

Low-temperature plasma-chemical pyrolysis of a mixture of fuel oil and water

*D A Shirokov*¹, *A A Udalov*¹, *D Y Titov*^{1*}, *E R Bodrikova*¹, and *E S Serova*¹

¹Nizhny Novgorod State Technical University named after R.E. Alekseev, 24, Minin Street, Nizhny Novgorod, 603155, Russia

Abstract. Plasma chemical aquatermolysis of heavy oil feedstock allows increasing the depth of oil refining and the yield of light hydrocarbons. In the present work, the process of NTP-pyrolysis of a mixture of fuel oil with water (10 wt%) in the liquid phase at 700V was carried out. The introduction of water (10 wt%) into the fuel oil leads to changes in the conversion rate, product composition and energy consumption. Addition of 10 wt% of water to fuel oil increases the conversion rate from 18.6 to 25.9 wt% and reduces energy consumption. The main products are carbon materials, acetylene, ethylene and C₃-C₆ hydrocarbons.

1 Introduction

Decreasing production of light oils forces to use heavy oil, the reserves of which significantly exceed the traditional oil [1]. Despite the significant resource base, there is a problem with the extraction and processing of heavy hydrocarbons due to the high content of heteroatomic compounds, asphaltenes, resins, and high viscosity [2-3]. Current technologies for extraction and processing of heavy hydrocarbon feedstock require modernization, as the currently used methods are not capable of providing high processing depth while maintaining economic profitability [4].

NTP-pyrolysis of heavy crude oil and petroleum products is one of the promising methods for processing heavy hydrocarbon feedstock with low carbon footprint using a renewable source of electricity [5-6]. Excitation of organic substances by non-thermal plasma action is possible at low temperatures in the reactor and does not require preheating and catalysts [7-8].

Due to the high carbon to hydrogen ratio in heavy petroleum products, the yield of light products is limited and viscosity increases significantly in the NTP pyrolysis process. The addition of water to heavy hydrocarbons will increase the degree of conversion, yield of demanded products and facilitate the technological process by reducing viscosity. Water molecules can generate radical particles (oxygen, hydrogen and others) when decomposing under the action of plasma. NTP-pyrolysis of a mixture of water and fuel oil leads to an increase in hydrogen yield [9-12].

The present work is devoted to the study of the influence of water on the NTP-pyrolysis of fuel oil in the liquid phase at 700V. Analysis of gaseous and solid products will help to

* Corresponding author: d.titov@nntu.ru

predict the mechanism of reactions in the process of NTP-pyrolysis of binary fuel oil-water system. Calculation of energy costs and conversion of the process will show the advantage of NTP-pyrolysis of fuel oil in the presence of water.

2 Material and methods

2.1 Characteristics of raw material

Fuel oil was used as a model compound of heavy petroleum product, which was mixed with distilled water (10 wt%). An ultrasonic laboratory dispersant was used for better mixing of the binary system. Fuel oil (density - 0.905 g/cm³ at 20°C, viscosity - 31.2 mm²/s, sulfur content - 2.7 wt%) was used as a model heavy oil compound.

2.2 Experimental setup

The experimental setup of NTP-pyrolysis [13] is presented in Figure 1. The unit consists of several reactors with a volume of 300 cm³ and a control system that allows setting the parameters of electric discharges. The voltage is set using a constant current source EA-PSI 9750-06 2U. At the reactor outlet there is a unit for collecting, capturing and measuring the volume of gaseous pyrolysis products. Current and voltage values are recorded by a Rigol MSO5074 oscilloscope with an interval of 2 minutes.

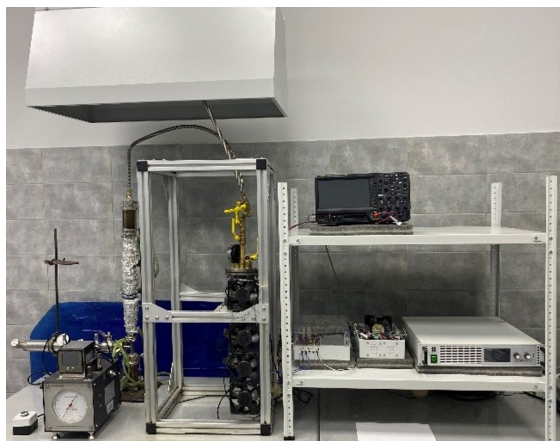


Fig. 1. Experimental installation of NTP-pyrolysis.

