Journal of Engineering Physics and Thermophysics, Vol. 81, No. 4, 2008

PRODUCTION OF COMMERCIAL HYDROGEN AND ACETYLENE FROM PROPANE-BUTANE AND LIQUID HYDROCARBONS IN AN ELECTRIC-ARC PLASMA REACTOR

A. L. Mossé, A. V. Gorbunov, A. A. Galinovskii,
V. V. Savchin, and A. V. Lozhechnik

UDC 533.9:536.45

A fundamentally new structure of a plasma reactor for production of acetylene and commercial hydrogen from gaseous and liquid hydrocarbons has been developed and proposed. In this device, the plasma jet of synthesis gas is submerged in the volume of liquid hydrocarbons to form a gas volume in which the second stage of pyrolysis reactions is realized. Experimental investigations have been carried out.

Introduction. Acetylene is the basic raw material for production of various products of organic synthesis in the chemical industry. Furthermore, it is widely used in mechanical engineering, construction, etc. The presence of the triple bond in acetylene explains its extremely high reactivity, which is used in highly diverse syntheses based on addition, condensation, and polymerization reactions. The chemical industry currently produces a wide range of products of heavy organic synthesis (acetaldehyde and acetic acid, ethyl alcohol, acetone, etc.) on the basis of acetylene and its simplest homolog: vinylacetylene. Acetylene and vinylacetylene are the starting products for production of various solvents, different kinds of synthetic rubbers, plastics, ethers and esters, polyamide resins, etc.

Acetylene can be produced from hydrocarbons or by the carbide technique. Selection of one method or the other depends mainly on the availability of the petroleum raw material, natural gas, coke, and power resources to the supplier [1–4].

The carbide technique of production of acetylene eliminates the necessity of isolating it from reaction gases and purifying specially; furthermore, it is suitable for many uses of organic synthesis. However, the rapidly growing demand for acetylene-processing products stimulates the development and propagation of new, more economic techniques of acetylene production that are based on the pyrolysis of gaseous (mainly methane and propane-butane) and liquid hydrocarbons in electric arcs or due to the energy released in combustion of a part of the raw material — thermooxidation pyrolysis. Since the supplies of natural hydrocarbons are limited, new forms of raw material have intensely been sought for recently; the waste of a number of organic industries and solid fuel — coke and different types of coals — can primarily be used as these forms.

It has been established that the chemical composition of the raw material substantially influences of the acetylene yield. It is the largest in pyrolysis of paraffins of normal structure. Aromatic hydrocarbons prove to be the least suitable, since a great amount of soot and resins and little acetylene is formed in their decomposition. The energy intensity of the process is dependent on the molecular weight of the starting hydrocarbon: the larger the weight, the lower the specific expenditure of energy. Also, the composition of the raw material determines the temperature and pressure of the process: the optimum temperature is lower for the larger molecular weight of hydrocarbons and no increase in the pressure is needed. Hydrogen with a fairly high concentration in the waste gases is formed simultaneously with acetylene. Commercial hydrogen can subsequently be produced after isolation and purification.

Formulation of the Problem. To develop and investigate a new variant of the technology of pyrolysis of hydrocarbon raw material with the aim of producing acetylene and commercial hydrogen we have reviewed and analyzed the technological and instrumental versions proposed earlier. The thermodynamic and kinetic calculations of the process and performance evaluation of the selection of the starting raw material have been carried out and, unlike [5, 6], a fundamentally new flow diagram of the process has been proposed.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 81, No. 4, pp. 630–636, July–August, 2008. Original article submitted April 18, 2007.

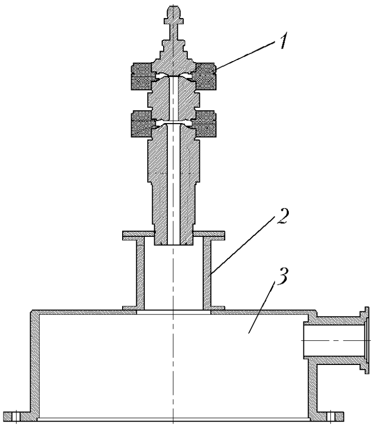


Fig. 1. Diagram of the reactor with a PDS-3D plasmatron for production of commercial hydrogen and acetylene: 1) plasmatron; 2) reactor; 3) bunker.

