Investigation of Electric-Discharge Conversion of Gas Hydrocarbons

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Abstract – The investigation of conversion of propane, methane and his mixture is represented. The propane-to-liquid product conversion degree achieves 30–45%. The methane-propane mixture conversion degree at the volume content of propane 50% is close to the propane conversion degree. The possibility of methane-to-hydrogen conversion realization is shown.

1. Introduction

The gaseous hydrocarbon raw materials are a significant part in the fuel balance of the country. In Russia annually up to 15 milliards m^3 of accompanying oil gas which contains methane, propane, butane is combusted.

Traditionally for gas hydrocarbon conversion the catalytic thermal processes such as GTL (Gas to Liquid), MTG (Methanol to Gasoline), SMDS (Shell Middle Distillate Synthesis) are used. These processes go at high temperatures (~700–800 °C) and pressures (3–5 MPa) and require the application as constructive materials of high-priced steels and powerful heat-reflection. The capital output ratio, high power inputs, process sluggishness and negative influence on the environment are characteristics for these technologies.

There are no such disadvantages in the plasmochemical technology of gas hydrocarbon conversion. Due to the high electrons temperature and concentration in the reaction zone the volume velocity of chemical processes increases by order and more. The heat losses to the environment decrease because the energy is liberated directly in the reaction zone. The non-equilibrium of the plasmochemical processes allows to adjust selectively the chemical reaction channels. The conversion process is easy to be automated.

The barrier discharge type is used for plasmochemical reactions more often because it is well-investigated and simple in the technical performance. It is characterized by high stability; it means the parameters constancy even under the discharge condition change (pressure, temperature, gas).

2. Experimental Set-up

The gas hydrocarbons go through the flow gauge to the reactor (see Fig. 1). The pulsed voltage from the pulsed generator and water for cools both reactor electrodes are led to the reactor. The liquid products of conversion are accumulated in absorber. Gas products move away to the atmosphere or are taken for the analysis.

The nanosecond high-volt pulse generator is carried out according to the magnetic compression device. The parameters of generator pulses at the matched resistive load with generator impedance are given in the Table 1.

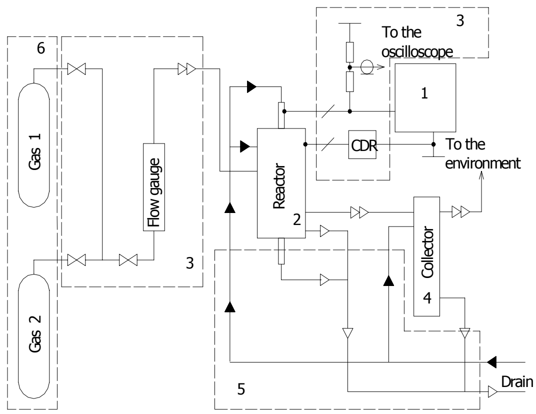

Fig. 1. The set-up scheme for gas conversion

The general drawing of the reactor of coaxial construction with dielectric barriers on the electrode is shown in Fig. 2.

The pulsed discharge parameters are measured by the current shunt and by the HV-divider. They are registered by the oscilloscope. The realized energy in plasma of barrier discharge was determined by the current and voltage oscillograms according to the known correlations. Its value is $W = 0.036$ J and does not depend on the pulse repetitive rate and velocity of gas supply to the reactor.

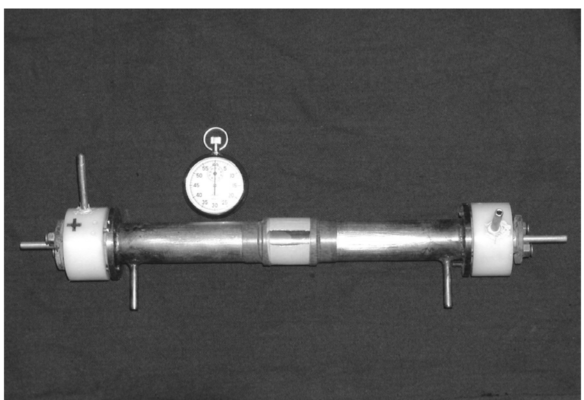

Fig. 2. The general drawing of the reactor

Table 1. Electric parameters of pulse generator

– pulse repetition rate	– 50, 250, 400, 1000, 1500 Hz
– electric power at the matched load (1500 Hz)	– 153 W
– energy per pulse	– 0.102 J
– voltage amplitude	– 30 ÷ 35 kV
– impedance	– 150 Ohm
– pulse duration at the half-height	– 100 ns

3. Plasma Propane Conversion

The preliminary experiments showed that at the pulse repetitive rate of 400 Hz and lower the conversion of domestic propane into liquid hydrocarbons is absent.

