

Oxygen-induced Cracking Distillation of oil in the Continuous Flow Tank Reactor

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ABSTRACT

The article analyses problems of processing black oil fuel and addresses the possibility of increasing the depth of oil refining by a new processing scheme. The study examines various methods of increasing the depth of oil refining reveals their inadequacies and highlights a need to introduce a new method of processing atmospheric and vacuum residues by initiation a reaction of cracking by ambient oxygen. We identify the main physical and chemical parameters of source materials and reaction products. We used a continuous flow reactor with an active volume of 1,5 liters and a continuous supply of oxygen which allowed us to process up to 3 kg of feedstock per hour at temperatures of up to 500°C and pressure up to 10 atm. The conducted experiments using initiated cracking showed the possibility of a substantial increase the yield of light fractions (up to 50-70%), which is substantially higher than yield of these products on existing installations of thermal cracking. On the basis of experimental data we propose creating an industrial installation which would allow to considerably increase the depth of oil refining without significantly changing the existent technology while also preserving the flexibility and the cost-effectiveness of the process.

KEYWORDS

Black oil fuel, oil refining, continuous flow reactor, increasing the depth of oil refining, cost-effectiveness

ARTICLE HISTORY

Received 19 May 2016
Revised 25 June 2016
Accepted 11 July 2016

Introduction

At present the amount of oil which is produced and refined in the world is huge. The depth of oil refining (DOR) is a crucial parameter in these processes. It shows what part of oil is converted into useful products. In countries with

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highly developed oil refineries the DOR makes up over 90 % and often approaches 95-98 %. However, in Russia, the DOR is approximately 72% (Baldin, Danilov & Khudyakova, 2014; Hao, 2016; Bouzarovski, 2014). Given high prices of oil, many Russian companies are accustomed to processing large volumes of it with a low DOR and selling the rest of oil to advanced countries. However, under conditions of decreased cost of oil the question of DOR becomes especially relevant. At present industrialized countries various technologies which allow raising this indicator are employed, but they are quite costly and energy-consuming (Liew, Hassim & Denny, 2014; Boateng, 2015).

Literature Review

Thermal cracking was the first elaborated process for increasing the yield of light fractions (atmospheric distillate, included gasoline and diesel with boiling range from initial boiling point up to 350°C) from oil stock. At present the method is almost never used in its original form since it is outdated. The working plants most frequently have a two-furnace scheme for recycle cracking (Gruse & Stevens, 1964).

Visbreaking is a flexible and relatively effective thermal process of vacuum residues, which became widespread in the 1980s. The main goal of the process is to decrease the viscosity of the processed residues for using them as fuel oil (Kapustin & Gureyev, 2007). At present there are two types of the manufacturing process: coil visbreaking and soaker visbreaking. The processes result in as little as 5-20 % wt. and 16-20 % wt. of light fractions in refining vacuum and atmospheric residues respectively.

Because of the low yield of light fractions, visbreaking is not widely applied in countries with highly developed oil refineries. In Russia, in spite of the low quantity and quality indicators of visbreaking plants, this method is used for processing most of the vacuum residue. This is mostly accounted for by the relatively low cost and technological simplicity of the instrumentation, stability and flexibility of plant operation in case of variation of feedstock's quality (Batzhev, 2005).

Coking is the most rigid form of thermal cracking. Black oil fuel or heavy still bottoms of various production processes can be used, namely vacuum residue, black oil fuels, pyrolysis resins, cracked residues etc. (Obukhova et al., 2011). There are two main types of coking, namely delayed coking and continuous (fluid) coking.

Hydro-visbreaking, which is thermal hydrocracking, is a process of thermal cracking in the presence of hydrogen. It allows to increase the yield of light products and simultaneously reduce the content of sulfur in them (Pivovarova et al., 2002).

Hydrogen-donor solvent thermal cracking takes place not in the presence of molecular hydrogen but in the presence of hydrogen donor, i.e. a liquid-phase solvent. Tetrahydronaphthalene (tetralin) is a classical hydrogen donor, which is capable of dehydrogenating under conditions of radical cracking (Semenov & Taranov, 2010).

Plasma chemical cracking is based on the bombardment of feedstock by ions of hydrogen and of the hydroxyl group in the reactor without access of ambient oxygen. The ions are supplied to the chamber as plasma (Khakimov & Belichenko, 2011). High manageability and high selectivity as regards the end

product of plasma chemical reactions are achieved by controlling the rate and volume of feedstock's supply to the reaction chamber (Vinokurov, Sharafutdinov & Tychkov, 2005).

