Energy Input Areas Initiated by Electric Discharge in Supersonic Flow of Reactive Gases

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The world hydrocarbon-fuel resources are predominantly concentrated in the form of natural-gas resources, consisting of lower-paraffin substances such as methane and ethane. The high stability of CH_4 and C_2H_6 (formation enthalpies 74.8 and 84.7 kJ/mole, respectively) hampers, or even makes impossible, using these substances in polymer production. The basic input materials in polymer production are unsaturated hydrocarbons, such as ethylene and acetylene. In chemical industry these materials are normally called semi-products. In the XXI century the methane conversion problem, i.e. the development of a highly efficient chemical process for methane conversion into chemical semi-products, has become a high-priority problem in connection with the reorientation of chemical industry to alternative raw materials. In this field, researches encounter the following three fundamental difficulties. First, the conversion requires considerable energy inputs (for one mole of acetylene to be produced from methane, at least 375 kJ of energy are required). Second, the conversion proceeds at high temperatures ($T \approx 1700 \div 2500$ K). Third, both ethylene and acetylene are intermediate products in the methane transformation sequence unstable at transformation temperatures. A rapid supply of energy to reactants followed by rapid cooling of the reacting mixture is a necessary condition for any natural-gas conversion pyrolysis process (rates of heating $10^{10} \div 10^{11}$ K/s, rate of cooling $10^8 \div 10^9$ K/s). The existing pyrolytic plants with many-ton annual production of end products are based on electro-arc and plasma-chemical energy input methods. In those plants, the energy supply and the chemical transformation proceed as parallel processes. A high rate of power input and a uniform distribution of supplied energy over reactants are very hard to be achieved simultaneously, this circumstance defining both the low energy efficiency of presently existing conversion facilities (typically, about 30%) and the low selectivity of the apparatuses in term of end products. Intensive research of nonequilibrium plasma application is carried out worldwide, e.g. [1-5]. The authors of [6] proposed a pyrolytic process in which energy supply and chemical transformations are organized as sequential processes. In the new technology, the energy supply is exercised without heating reactants while the supplied energy is accumulated in the form of stream kinetic energy. By force of the nonadmission condition for chemical transformations at the stage of energy input, the kinetic restricts the stream temperature from above. On the other hand, energy considerations for the

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conversion put limit to stream velocity from below. Both conditions define a supersonic regime of apparatus operating by the proposed method. The reaction is initiated in the normal shock wave.

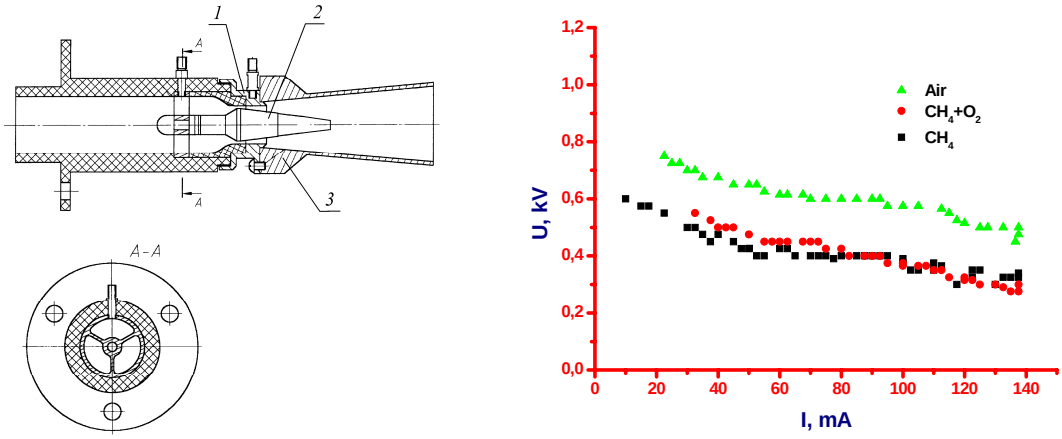

Figure 1. Left: Supersonic energy input chamber geometry, where 1, 2 – electrodes; 3 – diffuser. Right: Current-voltage characteristics of discharges in air, methane, and methane-oxygen mixture.