In the version proposed, a nonhydrocarbon raw material is injected into the high-temperature reaction zone, and a hydrocarbon-containing plasma jet is submerged in the volume of liquid hydrocarbons to form a gas volume in which we also have pyrolysis and thermosynthesis reactions. In the gas volume, as in an unusual kind of reactor, direct contact between the pyrolysis products and cold walls is eliminated; in so doing, the operating regime of the device is stabilized. An additional advantage of the process is a considerable decrease in the heat loss whose presence in the existing devices is caused by the necessity of cooling the elements of the setup. In the diagram proposed, the resulting reaction products are cooled by the ambient liquid, undergoing the quenching stage. Furthermore, devices for freeing a pyrogas of soot become unnecessary in such a flow diagram. The soot is mainly absorbed in the layer of liquid hydrocarbon raw material and can be deposited, periodically be removed from it, or circulate with the flow of liquid hydrocarbons which are subsequently filtered and purified. Also, the universal character of the process, as far as the possibility of using different liquid hydrocarbons — from light gas condensates to mazuts and even crude — and the waste of petroleum-producing and refining industries, waste oils, etc. is concerned, is of importance.

According to the results of the developments and experimental investigations performed, we propose a two-step process of pyrolysis of gaseous and liquid hydrocarbons for production of acetylene and commercial hydrogen. The process has been realized by heating the mixture of hydrocarbon gas, i.e., propane-butane, and nitrogen in a low-temperature-plasma generator and by drawing subsequently the plasma pyrogas jet in the volume of liquid hydrocarbons — diesel fuel. To determine the contribution of the technological version proposed, we have carried out experimental investigations and have compared the obtained results to the other two technological versions: 1) quenching of the pyrolysis products by water jets (existing technique) and 2) submergence of the nitrogen-plasma jet in the volume of diesel fuel.

In all the investigated and compared variants, for testing the process of production of acetylene from hydrocarbon raw material we used a PDC-3-type dc plasmatron and its modification PDC-3D intended for operation with hydrogen, methane, and propane-butane and their mixtures with other gases. The results of investigationg the characteristics of the plasmatron and the description of its modification have been presented in [7, 8].

Experimental Technological Setup. This is represented by a plasma reactor (Fig. 1) consisting of a PDC-3D plasmatron, a sectioned reactor, and a quenching device manufactured in two variants: a quenching section ensuring the distributed injection of water jets perpendicularly to the motion of a plasma jet (the schematic diagram of the entire setup is shown in Fig. 2) and a quenching bunker (see Fig. 1) where pyrolysis gases were quenched by submerging them in the volume of the quenching medium — diesel fuel (the complete schematic diagram of the setup is presented in [9]). Mixtures of propane-butane and air were used as a plasma-generating gas for production of hydrogen and acetylene. The total flow rate of the gas mixture was 12–20 kg/h; its velocity at exit from the plasmatron was 40–95 m/sec and 20–50 m/sec at entry of the pyrogas into the quenching medium (diesel fuel). Both technological setups, as is seen in Fig. 2, also incorporated systems for feeding the plasma-generating gas — nitrogen — and the starting hydrocarbon raw material — propane-butane (liquefied gas), water supply of the plasmatron, the sections of the reactor and the quenching, bunker, and for sampling pyrolysis products for an analysis.