A magnetic field increases the homogeneity of the oil system as well as the depth of processing while simultaneously decreasing the formation of coke (Musayeva, Takayeva & Akhmadova, 2011).

A considerable number of studies are devoted to the processes of thermal cracking of fuel-oil residues with the use of various particulate materials, namely fossil fuels (shale and coal) (Maloletnev, Yulin & Vol-Epshtein, 2011), fresh or waste zeolites and catalysts (Golovko et al., 2009), mixtures of shale and zeolites, including with addition of organic compounds (condensed aromatic compounds, shale oil etc.) (Kotov & Gorlov, 2007).

Thermal cracking of heavy oil stock in the presence of homogeneous additives, which may include a wide range of substances, paraffins, isoparaffins, oxides, hydroxides, carbons of alkali metals and earth metals (Ralph et al., 1970), and salts of aromatic sulfonic acids (Varadaraj & Brown, 2005).

A great deal of research is concerned with the use of initiators of radical reactions that are capable of segregating into radicals in the process. Such initiators may include peroxides and azo compounds (Ki-Hyouk, 2009), substances containing mercaptoethylthial groups and mercaptans (Huang, 1979), alcohols (Oehr, 2013), benzoinform (Karpov, Krivstov & Golovko, 2011), iodine (Peiqing et al., 2012), nitre compounds (Cotte & Machin, 2002), simple ethers (Wiehe, Gorbaty & Olmstead, 1989) etc.

The article examines a new technology which presents a possibility in principle of low-cost modernization of plants for thermal cracking and visbreaking which provide for raising the DOR to 90-95 %. The proposed technology makes it possible to use refractory heavy oil residues for obtaining additional quantities of petrol, diesel fuel and bitumen. This technology allows to recycle heavy oil residues, such as vacuum gas oil, tar, fuel oil et al., which can reduce the costs for their disposal, further giving a certain amount of gasoline, diesel oil and bitumen. As an example, the article gives a detailed study of the process of initiated cracking of fuel oil of Ryazan Refinery.

Aim of the Study

The main goal is to analyze problems of processing black oil fuel, to examine a new technology which presents a possibility in principle of low-cost modernization of plants for thermal cracking and visbreaking which provide for the possibility of increasing the depth of oil refining by a new processing scheme.

Research questions

To identify the main physical and chemical parameters of source materials and reaction products and to carry out experiments using initiated cracking.

On the basis of experimental data to propose the creating an industrial installation which would allow to considerably increase the depth of oil refining without significantly changing the existent technology while also preserving the flexibility and the cost-effectiveness of the process.

Methods

The scheme of the installation is presented in Figure 1.

The raw feedstock from container C_1 with a volume of 40 liters, which is equipped with safety valve SV_3 for emergency depressurization and a ball valve for run-off of the feedstock with temperature 60-120°C and a plunger-type, proportioning pump (PPP) was fed into the heater F_1 . In order to prevent congelation of the feedstock, container C_1 , the head part of the PPP, the connecting piping, as well as tap T_1 were heated with external electric heaters.

Furnace F_1 heated the raw feedstock to the operating temperature 430-450°C. In order to increase the rate of heat transfer, furnace oil was stirred with blade mixer with the help of electrical drive ED_2 with the rate of rotation of 3000 revs per minute. The feedstock was then fed into reactor R with the active volume of 1,5 liters, which maintained the temperature within the limits of 430-450°C via electric trace heating. The pressure and the liquid level in the reactor were regulated with two valves V_2 и SV_1 according to the position of float gage and the pressure gage readings. The reactor was also equipped with safety valve V_1 for emergency depressurization.

