

# Plasma-chemical pyrolysis of a mixture of fuel oil and methyl tert-butyl ether

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**Abstract.** NTP-pyrolysis of heavy petroleum products is a difficult task due to high viscosity, low hydrogen-to-carbon ratio and tendency to polycondensation with formation of high-molecular products. The use of oxygen-containing compounds for NTP-pyrolysis can reduce the yield of polycondensation products due to internal oxygen. In the present work, NTP pyrolysis of fuel oil in the presence of oxygen-containing additive (methyl tert-butyl ether) was carried out at a current source voltage of 700V. The influence of the content of the doping component in the range of 5-15 wt% on conversion, energy consumption and product composition was investigated. At increase in the content of methyl-tert-butyl ether up to 15 wt% in fuel oil the energy consumption decreases and the yield of gaseous products increases from 21.7 to 47.9 wt%. Carrying out NTP-pyrolysis process in the presence of oxygen-containing additive leads to an increase in the depth of processing of heavy fractions.

## 1 Introduction

The continuous growth of global energy demand leads to a continuous search for new oil resources that would be able to meet the demands of society [1-2]. Unconventional oil reserves significantly exceed light hydrocarbon resources and account for about 70% of total reserves, and can serve as an alternative to existing natural energy carriers [3-4]. Despite the possibility of high production of high-viscosity oils and bitumens, there is still a problem of their processing due to the low content of light fractions, high content of heteroatomic compounds and others [5-6]. The technologies used in the modern oil industry (visbreaking, catalytic cracking, delayed coking) cannot provide the necessary depth of processing, require maintaining high temperatures during the process, the use of catalysts, and also face a number of capital and energy costs [7-9].

The processing of heavy oils and petroleum products using nonthermal non-equilibrium plasma (NTP) pyrolysis in the liquid phase is currently being investigated by many scientific teams [10-11]. The advantage of NTP-pyrolysis is the absence of carbon dioxide emissions during the process, as well as the possibility of using renewable energy [12-13]. NTP is generated using electrical discharges in the liquid phase. Nonthermal plasma is able to circumvent the limitations associated with high temperatures, providing deep processing and high yields of sought-after products at near room temperature conditions [14-16].

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The use of doping components during the NTP-pyrolysis process allows increasing the yield of high-margin products. Introduction of oxygen-containing additives allows to obtain modified carbon structures in the solid phase. Dosed introduction of oxygen will allow to obtain oxidized high-molecular compounds that can be used as components of bituminous materials [17].

In the present work, the effect of methyl tert-butyl ether (MTBE) content on NTP-pyrolysis of fuel oil at a current source voltage of 700V was investigated. Material balance calculation, analysis of gaseous and solid phase products were carried out. Low energy costs for the process of NTP-pyrolysis and increase in conversion show the advantage of this technology using oxygen-containing compounds.

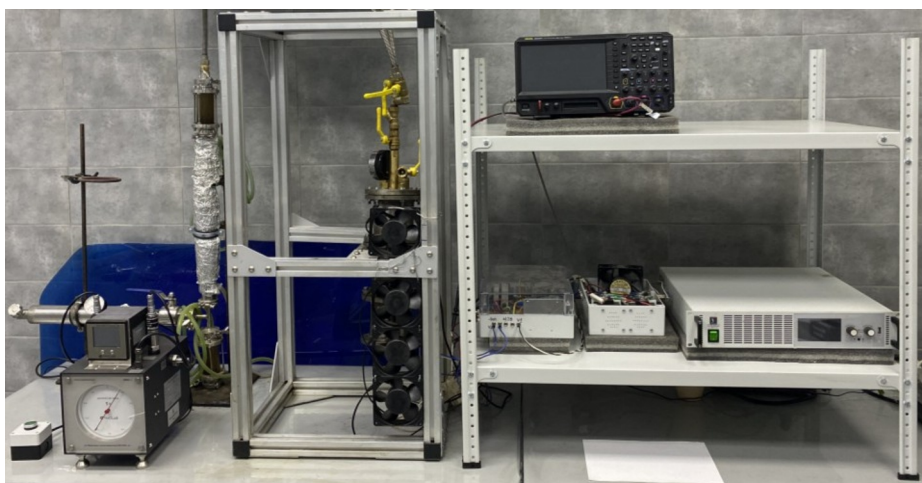
## 2 Material and methods

### 2.1 Characteristics of raw material

As a feedstock for NTP-pyrolysis was used fuel oil with sulfur content - 2.8 wt% and density at 20°C - 0.955 g/cm<sup>3</sup>, kinematic viscosity at 100°C - 31.2 mm<sup>2</sup>/s. Methyl tert-butyl ether with the content of 99.5 % was used as an oxygen-containing doping component. The mixture of fuel oil with MTBE was prepared in the ratio of 5, 10, 15% of the doping component to the initial oil product using a top-drive laboratory stirrer STEGLER MB-6.

