Fragmentation of Toluene by Non-Thermal Plasmas in Liquids

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Abstract. The influence of the energy of low-voltage discharges in the liquid phase on the directions of fragmentation of toluene is studied. The discharges were generated by a 60 V DC source with a capacitor of 90 μF, 20090 μF, and 40090 μF. Fragmentation of toluene leads to the formation of carbon structures on the surface of graphite electrodes and in a liquid medium. It was revealed that an increase in the power of electric discharges leads to the growth of carbon structures on the surface of electrodes, reduces the output of the gas phase and finely dispersed carbon structures. The morphology and composition of solid phase products were determined by scanning electron microscopy and energy dispersive X-ray spectroscopy. Nanosized carbon structures are obtained in the form of aggregates - carbon nanohorns, which actively absorb oxygen (content 0.9-3.6 at%). The composition of gaseous products was determined by gas chromatography. It was revealed that with an increase in the power of electric discharges, the hydrogen content slightly increases from 74.8 to 75.15 mol%, methane from 5.86 to 6.55 mol%, neopentane from 0.02 to 0.55 mol%. At the same time, the acetylene content in gaseous products decreases from 18.14 to 16.36 mol%.

1. Introduction

Investigations of the directions of transformation of substances occurring in liquids under the influence of electric discharges are of priority in the field of physics of low-temperature plasma [1-6].

The creation of plasma in liquid hydrocarbons can provide for the creation of reactors of small size with high productivity and process selectivity, different from the plasma formed in gaseous hydrocarbons. Under the action of plasma, cracking and reforming of liquid hydrocarbons occurs with the formation of carbon structures [7-11], hydrogen and light hydrocarbons [12,13].

Carbon particles can represent nanohorn-type structures (CNH). These structures are short tubes with a conical tip located in quasi-spherical aggregates. Single-wall carbon nanohorns (SWNHs) were synthesized in [14-16] by the method of ablation of pure graphite with a CO₂ laser with a high yield at room temperature. The individual tube SWNH has a diameter of about 2-3 nm and a length of 30-50 nm. Carbon nanohorns form spherical assemblies about 80 nm in diameter. CNH can be used for gas storage [17], in medicine [18,19] and electrochemical technologies [20-22]. The addition of toluene during arc evaporation of graphite increases the length of the CNH and leads to the functionalization of the surface [23].
This article is devoted to revealing the directions of fragmentation of toluene induced by low-voltage pulsed discharges in the liquid phase. The influence of the capacitance of the capacitors on the direction of the reaction is investigated. The results obtained in this work indicate that the action of low-voltage pulsed discharges on toluene in the liquid phase is an effective method for the preparation of nanosized carbon structures, hydrocarbons, and hydrogen.

2. Experiment
Toluene was used as a reagent (≥99.5%, Sigma Aldrich). Figure 1 shows the setup of the working reactor (made of Teflon, 40 cm³ capacity) used in this study; graphite electrodes (6 mm diameter) were mounted inside it. A 60 V DC voltage source (VS) with a capacitance of 90 μF, 20090 μF and 40090 μF was used to generate low-voltage discharges by varying the distance between the electrodes. The duration and power of discharge was controlled using a control unit. A detailed description of the discharge-control unit and impact-energy calculation can be found elsewhere [24, 25].

Table 1 shows the parameters of electric discharges during fragmentation of toluene under the action of electric discharges in the liquid phase.

**Table 1.** Dependence of the characteristics of electrical discharges on the capacitance of the capacitor C_ex.

| Characteristics of electrical discharges | Capacitor capacity, μF |
|-----------------------------------------|------------------------|
|                                        | 90         | 20090     | 40090     |
| Average pulse duration, ms              | 0.16       | 0.79      | 1.19      |
| Average pulse frequency, Hz             | 53         | 84        | 84        |
| Average pulse amplitude, A              | 30         | 31        | 30        |
| Average pulse energy, J                 | 0.004      | 0.02      | 0.04      |

A reflux condenser RC was used to prevent the reactant from evaporating (maintained at -15 °C). The temperature in the reactor does not exceed the boiling point of the reactant. The resulting gas was cooled and trapped in a gas trap (GT). The setup is such that pressure in the reactor is almost constant.

Table 2 presents the experimental data on the conversion of toluene and the yield of products with an experiment time of 30 minutes.
Table 2. Influence of the capacitance of the condenser on the degree of conversion of toluene and the yield of fragmentation products.

| Fragmentation parameters                      | Capacitor capacity, μF |
|----------------------------------------------|------------------------|
|                                              | 90         | 20090     | 40090     |
| Conversion, wt%                              | 9.2        | 17.1      | 20.6      |
| Yield of gaseous products, wt%               | 71.2       | 69.5      | 66.8      |
| Yield finely dispersed carbon structures, wt%| 28.8       | 20.2      | 16.2      |
| Yield of large carbon structures, wt%        | -          | 10.3      | 17.0      |

The morphology and elemental composition of solid products of toluene transformation were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a Supra 50VP scanning electron microscope (Carl Zeiss AG, Germany) with an INCA microanalysis system (Oxford Instruments). The composition of the gas phase products was determined by GC-FID on a Kristall 5000.2 gas chromatograph.