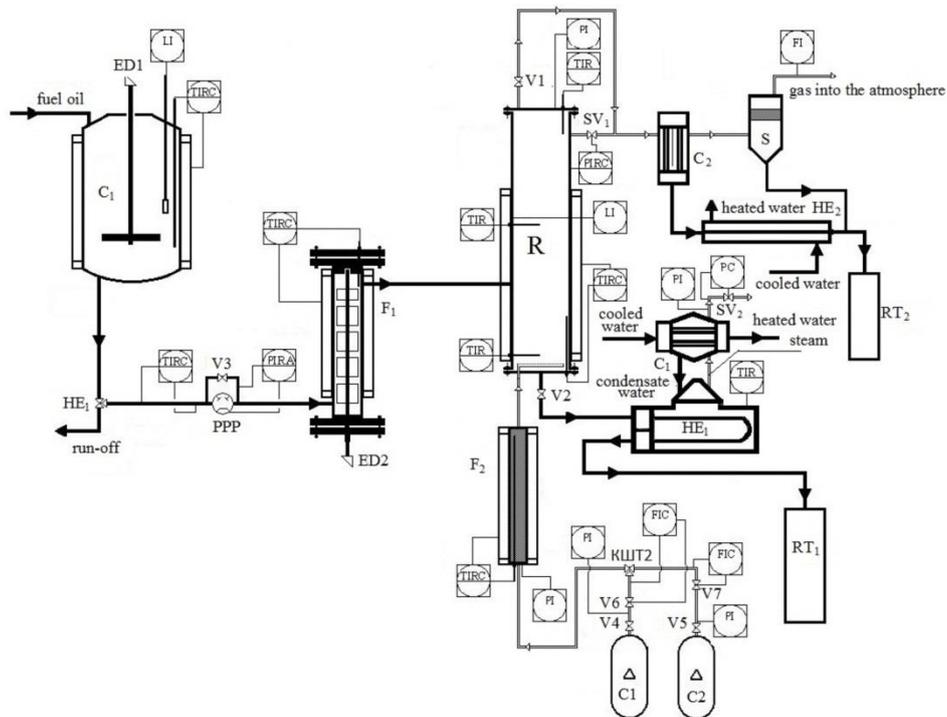


Figure 1. Scheme of flow-through installation of thermal-oxidative cracking. C_1 - container with feedstock, $F_{1,2}$ - furnaces, R - reactor, $HE_{1,2}$ - heat exchangers, $C_{1,2}$ - condensers, PPP - plunger-type, proportioning pump, $RT_{1,2}$ - receiving tanks

At zero time, i.e. during the heating of the reactor, a distribution device was used to supply fixed doses of nitrogen to its lower part from cylinder C_1 and when the process was stabilized, the supply of nitrogen was switched off and air was delivered from cylinder C_2 . Air was supplied at a rate which excludes the

appearance of oxygen at the reactor outlet. In most experiments, the amount of water formed during the conversion corresponds to all oxygen fed into the water. So explosive concentrations in the reactor zone were not created. Additionally, the lack of oxygen is the reason why we didn't examine formation of oxygenated compounds. The gases supplied to the distribution device had been previously heated to the temperature of the reaction (430-450 °C) in the electric furnace F₂, and the gas flow was controlled with variable area flow meters and regulated with the help of valves V₄ – V₇.

The cracking residue was collected from the reactor according to the level with the help of valve V₂ and sent to heat exchanger HE₁, where it was cooled to 100-150°C and collected in receiving tank RT₁.

Reaction gases mixed with nitrogen were deflected from the upper part of the reactor through V₁, which also played the role of the pressure controller in the reactor. The pressure in the reactor was adjusted so that the exhaust gas temperature does not exceed 280 °C and maintained within 0.1 atm. Then the exhaust gases were gradually channeled to refrigerating condenser C₂ и refrigerator H₁. There all the liquid products of the reaction were condensed and cooled to ambient temperature.

The cooled gas-liquid mixture was sent to gas-oil separator S. The gas phase which contained mostly nitrogen and cracked still gases (methane, ethane, ethylene, propane, propylene etc) was supplied to wet-gas meter, with the help of which their quantities were measured and then the gases were sent to burn. The liquid products from the separating vessel were collected in receiving tank RT₂ and analyzed for fractional composition, chemical composition, sulfur content, iodine value and others.

Basic properties of raw material (fuel oil of Ryazan Refinery) are summarized in Table 1.

Table 1. Basic properties of raw material - fuel oil of Ryazan Refinery

Property	Value
Sulfur content, wt. %	2,55
Flash point in open crucible, °C	118
20°C Density, kg / m ³	946
Fractional composition, °C:	
Start boiling	214,6
5%	314,7
10%	351,5
Yield up to 350 °C, % vol.	9,8
Yield up to 360 °C, % vol.	11,1
Viscosity at 100 °C	3,3
Kinematic viscosity at 100°C mm ² / s	22,2

In the process of investigation the following parameters were determined: composition of exhaust gases, the density of the experimental samples fractions, the sulfur content, the content of unsaturated hydrocarbons, aromatic hydrocarbons, solids content in the experimental samples of boiler fuels, conventional viscosity, the penetration of the needle depth, the softening temperature by the ring and ball experimental samples of bitumen. In all cases apparatus and methods were used according to Russian State Standards.