The process of NTP-pyrolysis of fuel oil and fuel oil-water mixture (10 wt%) was carried out at 80-100°C. Table 1 shows the characteristics of electrical discharges during NTP-pyrolysis of fuel oil and fuel oil-water system at 700V.

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

Water content (wt%)	0	10
Average pulse duration, ms	2.3	2.1
Average pulse frequency, Hz	42.8	45.5
Average pulse amplitude, A	14.4	9.4
Average pulse energy, J	1.1	0.6

Gaseous products were analyzed by gas chromatography using a chromatographic gas complex "Chromatek-Crystal 5000.2". The gas flow was measured using a drum gas meter with liquid shutter VIKS-1 for measuring the volume of gas media. Determination of the elemental composition of solid pyrolysis products of the fuel oil-water reaction system was carried out using an elemental analyzer EMA 502 CHNS-O. 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

Table 2 shows the results of the pyrolysis process of fuel oil and fuel oil-water mixture (10 wt%). In the gas phase, the major products were acetylene (12.3 wt%), light naphtha (4.7 wt%), propane-butane fraction (3.0 wt%), ethylene (3.0 wt%), and minor contents of hydrogen and ethane. Solid products of NTP-pyrolysis of the fuel oil-water system are amorphous carbon.

Table 2. Characteristics of NTP-pyrolysis of fuel oil and fuel oil-water system and composition of gaseous products at voltage 700 V.

Water content, wt%	0	10
Experiment time, min	113	100
Conversion rate, wt%	18.6	25.9
Gas yield, wt%	30.7	30.1
Solid product yield, wt%	69.3	69.9
Energy consumption, kWh/kg of raw material	10.5	7.5
Energy consumption, kWh/ kg of gas	34.1	25.0
Gas flow, ml/min	287.3	479.8
NTP-pyrolysis products, wt%		
Acetylene	14.7	12.3
Light naphtha	4.1	4.7
Propane-butane	4.6	3.0
Ethylene	4.4	3.0
Hydrogen	1.3	2.3
Methane	1.4	2.3
Ethane	0.3	0.2
Carbon structures	69.3	72.2
Total, %	100	100

Table 2 shows that at NTP-pyrolysis of fuel oil-water mixture in comparison with fuel oil pyrolysis the yield of solid-phase products increases from 58.9 to 72.2 wt% and hydrogen from 1.3 to 2.3 wt%. Probably, water acts as a donor of hydrogen radicals and increases the intensity of their formation in the reaction medium.

3.2 IR spectroscopy of cubic residues of NTP-pyrolysis of the fuel oil-water system

Figure 2 shows IR spectra of fuel oil, fuel oil cube residue and fuel oil-water mixture after pyrolysis at 700V. In the IR spectra of the pyrolysis residue of fuel oil-water mixture, more intense bands in the region of polyaromatic compounds are observed.

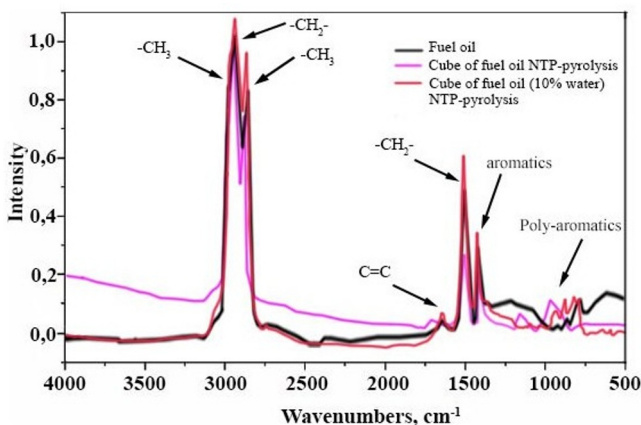


Fig. 2. IR spectra of cubic residues after NTP-pyrolysis at a water content of 10 wt%.

