The effect of electrically conductive additives on the plasma pyrolysis of heavy hydrocarbons

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Abstract. It’s shown that the electric discharge initiation of in-situ combustion can be executed by entering conductive additives to hydrocarbon raw materials. It is observed, that the most of all the soot is formed from aromatic hydrocarbons during the plasma pyrolysis. Cracking of hydrocarbons by electric discharge, with conducting additives and precursors of catalysts, leads to formation of carbon and metal nanoparticles.

1. Introduction

In the conditions of exhaustion of traditional energy resources, constantly increasing need of economy for hydrocarbons, oil production, and processing of heavy oils is an actual problem. One of the ways of extracting hardly removable oil is intra sheeted burning - a process at which the thermal energy is used received by burning oil in the formation when downloading in air layer is used. As a result of intra sheeted burning, the oil adjacent to a burning zone is diluted and gradually forced out to the second well, from which it is subsequently pumped out. The initiation of the formation of combustion occurs either forcibly or spontaneously. For acceleration of process of burning in layer initiation can be carried out using a gas burner, which is lowered into the bottom hole zone. Also the Immersed electric heaters and incendiary chemical mixtures are also used. Further maintenance of burning is carried out by downloading necessary the amount of oxygen (air). There were attempts of creation of the centers of burning by means of induction currents [1] and electric discharge of radio-frequency range.

In recent years, electrical discharges in the oil industry have began to be applied as the tool. For example, in work [2] the method of pulse plasma processing of the well was discussed with the purpose of elimination of contamination of the punched part and increasing the return of layers. Modern innovative technologies for well-drilling, especially when drilling hard rocks, suggest the use of plasma tools instead of rotating drills [3]. Various ways of influencing electric discharges on liquid hydrocarbons are discussed [4].

In this paper, we propose a new method for initiating intra sheeted burning using an electric discharge of direct or alternating current in a medium of electrically conductive liquid hydrocarbons.
2. Initiation of intra sheeted burning by electric discharge

The main idea of initiation of intra sheeted burning by electric discharge consists that the high-voltage electrode is lowered to the well, and include high voltage in an estimated zone of burning. An electrical discharge occurs between the electrode and oil treated processed by electroconductive additives. Further, when air is injected, the combustion zone extends to all depth of the oil tank. Figure 1 presents a schematic diagram of the initiation of intra sheeted burning by electric discharge.

![Figure 1. Schematic diagram of the initiation of intra sheeted burning by means of an electric discharge.](image)

For the primary processing of oil in the conditions of the layer, enter precursors of catalysts which get a burning zone, are restored to catalytically active metal complexes into a zone of burning. The Catalytic complexes in the conditions of intra sheeted burning promote primary oil refining by decomposition of heavy hydrocarbon components of oil into easier fractions. Precursors of of catalysts download in layer in the form of solutions of organometallic complexes in organic solvents. Therefore, it would be advisable to pump electroconductive additives together with a solution of precursors of catalysts.

In the processes of intra sheeted burning of one of the main problems is the coking of sand, it reduces the completeness of extraction of hydrocarbon raw materials. Therefore, another task of this work was to determine the conditions under which the chemical processes of burning (oxidation) soot is the most of all formed.

Proceeding from the above, the study of the interaction of an electric discharge with hydrocarbons of oil in the presence of organometallic complexes is an actual task.

3. The experimental part

As it is well-known, fluid hydrocarbons poorly carry electric current, therefore, it is rather difficult to organize an electrical discharge between electrodes, one of which is a hydrocarbon feedstock. To solve this problem, electroconductive additives soluble in fluid hydrocarbons were used in this paper. One of the effective formulations was a solution of sodium formate in acetone. The saturated solution of sodium formate was prepared in acetone with the concentration of 0.037 mg / ml. From this initial solution, tests of hydrocarbons with different specific resistivities were prepared. At an electroconductive concentration of 20%, the resistance of the hydrocarbon test was 1 MΩ. This concentration was chosen for the experiments. For the experimental studying of the plasma pyrolysis process, individual alkane hydrocarbons and aromatic hydrocarbons were used.

The experimental setup consisted of a reactor, a gas supply device, a power source and measuring devices. The reactor was made of the transparent heat-resistant glass, in which there was a metal
container for fluid hydrocarbon samples. The test of liquid hydrocarbons was a cathode. An anode was entered into the reactor from above. The anode consisted of coaxially arranged tubes, at the end of which there was an insert of silicon carbide. The tip had a central hole through which a working inert gas, helium, was carried out. The gaseous products which are formed in the discharge zone were discharged through the side openings of an external tube.

4. The results of experiments
To determine the optimum input power, the volt-ampere characteristics for various tests of hydrocarbon were taken. The volt-ampere characteristic of a discharge for a sample of oil with an electrically conductive additive is presented in Figure 2. At the current strength of 250 mA, the discharge power was 115W. Plasma pyrolysis of hydrocarbon feedstock passed efficiently both on a direct current and alternating current at a frequency of 50 Hz. During the experiments it was noticed that at increase in current intensity plasma pyrolysis occurred more intensively.

To ignite hydrocarbons in air, at atmospheric pressure it is required to carry out the electrical breakdown of the gas which is between the electrode and hydrocarbons. During the experiment it was necessary to determine the interelectrode distance at which there will be an electrical breakdown of air__ at atmospheric pressure and voltage 2100 V. The value of the interelectrode distance for air at atmospheric pressure calculated according to Paschen's law made 0.36 mm. The experiment was carried out in the air environment, the glass reactor vessel was dismantled. During the experiment, it was demonstrated the possibility of igniting fluid hydrocarbons with electrically conductive additives by means of an electric discharge.

Figure 2. Voltage-current characteristic of a discharge on a direct current.

During the experiments in all cases, soot and hydrocarbon gas were formed. Experiments were carried out on individual hydrocarbons, such as, octane, toluene and mixtures thereof. The most fine-grained was the soot obtained in the plasma pyrolysis of toluene, the size of the soot particles was 10-50 nm. The amount of soot formed in the case of toluene was maximal.

The influence on the plasma pyrolysis of liquid hydrocarbons of additives - transition metal resins in the amount of 1% of the total mass of liquid hydrocarbons was studied. The addition of resins did not have a significant effect on the current-voltage characteristics of the discharge. Carbon black, obtained by the pyrolysis of liquid hydrocarbons with the addition of copper rubber, had a red metallic tint, which is probably due to the presence of copper particles in this carbon black. An analysis of the elemental composition of this soot was carried out. The measurements were carried out on an auto-emission high-resolution scanning electron microscope Merlin (Carl Zeiss). The microscope is equipped with the AZtec X-Max energy dispersion spectrometer. Elemental analysis was performed
with an accelerating voltage of 20 keV and a working interval of 10 mm. The depth of sounding is about 1 micron. Elemental analysis of soot particles obtained by plasma pyrolysis of toluene with the addition of copper resinate showed that this soot contains about 1% copper. As you increase, you can see that the copper particle size is less than 90 nm, Figure 3.

![Figure 3](image.png)

**Figure 3.** The image of particulate matter at 20,000 times magnification.

5. **Conclusions**
During the experiments, it was shown that this method can be used to ignite hydrocarbons in the conditions of the formation. The amount of soot formed in the case of aromatic hydrocarbons was maximal, i.e. The main source of coke formation is aromatic compounds. The dispersion of different soot samples was determined. The most fine-grained was the carbon black, obtained by plasma pyrolysis of aromatic hydrocarbons. Copper nanoparticles were also produced, which were formed from copper.

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