Data, Analysis, and Results

In order to be able to compare the results of initiated and non-initiated cracking as well as to discover the advantages of the developed technology, we conducted a number of experiments on initiated cracking of fuel oil at Ryazan Oil Refinery without addition of air.

The experiments were performed on the installation shown in Figure 1. The first stage included a series of experiments on varying the time of feedstock's stay in the reaction zone given diverse fixed temperatures and pressure. We identified the process mass balance, the qualitative composition of light fractions as well as properties of the cracked black oil fuel.

The findings of the experiments on the yield of light fractions, their group composition and typical distillation curve as well as of the research of properties of the heavy residue in this series of experiments are presented in Table 2 and Table 3, and in Figure 2 and Figure 3.

Table 2. The results of cracking of atmospheric fuel oil at P=3 atm, in the absence of initiator with different retention times of the reaction mixture in the reactor

Thermal cracking of fuel oil. Conditions: T=450°C, P=3 atm					
t, Retention time (min)	10.0	15.0	20.0	25.0	30.0
Yield of light fractions, % wt	14.4	26.2	35.3	39.3	44.5
Thermal cracking of fuel oil. Conditions: T=440°C, P=3 atm					
t, Retention time (min)	10.0	15.0	20.0	25.0	30.0
Yield of light fractions, % wt	12.5	22.7	30.7	34.7	38.7
Thermal cracking of fuel oil. Conditions: T=430°C, P=3 atm					
t, Retention time (min)	10.0	15.0	20.0	25.0	30.0
Yield of light fractions, % wt	10.3	17.2	23.8	29.1	32.8

Table 3. Group composition of light fractions of thermal cracking of fuel oil at various temperatures and retention time 20 min

Temperature, 0C	430	440	450
Olefins	12.6	17.9	23.5
Paraffins	64.8	58.1	52.7
Aromatic hydrocarbons	22.6	24.0	23.8

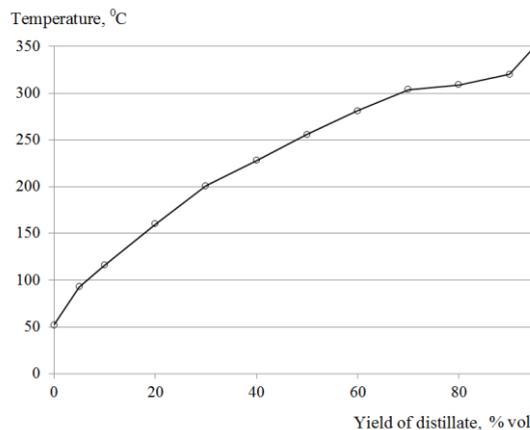


Figure 2. A typical distillation curve of Ryazan fuel oil cracking in the absence of an initiator

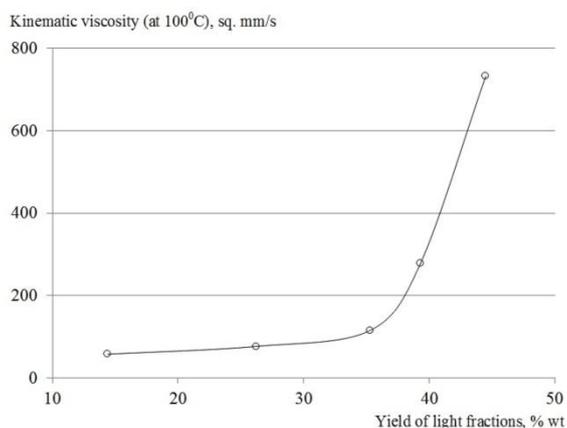


Figure 3. Dependence of kinematic viscosity (at 100°C) of the heavy residue of thermal cracking on the yield of light fractions at $T=450^{\circ}\text{C}$ and $P= 3 \text{ atm}$

As Tables 2, 3 and Figure 3 suggest, when the temperature and the duration of the reaction are increased, the yield of light fractions increases as well. This corresponds to the main kinematic and physical chemical characteristics of this process. The maximum yield of light fractions (44.5 % wt.) is recorded at maximum temperature and maximum time of stay ($T=450^{\circ}\text{C}$, t of reaction 30 min). However, we should note that the viscosity of black oil fuel increases when lighter fractions are removed from it (Figure 3). It is also noteworthy that the quality of residue does not satisfy the requirements of fuel oil and bitumen in case of maximum yield of light fractions. Moreover, it is necessary to explain that the obtained black oil fuel is impossible to use industrially. It must be disposed of, which implies extra spending.