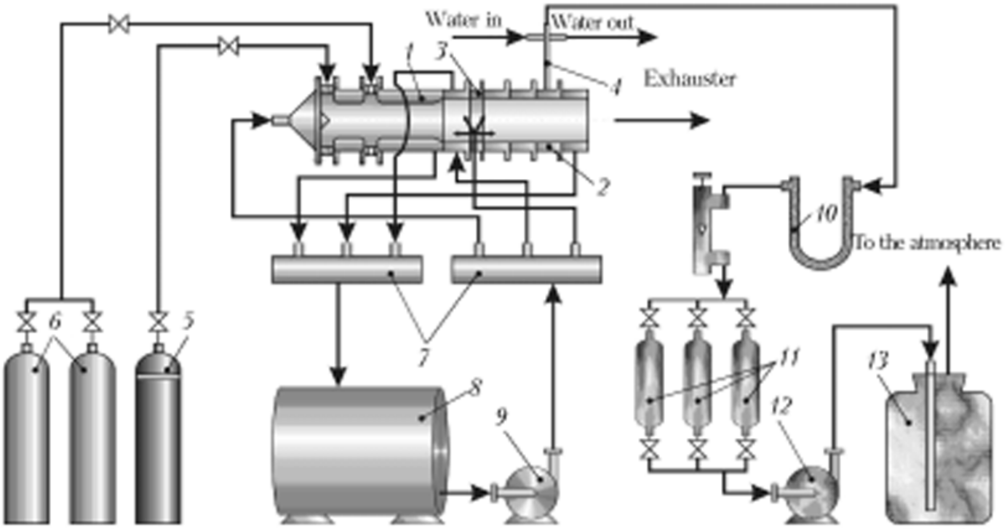


Fig. 2. Flow diagram of the plasma setup with a dc plasmatron for production of acetylene and commercial hydrogen (quenching by water jets): 1) plasmatron; 2) sectioned reactor; 3) quenching chamber; 4) sampler; 5) cylinder with propane-butane; 6) cylinder with nitrogen; 7) combs of the water-supply system; 8) vessel with water; 9) water pump; 10) filter for freeing the gas of soot; 11) pipets for sampling; 12) vacuum pump; 13) water gate.

A chemical analysis of the gas samples was made by the gas-adsorption-chromatography method. The gas samples for analysis were taken from the plasma reactor into gas pipets via a special filter with glass wool for separation of moisture and precipitation of solid soot particles using a water-cooled sampler and a vacuum pump [7]. A gas chromatographic analysis of hydrocarbon gases S1-S4 in the samples taken was made with a Tsvet-100M chromatograph (model 164) fitted with a plasma-ionization detector.

An LKhM-8MD gas chromatograph fitted with a heat-conduction detector was used for measuring the concentrations of hydrogen, oxygen, nitrogen, and methane in the pyrogas samples.

Results of Studying the Process of Pyrolysis of Propane-Butane. To produce acetylene and commercial hydrogen we have carried out investigations according to different flow diagrams in three runs of experiments characterized by the following parameters and composition of the gaseous products.

1. Quenching of pyrolysis gases by water jets using the mixture of propane-butane and nitrogen as a raw material: electric-power input of the dc plasmatron 32.2–35.2 kW, plasma-generating gas propane-butane (10.8 g/sec) mixed with nitrogen (5.4 g/sec), arc-current strength 140–150 A, mass-mean temperature of the gas at exit from the plasmatron 2300–2500 K, plasmatron-arc voltage 220–230 V, and plasmatron efficiency 0.7.

Composition of the pyrogas (in vol. %): C_2H_2 — 12.1–16.3, CH_4 — 4.0–5.5, C_2H_4 — 6.65–7.95, C_3H_8 — 8.9–9.4, C_4H_{10} (*n*-butane) — 1.36–1.86, C_4H_{10} (isobutane) <0.1, C_2H_6 < 0.1, C_3H_6 <0.1, the remaining — H_2 (to 17.5%), N_2 (to 46%), and O_2 (to 2.1%). Specific energy expenditure 14.0–18.6 kW·h/kg C_2H_2.

2. Submergence of the nitrogen-plasma jet in the volume of diesel fuel without propane-butane supply: electric-power input of the dc plasmatron 28.0–46.8 kW, plasma-generating gas nitrogen (3.6–9.0 g/sec), arc-current strength 160–230 A, mass-mean temperature of the gas at exit from the plasmatron 5200–6200 K, plasmatron-arc voltage 155–210 V, and plasmatron efficiency 0.6–0.75.

