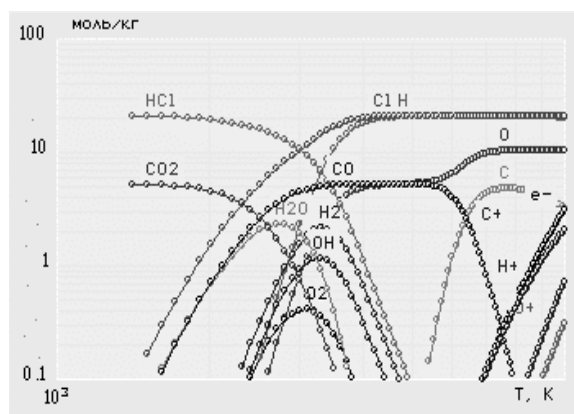

Fig. 3

Due to this the non-equilibrium processes of hydrocarbon gas conversion in the mixture with oxygen initiated by pulsed electron beam are perspective for synthesis of both oxygenates and hydrocarbon compositions which do not contain oxygen.

References

[1] V.N. Kondariev, E.E. Nikitin, *Chemical Processes in Gases*, Moscow, Nauka, 1981, 264 pp.

[2] V.S. Arutyunov, O.V. Krylov, *Oxidative conversion of methane*, Moscow, Nauka, 1998, 361 pp.

[3] Y.A. Kolbanovsky, I.V. Bilera, *Generation of Synthesis-gas in the Electric Power Installations, Gas chemistry in twenty first Century. Problems and Perspectives*, Edited by A.I. Vladimirov, A.L. Lapidus, Moscow, Oil and Gas, 2003, 288 pp.

[4] V.D. Rusanov, A.I. Babaritskiy, A.I. Gerasimov et al., *in: Proc. of Academy of Science* **389**, No. 3, 324–327 (2003).

[5] T. Kappes, T. Hammer, A. Ulrich, *in: Proc. of 16th International Symposium on Plasma Chemistry*, Italy, June 22–27, 2003.

[6] V.D. Rusanov, A.A. Fridman, *Physics of Chemically Active Plasma,* Moscow, Nauka, 1984, 416 pp.

[7] V.D. Rusanov, A.A. Fridman, G.V. Sholin, Technical Physics **49**, No. 10, 2169–2175 (1979).

[8] K. Shmidt-Szalowski, J. Sentek, K. Krawczyk, J. Ruszniak, and K. Radomyska, *in: Proc. of 16th*

International Symposium on Plasma Chemistry. Taormina, Italy, June 22–27, 2003.

[9] A. Suslov, E. Kolman, Yu. Novoselov, V. Ryzhov, *in: Proc. of 4th International symposium on pulsed power and plasma applications*, Nagaoka, Japan, 2003.

[10] S. Kado, Y. Sekine, N. Muto, T. Nozaki, and K. Okazaki, *in: Proc. of 16th International Symposium on Plasma Chemistry*, Taormina, Italy, June 22–27, 2003.

[11] H.E. Harlampidi, Sorovsky Educational Journal, Chemistry, No. 1, 41–46 (1999).

[12] *Cain Reactions of Hydrocarbon Oxidation in the Gas phase*. Work Collection, Moscow, Academy of Sciences of USSR, 1955, 190 pp.

[13] A.M. Starik, N.S. Titova, Technical Physics Magazine **73**, pp. 59–68.

[14] A.Y. Starikova, Combustion and Explosion Physics **39**, No. 6, 12–19 (2003).

[15] G.Y. Gerasimov, Chemistry of High Energies **36**, No. 6, 408–412 (2002).

[16] A.A. Seleznev, A.Y. Aleynikov, V.V. Yaroshenko, Chemical Physics **18**, No. 5, 65–71 (1999).

[17] G.E. Remnev, A.I. Pushkarev, *in: Proc. of 11th International Scientific School-Seminar "Physics of Pulsed Discharges in the Condensed Environment",* Nickolaev, 2003, pp. 75–77.

[18] V.S. Bogdanov, Proceedings of Academy of Sciences **136**, 121–124 (1961).

[19] S.P. Bugaev, V.S. Kozlov, A.V. Kozirev, M.V. Panchenko, N. S Sochugov, Atmosphere and Ocean Optics **12**, No. 8, 736–743 (1999).

[20] A.V. Kozirev, A.G. Sitnikov, *in: Proc. of 6th International Coinference "Physics Chemistry of Ultradispersed (Nano)systems,* Moscow, MIFI (2002), pp. 91–92.

[21] G. Remnev, E. Furman, A. Pushkarev, S. Karpusov, N. Kondratiev, and D. Goncharov, *in: Proc. of 4th International symposium on pulsed power and plasma applications,* Nagaoka, Japan, 2003, pp. 172–175.