The second stage of research consisted in performing experiments on thermal-oxidative cracking with variation of the quantity of supplied inducer, i.e. ambient oxygen.



On the basis of reference data, the following conditions were selected for the first series of experiments on the study of the process of initiated cracking of fuel oil: pressure $P=3$ atm, retention time 15 min and $T=450^{\circ}\text{C}$ under which a sequence of experiments was conducted with variation of the quantity of supplied air.

The results of this series of experiments are shown in Figures 4. It is necessary to note that the kinematic viscosity of the heavy residue of thermal-oxidative cracking changes insignificantly when light fractions of up to 45 % wt. are extracted. However, as larger quantities of light fractions are withdrawn, the kinematic viscosity of the heavy charge increases considerably.

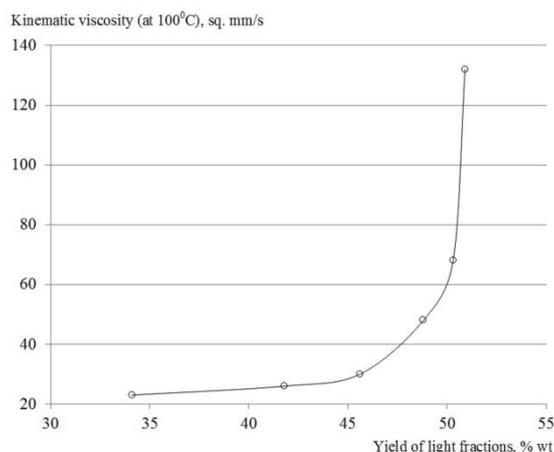


Figure 4. Dependence of kinematic viscosity (at 100°C) on the yield of light fractions with input initiator at $T=450^{\circ}\text{C}$, retention time 15 mins and $P=3$ atm (viscosity of the original straight-run fuel oil from Ryazan Oil Refinery is 22 sq.mm/sec)

Furthermore, a series of experiments was conducted to study the influence of temperature of thermal oxidative cracking on the yield of products. The results of these experiments are presented in Figure 5 and Figure 6.

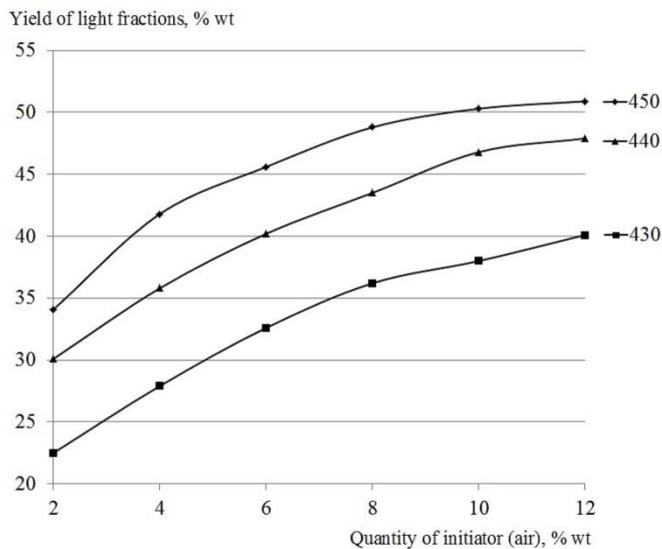


Figure 5. Dependence of the yield of light fractions of thermal-oxidative cracking of fuel oil on the quantity of the initiator. The light fractions were obtained at different temperatures with retention time 15 min and P=3 atm