3.3 Elemental analysis of NTP- pyrolysis products of fuel oil-water system

Elemental analysis of solid products of NTP-pyrolysis of fuel oil and fuel oil-water mixture is presented in Table 3.

Table 3. Elemental composition of plasma pyrolysis products of fuel oil-water system at 700V.

Water content (wt%)	0	10
Carbon	85.9	86.7
Hydrogen	7.8	7.9
Nitrogen	1.0	1.6
Sulfur	3.2	3.5
Oxygen	2.0	0.4
C/H ratio	10.9	11.0

It can be seen from the above results that water molecules in NTP-pyrolysis of fuel oil have a weak influence on the composition of solid products.

4 Conclusions

NTP-pyrolysis of the fuel oil-water system (10 wt%) was carried out at a DC source voltage of 700V. Analysis of the results of NTP-pyrolysis of fuel oil and fuel oil-water mixture indicates the positive influence of water molecules on the process. The results show that the addition of 10 wt% water increases the degree of fuel oil conversion from 18.6 to 25.9 wt%, and also reduces the energy consumption from 10.5 to 7.5 kWh per 1 kg of processed fuel oil. Addition of water molecules to the reaction mixture allows to increase the hydrogen yield and reduce the viscosity of the mixture. The process of NTP-pyrolysis of fuel oil in the presence of water can compete with existing technologies and yield valuable products using renewable energy.

Acknowledgement

This research was funded by Russian Science Foundation, grant number 24-23-00351, <https://rscf.ru/project/24-23-00351/>

References

1. Vamsi Krishna Kudapa, K.A. Suriya Krishna, Mater. Today: Proc. (2023)
2. Youssef Yatimi, Jihane Mendil, Meena Marafi, Ahmed Alalou, Muthanna H. Al-Dahhan, Arab. J. Chem., **17** (2024)
3. A.V. Vakhin, M.A. Khelkhal, A.L Maksimov, Catalysts, **13**, 99 (2023)
4. Di Yu, Zhiwei Li, Jie Li, Jun He, Bo Li, Yin Wang, J Hazard Mater, **462**, 132618 (2024)
5. He Li, Mengyang Xia, Xiixin Wang, Ben Chong, Honghui Ou, Bo Lin, Guidong Yang, Appl. Catal. B: Environ., **342**, 123423 (2024)
6. Naser S. Matin, William P. Flanagan, Int J Hydrogen Energy, **49**, 1405-1413 (2024)
7. Shanshan Shao, Zian Ye, Jiayuan Sun, Chengyue Liu, Jinlong Yan, Tieyi Liu, Xiaohua Li, Huiyan Zhang, Rui Xiao, Fuel, **330**, 125420 (2022)
8. Jiaxing Song, Jun Wang, Jingyuan Sima, Youqi Zhu, Xudong Du, Paul T. Williams, Qunxing Huang, Chemosphere, **338**, 139535 (2023)
9. Liru Wang, Bing Sun, Xiaomei Zhu, Yanbin Xin, Zhiyu Yan, Fuel, **293**, 120400 (2021)
10. Alexis Tirado, Chengdong Yuan, Mikhail A. Varfolomeev, Jorge Ancheyta, Fuel, **310**, 122286 (2022)
11. F.A. Aliev, I.I. Mukhamatdinov, S.A. Sitnov, M.R. Ziganshina, Y.V. Onishchenko, A.V. Sharifullin, A.V. Vakhin, Processes, **9**, 127 (2021)
12. Riyi Lin, Kai Chen, Mingqiang Miao, Liqiang Zhang, Xinwei Wang, Ye Jiang, Jianliang Zhang, Yue Wang, Huida Pan, Energy Fuels, **34**, 2781-2789 (2020)
13. E.Y. Titov, I.V. Bodrikov, A.L. Vasiliev, Y.A. Kurskii, A.G. Ivanova, A.L. Golovin, D.A. Shirokov, D.Y. Titov, E.R. Bodrikova, Energies, **16**, 4017 (2023)