Composition of the pyrogas (in vol. %): C_2H_2 — 10–18.9, CH_4 — 3.2–9.65, C_2H_4 — 7.25–13.9, C_3H_8 <0.1, C_4H_{10} (*n*-butane) <0.1, C_4H_{10} (isobutane) <0.1, C_2H_6 — 0.3–0.8, C_3H_6 — 1.78–2.8, the remaining — H_2 (12.0–22.0), N_2 (to 50%), and O_2 (to 1.5%). Specific energy expenditure 30.0 kW·h/kg C_2H_2.

3. Quenching of pyrolysis gases by submerging in the diesel-fuel volume using the mixture of propane-butane and nitrogen as a raw material: electric-power input of the dc plasmatron 19.0–30.8 kW, plasma-generating gas propane-butane (12.2–19.3 g/sec) mixed with nitrogen (2.9 g/sec), arc-current strength 190–305 A, mass-mean temperature of the gas at exit from the plasmatron 1300–2000 K, plasmatron-arc voltage 80–110 V, and plasmatron efficiency 0.7–0.75.

TABLE 1. Composition of the Pyrolysis Gas (vol. %)

Gas	Raw material (commercial propane-butane)	Sample No. 1, quenched	Sample No. 2, quenched	Average values
C_2H_2 (acetylene)	—	29.69	31.30	30.50
CH_4 (methane)	0.6	11.61	10.78	11.20
C_2H_4 (ethylene)	—	14.67	14.95	14.81
C_3H_8 (propane)	72.5	0.67	0.57	0.62
C_4H_{10} (*n*-butane)	12.2	0.1	0.1	0.1
C_2H_6 (ethane)	5.6	0.43	0.32	0.37
C_3H_6 (propylene)	—	1.87	1.89	1.88
C_4H_{10} (isobutane)	9.0	0.1	0.1	0.1
H_2 (hydrogen)	—	13.24	13.58	14.36
O_2 (oxygen)	—	2.05	1.61	1.45
N_2 (nitrogen)	—	25.82	24.99	24.84

Notes. 1. The plasma-generating gas — nitrogen — was fed to the first gas ring. 2. The plasma-generating gas — propane-butane — was fed to the second gas ring. 3. Pyrolysis gases were quenched by submerging of the plasma jet of the pyrolysis gases in the volume of liquid hydrocarbons (diesel fuel). 4. The reaction-zone length (from the plasmatron's nozzle exit section to the quenching-medium surface) is 0.36 m. 5. Partial pyrolysis of liquid hydrocarbons (diesel fuel) with a flow rate of nearly 2 kg/h was carried out in addition to the pyrolysis of propane-butane raw material. 6. The energy expenditure was ~4.2 kW·h/kg C_2H_2 (disregarding the pyrolysis of liquid diesel fuel and the efficiency of the current source). 7. The arbitrary degree of conversion of raw material to C_2H_2 η was equal to $(C_{C_2H_2}/(C_{C_2H_6} + C_{C_3H_8} + C_{C_4H_{10}}))$.

Composition of the pyrogas (in vol. %): C_2H_2 — 37.08–37.99, CH_4 — 5.9–9.32, C_2H_4 — 8.14–12.54, C_3H_8 <0.1, C_4H_{10} (*n*-butane) <0.1, C_4H_{10} (isobutane) <0.1, C_2H_6 <0.1, C_3H_6 — 1.79–2.46, the remaining — H_2 (to 15.5%), N_2 (to 22%), and O_2 (to 1.5%). Specific energy expenditure 4.1 kW·h/kg C_2H_2.

As is seen from the above results, nearly analogous ranges of operating parameters of the plasmatron, primarily the power, the flow rate of the plasma-generating gas, and the temperatures, were maintained in the runs of experiments presented. The operating regime of the plasma setup can be characterized as energy-expenditure-optimized only in the third variant.