The relative coefficient of conversion *C* of propane was investigated depending on the gas expense through the reactor *Q*, pulse repetition rate and voltage pulse polarity. The measurements were carried out mainly at the positive pulse polarity as at the negative polarity the conversion degree is lower.

Figure 3 presents conversion degree *C* and mass m of the accumulated liquid products depending on the propane expense *Q* to the reactor. Table 2 shows the fractional composition of liquid product of the treated propane. The conversion degree C was determined as a ratio of the liquid products mass to the brought propane mass for treatment. The conversion degree enhances with the input energy increase. The maximum point of the curve $m = f(Q)$ corresponds to the optimal degree of gas treatment in the given conditions.

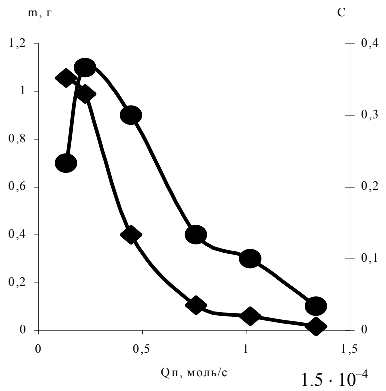

Fig. 3. The dependence of liquid product mass m and the propane conversion degree *C* on the gas expense *Q* (1.5 kHz)

Table 2. The fractional composition (% mass) of liquid product

Carbon atom number in the *n*-alkane molecule	Boiling *t*, °C	Fraction content C5-C13
C5	36.1	1.21
C6	68.7	4.16
C7	98.4	7.71
C8	124.7	17.42
C9	150.8	24.64
C10	174.1	24.54
C11	195.8	14.22
C12	216.3	4.98
C13	235.4	1.11
		100.00

The gas treatment time increases at the low *Q* values. This leads to the composition of already formed liquid products and to the decrease of their output. The radical concentration decreases at the increase of *Q* in the gas mixture. These radicals are capable to synthesize the liquid reaction products.

The maximal productivity of the experimental installation is $m = 1.1$ g of liquid for one operation hour. For this time 3.41 g or 0.08 mole of propane is collected in the reactor. The input energy to propane is $1.94 = 1.21 \cdot 10^{24}$ eV (electric energy $5.8 \cdot 10^{5}$ J is consumed). In the discharges 2.71 g or 0.061 mole of C_3H_8 was converted, and 0.816 $g = 0.0185$ mole of the untreated propane was left. In the conversion process more than 40 different new products were collected. The mass of liquid conversion products was 1.1 g, mass of gaseous products was 1.61 g including hydrogen – 0.0305 g or 0.0152 mole, methane – 0.26 g or 0.016 mole and ethane – 0.32 g or 0.011 mole. The power inputs for one molecule only of liquid product were 196 eV, only for one molecule of gaseous conversion products (hydrogen, methane, and ethane) were 47.4 eV and only for one molecule of hydrogen were 131 eV.

4. Methane-Propane Mixture Conversion

The accompanying gas is the mixture of methane, propane and other gases (the methane content in the mixture achieves 90%). To find out the possibility of methane-propane mixture conversion in the plasma of pulsed discharge seems to be the present-day task.

The experiments on methane-propane mixtures conversion were carried out at the positive polarity of voltage pulses, with the pulse repetition rate of 1500 Hz and treatment time of one hour. Figure 4 shows the dependence of the liquid conversion product mass m on the specific energy *W* for different methane-propane ratio. The methane in mixtures forms a larger part of the reacting treated molecules and particles. It takes the significant energy part realized to plasma. The concentration of active molecules and radicals which are capable to conglomerate to large molecules within plasma decreases, the possibility of their interconnection reduces. However, the mixture conversion effectiveness appears to be close to the propane conversion.