### 2.2 Experimental setup

NTP-pyrolysis of fuel oil-MTBE mixture was carried out using an experimental setup (Figure 1), which includes a sectional plasma-chemical reactor, a system for control and regulation of the process and discharge parameters, a unit for collection and recovery of the resulting gaseous products [18]. The process was carried out at a reactor temperature of 80-120°C and a pressure of 2-3 atm. The volume of feedstock loaded was 300 cm<sup>3</sup>. The EA-PSI 9750-06 2U constant current source was used to generate discharges.



**Fig. 1.** Experimental NTP-pyrolysis unit.

Table 1 presents the characteristics of electrical discharges during NTP-pyrolysis of the fuel oil-MTBE reaction system at 700V.

**Table 1.** Characteristics of electric discharges in the process of NTP-pyrolysis of reaction system fuel oil-MTBE.

| MTBE content (wt%)          | 0    | 5    | 10   | 15   |
|-----------------------------|------|------|------|------|
| Average pulse duration, ms  | 2.3  | 2.5  | 2.4  | 2.5  |
| Average pulse frequency, Hz | 42.8 | 43.3 | 42.8 | 42.6 |
| Average pulse amplitude, A  | 14.4 | 19.3 | 15.8 | 18.0 |
| Average pulse energy, J     | 1.1  | 1.6  | 1.2  | 1.5  |

Gaseous products were analyzed by gas chromatography using a chromatographic gas complex "Chromatek-Crystal 5000.2". The gas flow rate was measured using a drum gas counter with liquid shutter VIKS-1. Determination of elemental composition of solid pyrolysis products of the reaction system was carried out using an elemental analyzer EMA 502 CHNS-O. The IR spectra were measured using a Fourier IR spectrometer FSM-1202.

### 3 Results and Discussion

#### 3.1 Characteristics of NTP-pyrolysis and analysis of gaseous products

Depending on the MTBE content in the mixture, the composition of gaseous and solid-phase products, energy consumption, and the degree of feedstock conversion change. Table 2 shows the results of NTP-pyrolysis of fuel oil-MTBE mixture at the content of doping component up to 15 wt%. The main gaseous products are (wt%): acetylene (7.1-15.8), light naphtha (8.1-18.0), propane-butane fraction (2.7-5.3), ethylene (2.1-4.6), hydrogen (0.9-2.3), methane (0.7-1.6) and minor ethane content. Amorphous carbon is predominantly formed in the solid phase.

**Table 2.** Characteristics of plasma pyrolysis of fuel oil-MTBE system and composition of gaseous products at voltage 700V.

| MTBE, wt%                                  | 0     | 5     | 10    | 15    |
|--|-------|-------|-------|-------|
| Experiment time, min                       | 113   | 122   | 113   | 134   |
| Conversion rate, wt%                       | 18.6  | 30.8  | 25.0  | 34.5  |
| Gas yield, wt%                             | 30.7  | 36.8  | 21.7  | 47.9  |
| Solid product yield, wt%                   | 69.3  | 63.2  | 78.3  | 52.1  |
| Energy consumption, kWh/kg of raw material | 10.5  | 6.8   | 8.1   | 6.6   |
| Energy consumption, kWh/ kg of gas         | 34.1  | 18.5  | 37.2  | 13.7  |
| Gas flow, ml/min                           | 287.3 | 558.9 | 236.8 | 561.3 |
| Plasma pyrolysis products, wt%             |       |       |       |       |
| Acetylene                                  | 14.7  | 13.1  | 7.1   | 15.8  |
| Light naphtha                              | 4.1   | 12.6  | 8.1   | 18.0  |
| Propane-butane                             | 4.6   | 4.3   | 2.7   | 5.3   |
| Ethylene                                   | 4.4   | 3.5   | 2.1   | 4.6   |
| Hydrogen                                   | 1.3   | 1.9   | 0.9   | 2.3   |
| Methane                                    | 1.4   | 1.2   | 0.7   | 1.6   |
| Ethane                                     | 0.3   | 0.2   | 0.2   | 0.3   |
| Amorphous carbon                           | 69.3  | 63.2  | 78.3  | 52.1  |
| Total, %                                   | 100   | 100   | 100   | 100   |