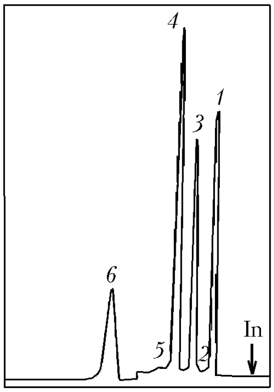
We emphasize that we did not find *n*-butane, isobutane, and propane in concentrations higher than 0.1% in the samples obtained. This points to the fairly high degree of conversion of the starting raw material, i.e., propane-butane. In the experiments of the third run, the pyrogas was quenched in the volume of both fresh diesel fuel and that used in the previous experiments. Taking into account that diesel fuel sorbs acetylene at temperatures below 160°C and desorbs it in heating during the plasmatron operation, we used fresh diesel fuel filled just before the experiment for quenching.

The composition of the gas products (in vol. %) in this special experiment was as follows: C_2H_2 — 29.7–31.3, CH_4 — 10.8–11.6, C_2H_4 — 14.67–14.95, C_3H_8 — 0.57–0.67, C_4H_{10} (*n*-butane) <0.1, C_4H_{10} (isobutane) <0.1, C_2H_6 — 0.32–0.43, remainder — H_2 (to 15.6%), N_2 (to 24.2%), and O_2 (to 1.37%). The specific energy expenditure was 4.01 kW·h/kg C_2H_2. Clearly, the content of acetylene was somewhat lower than that in the experiments of the third group.

Below, we present as an example results of one experiment of the third (optimum) run on production of hydrogen and acetylene from propane-butane in the direct-flow plasma reactor with a PDC-3D dc plasmatron with nitrogen as a plasma-generating gas (Table 1, Figs. 3 and 4).

The operating parameters of the PDC-3D plasmatron with two gas rings are as follows:

Current strength, A	280	Flow rate of propane-butane, kg/h	12.1
Voltage, V	110	Thermal power, kW	21.6
Power input, kW	30.8	Enthalpy of the mixture, MJ/kg	5.13
Flow rate of N_2, kg/h	2.9	Temperature of the mixture, K	1720–2000



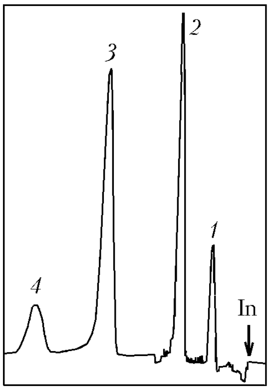


Fig. 3. Typical chromatogram of the hydrocarbon fraction of the vapor-gas phase of the samples, obtained on the plasma-ionization detector: 1) methane; 2) ethane; 3) ethylene; 4) acetylene; 5) propane; 6) propylene.

Fig. 4. Typical chromatogram of the gas phase of the samples, obtained on the heat-conduction detector: 1) hydrogen; 2) oxygen; 3) nitrogen; 4) methane.

Thus, it may be stated that the temperature and quality of diesel fuel (fresh or spent) influence the composition of pyrolysis gases. This fact is also confirmed by the pyrogas composition obtained in the check experiment where no propane-butane was fed at all, and acetylene in an amount of nearly 5.0% (by weight) was produced only by pyrolysis of diesel fuel in heating it by the plasma nitrogen jet. A substantial influence on the composition of the pyrogas and the degree of conversion of the raw material to acetylene is exerted by the relation of the flow rates of the plasma-generating gas — nitrogen — and the starting raw material — propane-butane. With an N_2/propane-butane relation of 12.9/16.9 = 0.17 to 2.9/19.3 = 0.15, the degree of conversion of propane-butane to acetylene is small and a certain amount of propane, *n*-butane, and isobutane remains in the pyrogas. With an N_2/propane-butane relation of 2.9/12.2 = 0.16, propane, *n*-butane, and isobutane are absent from the pyrogas, i.e., the degree of decomposition (conversion) of propane-butane approaches 100%. Such an operating regime of the setup seems optimum, as far as the specific energy expenditure is concerned.