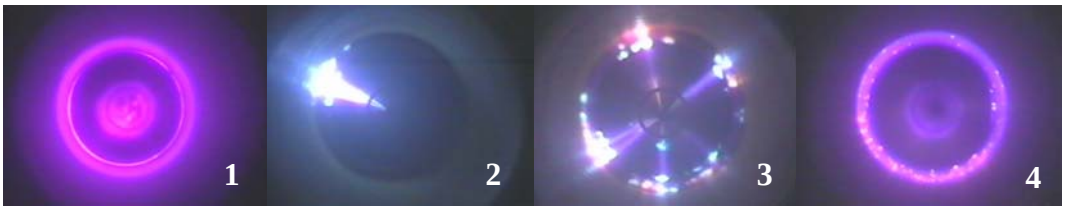

Figure 2. Glow discharge in supersonic flow: 1 – air; 2 – CH_4; 3 – CH_4+5%air; 4 – CH_4+15%O_2.

One method to organize the input of energy into the supersonic reactor is the initiation of the chemical reaction with electric discharges. The discharge stimulates the ignition of the air-fuel mixture by shortening the induction time and by lowering the ignition temperature, both factors being essential in developing new plasmochemical processes and in solving many problems in applied gas-dynamics. In the present work, a volumetric electric discharge ignited in an expanding reacting gas flow (methane, air, methane-oxygen mixture) was examined. The working mixture of methane with air or methane with oxygen entered the for-chamber out of a mixing chamber, where the components were premixed in rotating counter-flows. The electrode assembly (Fig. 1) was made integral with the supersonic nozzle (M=3.5). The central electrode was a contoured body of revolution, and the outer electrode was an annular electrode. Both electrodes were provided with geometric features used to position the discharge at the electrodes. The stream having passed the working section was ejected into a vacuum tank. In the experiments, the mass rate of the gas flow was 9-25 g/s, with the contribution due to the additional air or oxygen flow being, depending on particular adopted experimental conditions, 5 to 30%. The for-chamber pressure was 0.15–0.5 at. The discharge current was within 1 A, and the voltage, 0.3 to 0.8 kV. Figure 1 shows the current-voltage characteristics of gas discharges ignited in supersonic flows of air, methane, and methane-oxygen mixture. The descending current-voltage characteristics shown in the plot are typical of glow discharges. Figure 2 shows photographs of glow discharges which were taken along the stream axis (in the photographs, the gas moves to observer). It is seen that in pure methane we have a constricted discharge, presumably due to enhanced electron mobility in methane in comparison with air at low E/P ratios taking place in gas discharges [7]. Addition of an electronegative gas, such as oxygen, for instance, makes the discharge glow more uniformly.

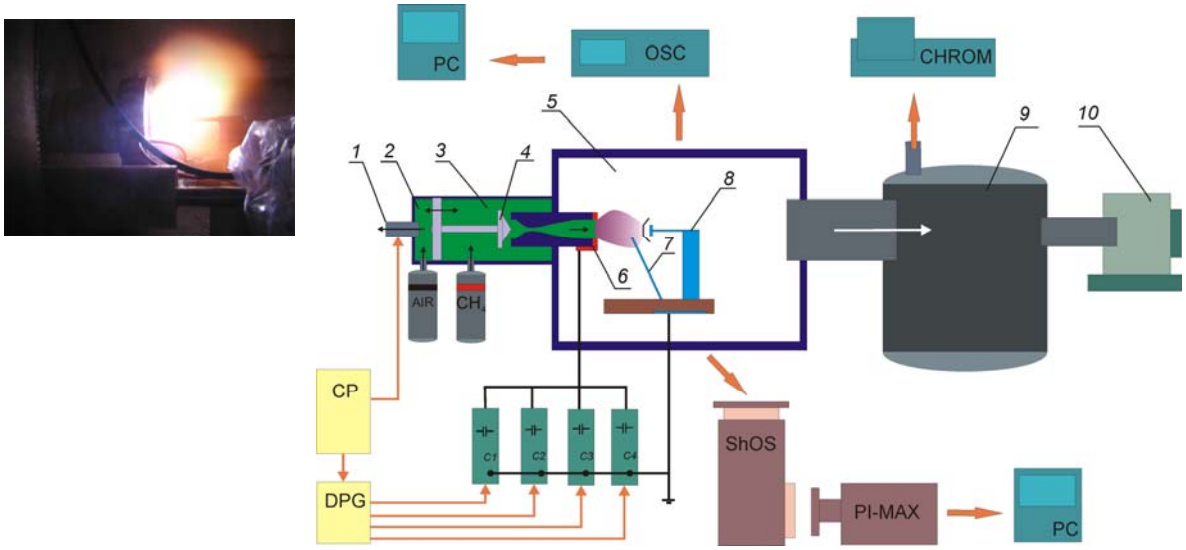

Figure 3. Supersonic reactor. Left: Photo of the impulse discharge in supersonic flow. Right: The reactor layout, where 1 – auxiliary-gas abutment pressure release valve; 2 – auxiliary-gas chamber; 3 – primary-gas chamber; 4 – «fast» valve; 5 – working chamber; 6 – annular anode; 7 – auxiliary electrode - cathode; 8 – pylon with installed target (electrode); 9 – low-pressure chamber; 10 – vacuum forepump; PC – personal computer; OSC – oscilloscope; CHROM – chromatograph; CP – control console; DPG – delayed-pulse generator; AIR – compressed-air flask; CH_4 – methane flask; C1, C2, C3, C4 – four capacitor-battery sections; ShOS – Schlieren optical system; PI-MAX – high-speed camera.