According to the experimental results (Table 2), the highest conversion and the lowest energy consumption in NTP-pyrolysis of fuel oil-MTBE mixture (15 wt%) were 34.5 wt% and 6.6 kWh/kg of raw material, respectively. In addition, the yield of gaseous products

increases from 21.7 to 47.9 wt%, and the yield of solid-phase products decreases from 78.3 to 52.1 wt%. As the doping component content increases, the yield of acetylene increases from 7.1 to 15.8 wt% and hydrogen from 0.9 to 2.3 wt%.

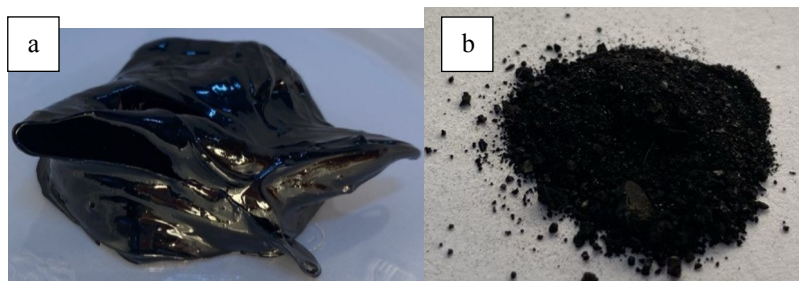
### 3.2 Characteristics of cube residues of NTP-pyrolysis of fuel oil-MTBE system

Table 3 presents the results of analysis of individual fuel oil and cube residues of NTP-pyrolysis of fuel oil-MTBE system. The results show that the content of solid structures decreases from 22.0 to 19.2 wt% as the content of the doping component increases.

**Table 3.** Characteristics of fuel oil and still bottoms of NTP-pyrolysis of mixture fuel oil-MTBE.

| MTBE, wt%                     | Fuel oil | Fuel oil (still bottom) | Still bottom |       |      |
|-------------------------------|----------|-------------------------|--------------|-------|------|
|                               |          |                         | 5            | 10    | 15   |
| Solid structures content, wt% | 28.4     | 13.7                    | 22.0         | 19.2  | 21.6 |
| Sulfur content, %             | 2.8      | 2.6                     | 2.3          | 2.7   | 2.8  |
| Non-volatile residue, %       | 30.6     | 56.3                    | -            | 47.6  | -    |
| Initial boiling point, °C     | 298.5    | 269.3                   | -            | 264.5 | -    |
| End-boiling point, °C         | 671.3    | 673.4                   | -            | 603.0 | -    |
| Evaporated, %                 | 69.4     | 43.7                    | -            | 52.4  | -    |

Figure 2 shows photographs of the cube residue (a) and solid product (b) isolated from the cube residue after NTP-pyrolysis of the fuel oil-MTBE reaction system (15 wt%).



**Fig. 2.** Photos of still bottom (a) and solid product (b) of NTP-pyrolysis of reaction system fuel oil-MTBE (15 wt%) at 700 V.

## 4 Conclusion

In the present work the influence of doping component (MTBE) NTP-pyrolysis of fuel oil was investigated. During the study of NTP-pyrolysis of fuel oil-MTBE reaction system, calculations of material balance, energy costs, as well as analysis of gaseous and solid-phase products were carried out. The results show that at addition of 15 wt% of methyl tert-butyl ether the highest conversion and the lowest energy consumption were observed, which amounted to 34.5 wt% and 6.6 kWh/kg of raw material, respectively. The main gaseous products during the NTP-pyrolysis process were acetylene, light oil, C<sub>3</sub>-C<sub>4</sub> hydrocarbons, ethylene, hydrogen, methane and ethane. The yield of gaseous products increased from 21.7 to 47.9 wt%. Amorphous carbon was predominantly formed in the solid phase, the content of which decreases from 78.3 to 52.1 wt%. The obtained results indicate that the process of NTP-pyrolysis in the presence of methyl tert-butyl ether is an alternative to existing methods of refining heavy oil and petroleum products.

## Acknowledgements

This research was funded by Russian Science Foundation, grant number 21-73-10119. <https://rscf.ru/project/21-73-10119/>.

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