A change of 0.27 to 0.36 m in the distance from the plasmatron's nozzle exit section to the surface of the quenching medium and accordingly the zone of penetration of the high-temperature pyrogas flow into the quenching medium exerts no substantial influence on the composition of the pyrogas and the degree of conversion of the raw material to acetylene in the experiments carried out. A more profound influence is exerted by such factors as the depth of penetration of the plasma pyrogas jet and/or the size of the quenching-medium surface (or the ratio of the diameter of the outlet cross section of the plasma reactor to the diameter of the surface of the quenching medium) and the relation of the flow rates of the plasma-generating gas (nitrogen) and the starting raw material (propane-butane). Thus, the use of a lance to organize the submergence of the plasma pyrogas jet (and to simultaneously reduce the "operating" surface of the quenching medium) in one experiment produced a decrease in the concentration of acetylene in the composition of the pyrogas. On the basis of these results, it may be stated that the selected distance from the plasmatron's nozzle exit section to the surface of the quenching medium of 0.27–0.36 m and a ratio of the diameter of the outlet cross section of the plasma reactor to the size of the quenching-medium surface of 50 : 500 are optimum for the quenching regime.

The resultant influence of these factors is likely to have an effect on the depth of penetration of the plasma pyrogas jet into the volume of the quenching medium, which determines the efficiency of the process of volume quenching.

Also, it is noteworthy that one basic problem arising during the experiments is the low pressure of propane-butane in the cylinder (no higher than 6.5 atm), which limits the possibility of increasing its flow rate in the plasmatron and degrade gasdynamic characteristics in the plasmatron's discharge chamber. This circumstance limits the possibility of increasing the power and output of the reactor during the testing of the process of acetylene production. Furthermore, it has been established experimentally that with feeding of propane-butane to the plasmatron's discharge chamber and reduction in the flow rate of the plasma-generating gas, i.e., nitrogen, a voltage drop across the plasma-

TABLE 2. Composition of the Gas Products Obtained on Quenching of Pyrolysis Gases by a Dispersed Water Jet (I), on Submergence of a Nitrogen-Plasma Jet in the Diesel-Fuel Volume (II), and on Quenching of Pyrolysis Gases by Submerging a Pyrogas Jet in the Diesel-Fuel Volume (III) (vol. %)

Gas	I	II	III
C_2H_2 (acetylene)	12.1—16.3	10.0—18.9	37.08—37.99
C_2H_4 (ethylene)	4.0—5.5	7.25—13.9	8.14—12.54
CH_4 (methane)	6.7—8.0	3.17—9.65	5.9—9.32
C_3H_6 (propylene)	< 0.1	1.80—2.80	1.79—2.46
C_3H_8 (propane)	8.9—9.4	< 0.1	< 0.1
C_4H_{10} (*n*-butane)	1.4—1.9	< 0.1	< 0.1
C_4H_{10} (isobutane)	< 0.1	< 0.1	< 0.1
C_2H_6 (ethane)	< 0.1	0.30—0.56	< 0.1
H_2 (hydrogen)	—	12.0—22.0	11.4—13.7

Notes. 1. The composition of the gas products included N_2 (to 22%) and the O_2 impurity (to 1.5%) in addition to the hydrocarbons indicated in Table. 2. The specific energy expenditure (kW·h/kg C_2H_2) was as follows: I) 10.0–12.2; II) 8.0–9.0; III) 4.1.

tron arc occurs and we are forced to increase the current strength to preserve the electric-power input, which is undesirable because of a possible degradation of the operating characteristics of the plasmatron electrodes. Unfortunately, we have to state that there are no data (except for [7–9] given by us) on the characteristics of plasmatron operation with propane-butane and its mixtures with other gases in the literature. Therefore, it is of independent interest to obtain, process, and generalize the volt-ampere, thermal, and operating characteristics of plasmatrons of different types and power in their operation with hydrocarbon gases.

As has already been noted above, we used a quenching device of two types: a quenching section ensuring a distributed injection of water jets perpendicularly to the motion of the plasma jet, and a quenching bunker for testing the efficiency of the technological process. Since water quenching of pyrolysis gases is a fairly well-known technique in use, the results of these experiments are not presented in the work. But it is, probably, of interest to compare them to the proposed two-step process of pyrolysis and quenching of the pyrogas by submerging in the volume of liquid hydrocarbons — diesel fuel. The results of such comparison are presented in Table 2.