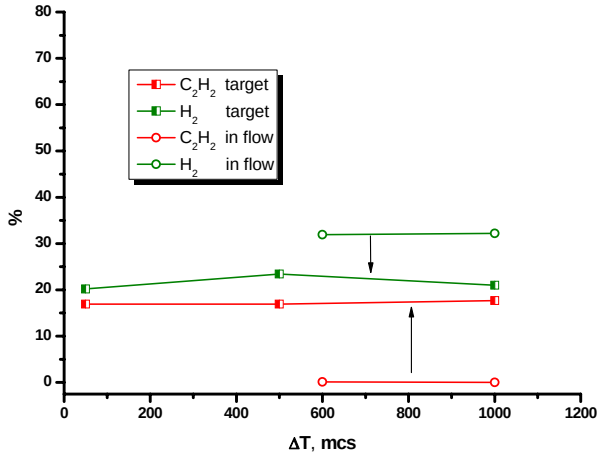

Figure 4. Percentage of acetylene and hydrogen in pyrolysis products obtained with energy supply in the form of a high-voltage pulse package and with flow deceleration at the target (the time delay between pulses is ΔT). The arrow shows the direction in which the percentage of the component of interest varies following the installation of the target.

A second method to organize the supply of energy to the reaction zone consisted in initiation of a high-power, high-current discharge there. The experiments in the present study were carried out in an experimental facility of ITAM. The facility consisted of 2-liter pre-chamber *3* filled, prior to the experiments, with working gas, methane, to a pressure of 5-10 at. (Fig. 3). After the «fast» pneumatic valve *4* was opened by relieving the abutment pressure, the working gas started emanating from the supersonic nozzle. At the nozzle outlet the gas directly entered the energy-input zone formed by annular anode *6* attached at the nozzle lip and by the point cathode located farther in the downstream direction at a distance L1. The target, on which, as a result of the deceleration of the reacting flow, the

methane underwent conversion with subsequent quenching of products during radial gas spreading, was located at a distance L2 from the cathode point (L1>L2). The energy was input into the reacting zone in the form of a packet of millisecond pulses formed by capacitor-battery sections, each section having a capacity 2.6 mF (Fig. 3). The pulses were generated with a delay ΔT. After the experiment, a gas sample was withdrawn from the exhaust pipe to analyze the exhaust gas chromatographically. The analysis of conversion products was carried out using Tsvet 500 and Kristall 2000M chromatographs.

A series of experiments with a nozzle allowing ejection of working gas at Mach number M=3.5 was carried out. The layout geometry of the electrodes and the obstacle was as follows: L1/L2=8, nozzle outlet-to-target diameter ratio – 3:1. The amplitude of the high-voltage pulses was as high as 1 kV, and the electric current was up to 10 kA. The delay value was varied in the range from 50 to 1000 μs. During one pulse, one section of the capacitor battery gave out into the stream 0.8-kJ energy.

Experimental series with energy inputs and with and without an installed target were carried out. The chromatographic analysis showed that, with the energy input into the supersonic flow, the main conversion product, in terms of hydrocarbons and hydrogen, was hydrogen (up to 35%). No acetylene was present in the sample. After the obstacle was installed in the experimental facility, the hydrogen content of the taken samples has reduced to 20% with simultaneous growth of the acetylene content to 18% (Fig. 4). As it is seen from the graph, a weak dependence of the produced amount of products (here, data for acetylene and hydrogen are shown) on the repetition frequency of pulses is observed. This result is consistent with our data on methane conversion in subsonic reactors at energy supply organized in pulsed-periodic mode [8].

To summarize, we have examined the possibility of initiating volumetric-uniform energy-release regions with the help of glow discharges ignited in a supersonic pyrolytic reactor. In pulse operation mode methane conversion up to 18% of acetylene was obtained. It was found that, by varying the discharge frequency, one can control the selectivity of final methane conversion products in sub- and supersonic reactors.

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