The mass of the accumulated liquid products depends on the propane concentration in the mixture and power inputs. In the mixtures with propane content less than 25–20% of volume conversion degree *C* to the liquid products decreases down to several per cents and evidently slightly depends on the power inputs.

5. Methane-to-Hydrogen Conversion

At the propane and methane-propane mixtures treatment by the pulsed discharges one of the conversion product is hydrogen. Its content in the gaseous conversion products achieves ~ 25%). The hydrogen output should increase if as an initial raw material the methane is used.

The experiments on the methane-to-hydrogen conversion were carried out at the same installation with the pulse repetition rate of 1500 Hz. The methane was supplied to the reactor with the expense of 1.5 cm^3/s. For an hour 5.4 liters (0.24 mole or 3.84 g) of methane were treated, 0.12 g of hydrogen (0.06 mole) was generated. The hydrogen content in the gaseous products of conversion, the methane-to-hydrogen conversion degree is 40%. The power inputs for hydrogen generation is $32.3 \cdot 10^5$ J/mole or $20.2 \cdot 10^{24}$ eV/mole.

6. Evaluation of Economical Effectiveness of Conversion Process

To estimate the economical process effectiveness we suppose that the target reaction products are liquid conversion products and hydrogen. The estimation will be done for the case of maximal generation of liquid products, see Fig. 3. For propane accumulation 0.58 MJ was spent for the electric main and 1.1 g of liquid products and 0.0305 g of hydrogen were obtained. Suppose that the accumulated products are expensed for electric energy production with the efficiency of 30 and 80%. The calorific efficiency of liquid products is taken as 51 kJ/g.

At the produced liquid combustion the energy $W_L = 0.55 \cdot 10^5$ J is liberated. At the hydrogen combustion the energy is $W_{H_2} = 0.34 \cdot 10^4$ J and total energy is $W_L + W_{H_2} = 58.4$ kJ. Then at the transformation efficiency of 0.3 the electric energy is $W_{0.3} = 17.5$ kJ and at the efficiency of 0.8 the energy is $W_{0.8} = 46.7$ kJ. So the power inputs for liquid products and hydrogen production are 27 and 12 times higher than the value of electric energy which can be obtained from these products with the efficiency of 0.3 and 0.8 correspondently. If to compare the electric energy liberated at the conversion products combustion with the realized to the discharge plasma energy these values will decrease by 3 times.

So due to the reactor and generator mode optimization the conversion effectiveness can be increased. To increase the process effectiveness the reactor without dielectric barriers at the electrodes would be used because the barrier discharge does not allow to use more than 50% of pulse generator energy.

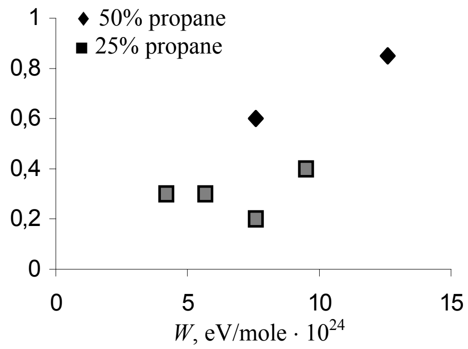

Fig. 4. The dependence of liquid product mass on the specific energy *W*

7. Conclusion

1. The methane-to-liquid product conversion was not observed under the influence on the gas by the pulses of nanosecond range in the discharges of barrier type. The special attention should be paid to the possibility of methane-to-hydrogen conversion realization.

2. The propane-to-liquid product conversion degree achieves 30–45%. The methane-propane mixture conversion degree at the volume content of propane 50 % is close to the propane conversion degree.

3. The power inputs of gas hydrocarbon conversion in the investigated range of parameters are ~ (7–20) · 1024 eV/mole. Nature gas conversion will be effective under the condition of power inputs decrease to 5–10 times.

4. The increase of conversion effectiveness is possible mainly due to the deep understanding of this process mechanism. To our mind the application of catalysis, organization of homolytical way of bond opening C-C and C-H can be perspective.

5. The application of some technical methods, for example, the increase of pulse generator efficiency will allow even now to decrease the energy imputs of conversion process by 2–3 times. The development of new reactor constructions, the application of different power supple and discharge types including nonsustain volume one should lead to the decrease of energy consumptions.