As is clear from Table 2, the quenching of pyrolysis gases by submerging them in the volume of the quenching medium, i.e., diesel fuel, is preferable as far as both the specific energy expenditure and the selectivity of C_2H_2 formation are concerned.

Thus, as a result of the investigations carried out, we propose a flow diagram of the plasmachemical setup for conversion of propane-butane to acetylene and commercial hydrogen with quenching of pyrolysis gases by submerging them in the volume of a quenching medium, i.e., diesel fuel. It has been established that, in certain operating regimes of the setup, the concentration of acetylene in pyrolysis products can attain 30.0–37.9 vol. %, when the concentration of acetylene theoretically possible under these conditions is 38.05 vol. %.

Conclusions. In investigating this process, we have revealed regimes with a high (95–99%) degree of conversion of the raw material — propane-butane (liquefied gas) — to C_2H_2), a high concentration of acetylene in the pyrogas, and a low energy expenditure (to 4.0 kW·h/kg). The technological process in the parametric range investigated with the use of dc plasmatrons of different power and with quenching of pyrolysis products in the volume of liquid hydrocarbons (in particular, diesel fuel) is fairly well optimized. The technology and equipment can be used in industry, with the secondary raw material — liquid hydrocarbons or waste containing different liquid hydrocarbons — being used as the quenching medium, which is the subject of further investigations.

REFERENCES

1. K. Iskenderova, P. Porshnev, A. Gutsol, A. Saveliev, A. Fridman, L. Kennedy, and T. Rufael, Methane conversion into syn-gas in gliding arc discharge, in: *Proc. 15th Int. Symp. on Plasma Chemistry*, Orleans, 9–13 July, 2001, Vol. 7, pp. 2849–2854.

2. A. Czernichowski, GlidArc-assisted preparation of synthesis gas from natural and waste hydrocarbons gases, *Oil Gas Sci. Technol. Rev. IFP*, **56**, No. 2, 181–198 (2001).
3. F. K. Lu, C. M. Roseberry, J. M. Meyers, D. R. Wilson, Y. M. Lee, and P. A. Czysz, Pyrolysis of Methane in a Supersonic Arc-Heated Flow. *American Institute of Aeronautics and Astronautics*, *Inc. Paper* (2004).
4. M. Deminsky, V. Jivotov, B. Potapkin, and V. Rusanov, Plasma-assisted production of hydrogen from hydrocarbons, *Pure Appl. Chem.*, **74**, No. 3, 413–418 (2002).
5. V. D. Parkhomenko, L. S. Polak, P. I. Soroka, et al., *Processes and Apparatuses of Plasma-Chemical Technology* [in Russian], Vishcha Shkola, Kiev (1979).
6. A. L. Mossé, V. A. Menkh, I. A. Krylova, and V. K. Zabrodin, Study of certain reactor designs as applied to the process of oil pyrolysis in a plasma jet, *Inzh.-Fiz. Zh.*, **20**, No. 3, 462–466 (1971).
7. V. E. Vogulkin, A. V. Gorbunov, A. L. Mossé, and A. A. Galinovskii, Thermosynthesis of acetylene in an electric-arc plasma reactor from propane-butane with quenching of the pyrolysis gas by a submerged jet, in: *Proc. Vth Minsk Int. Forum "Heat and Mass Transfer–MIF-2004"* [in Russian], 24–28 May 2004, Minsk (2004), pp. 414–415.
8. V. E. Vogulkin, A. V. Gorbunov, A. L. Mossé, and A. A. Galinovsky, Synthesis of acetylene from propane-butane in the dc plasma reactor with downed jet quenching of pyrogas, *High Temp. Mater. Processes*, **9**, No. 3, 463–471 (2005).
9. A. F. Bublievskii, A. A. Galinovskii, A. V. Gorbunov, S. A. Zhdanok, L. I. Sharakhovskii, and A. L. Mossé, Plasma pyrolytic synthesis of carbon nanostructures in a mixture of nitrogen and propane–butane, *Inzh.-Fiz. Zh.*, **79**, No. 2, 3–9 (2006).