3. Results and discussion
Exposing toluene to an electrical discharge causes instant darkening of the liquid and rapid formation of gaseous products. The darkening of the liquid occurs due to the accumulation of carbon structures. During the experiment, solid structures are formed both in the liquid phase in the form of fine particles and in the form of large growths on the surface of graphite electrodes. These build-ups have poor adhesion to the surface of the electrodes and can be eroded into a liquid medium. An increase in the power of electrical discharges (Table 2) causes an increase in the rate of formation of solid structures. At discharges with an average pulse energy of 0.004 J, only nanoscale structures (yield 28.8 wt%) are formed in a liquid medium (Fig. 2a). An increase in the discharge energy to an average pulse energy of 0.02 and 0.04 J leads to the growth of carbon structures (2–5 mm in diameter) on the surface of the electrodes (yield 10.3 and 17.0 wt%, respectively). The yield of finely dispersed structures in a liquid medium decreases and amounts to 20.2 and 16.2 wt%, with a capacity of 20090 and 40090 μF, respectively. By morphology, carbon structures (Fig. 2) are carbon nanohorns in the form of tiny sheets of graphene wrapped in horn-shaped cones with a semi-fullerene cap, 30–50 nm in length and 2–5 nm in diameter [26]. They are structured into aggregates (spherical clusters or bundles), similar to flowers or «dahlia» buds.

Figure 2. Scanning electron micrographs of the solid products: 90 μF (i), 20090 μF (ii), 40090 μF (iii).
According to the results of analysis of the surface of carbon structures by energy dispersive X-ray spectroscopy, it can be seen that carbon structures obtained by fragmentation of toluene contain oxygen in their composition. When using a capacitor with a capacity of 90 μF, the carbon content is 98.8-99.1 at%, oxygen is 0.9-1.2 at%; 200 μF - carbon 96.4-97.8 at%, oxygen 2.2-3.6 at%; 400 μF - carbon 97.6-97.9 at%, oxygen 2.1-2.4 at%. The presence of oxygen in carbon structures is caused by its adsorption from air [27] during drying of samples.

The change in the discharge power also affects the composition of the formed gaseous products (Table 3). The composition of the main products formed in the gas phase is confirmed by the results of quantum-chemical prediction given in [28]. According to the data of quantum chemical analysis, fragmentation of toluene occurs through two competing parallel channels: C₇H₇ + H и C₆H₅ + CH₃ [28]. The formation of benzyl is the dominant channel, which upon further decomposition leads to the formation of hydrogen, acetylene and methane [29].

The yield of gaseous products decreases from 71.2 to 66.8 wt% with an increase in the discharge energy from 0.004 to 0.04 J. In this case, an increase in the content of hydrogen, methane, 2,2-dimethylpropane and C₆ hydrocarbons occurs. A decrease in the fraction of acetylene in the gas phase with an increase in the discharge power is probably due to its further decomposition [30], which is confirmed by an increase in the fraction of the solid phase and hydrogen.

| Component      | Capacitor capacity, μF |
|----------------|------------------------|
|                | 90         | 20090     | 40090     |
| H₂, mol%       | 74.80      | 74.94     | 75.15     |
| C₂H₂, mol%     | 18.14      | 17.40     | 16.36     |
| CH₄, mol%      | 5.86       | 6.15      | 6.55      |
| C₃H₄, mol%     | 0.58       | 0.55      | 0.67      |
| C₃H₄, mol%     | 0.53       | 0.43      | 0.55      |
| C₂H₆, mol%     | 0.04       | 0.03      | 0.03      |
| C₃H₈, mol%     | 0.02       | 0.03      | 0.03      |
| neo-C₅H₁₂, mol%| 0.02       | 0.39      | 0.55      |
| C₆₉⁺, mol%     | 0.01       | 0.08      | 0.11      |

4. Conclusions
Low-voltage electrical discharges generated in a liquid medium can be effectively used to fragment toluene. Changing the power of the electric discharge makes it possible to vary the directions of fragmentation of toluene. When discharges with an average pulse energy of 0.004 J are used, the yield of carbon nanohorns is 28.8 wt%; the growth of carbon structures on the electrode surface is not observed. With an increase in the average pulse energy from 0.004 J to 0.02 and 0.04 J, the yield of nanosized structures decreases from 28.8 wt% to 20.2 and 16.2 wt%, respectively. It was revealed that the obtained carbon structures actively adsorb oxygen from the air. Depending on the structure, the oxygen content in carbon structures varies in the range 0.9-3.6 at%. An increase in the power of the electric discharge leads to a decrease in the output of the gas phase. With an increase in the power of the electric discharge, an insignificant increase in the proportion of hydrogen from 74.8 to 75.15 mol% is observed, methane from 5.86 to 6.55 mol%, neopentane from 0.02 to 0.55 mol%. At the same time, the acetylene content in gaseous products decreases from 18.14 to 16.36 mol%.
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