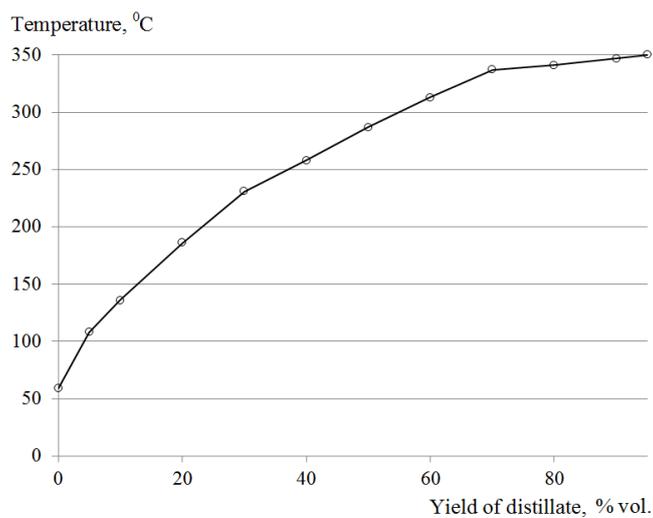


Figure 6. A typical distillation curve of Ryazan fuel oil cracking in the presence of an initiator

To follow up on this series of experiments, we conducted additional experiments at various temperatures, the results of which are shown and summarized in Figure 7.

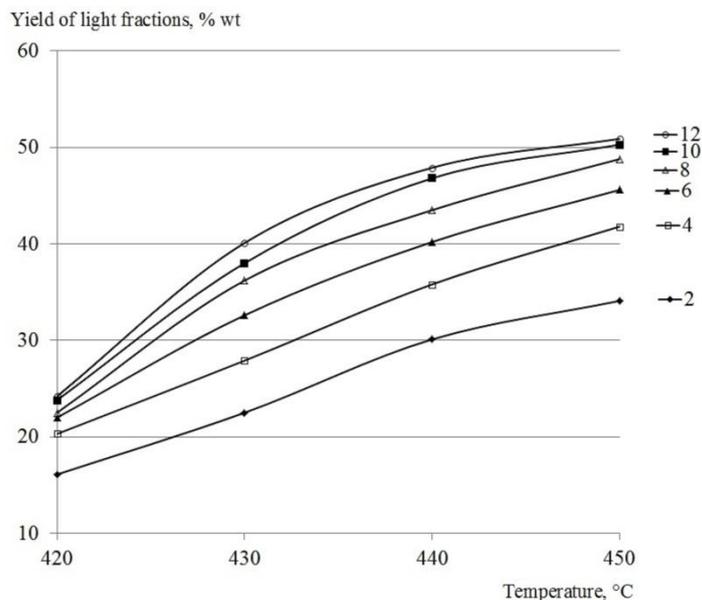


Figure 7. Dependence of the yield of light fractions in thermal-oxidative cracking of fuel oil on temperature. The input of initiator was varied

Discussion and Conclusion

In all the above experiments the dependence of the viscosity of the residue on the quantity of extracted light fractions is similar to the correlation in Figure 4.

On the basis of the above dependences of light fractions on the quantity of supplied initiator and temperature it is possible to conclude that when more than 8 % wt. of the initiator is supplied, the yield begins to decline.

Moreover, when analyzing the data shown in Figure 4-7, it becomes clear that when a substantial quantity of initiator is supplied, the yield of light fractions and kinematic viscosity of the heavy charge of thermal-oxidative cracking increases rapidly. The quality of light fractions is not fundamentally changed. Accordingly, most of the experiments were carried out in the range of initiator (6-8 % wt.).

The next sequence of experiments were conducted with variation of retention time of the feedstock in the reactor. According to earlier obtained data, scientific papers and our calculations, the estimated retention time in the reaction zone over which a noticeable increase in the yield of light fractions (compared to non-induced cracking) is achieved makes up 20 min. In view of this, the whole investigation was carried out with variation of retention time from 10 to 30 min.

The results of these experiments are presented in Figure 8.

As the obtained data suggest, when the quantity of input initiator (air) is increased to 8% wt, the yield of light fractions rises appreciably. However, when the initiator is increased to more than 8% wt, the yield increases but slightly.

Thus, the obtained data speak in favor of the earlier made selection of the quantity of the initiator between 6 and 8 % wt.

Moreover, when the time of the reaction is increased, the yield of light products of thermal-oxidative cracking rises. However, the obtained dependence is not linear and when the retention time exceeds 25 min, the rise in the yield is not substantial. Moreover, it is necessary to note that when the reaction time exceeds 25 min, the depth of needle penetration, i.e. one of the indicators of the quantity of bitumen, diminishes considerably (Figure 8).

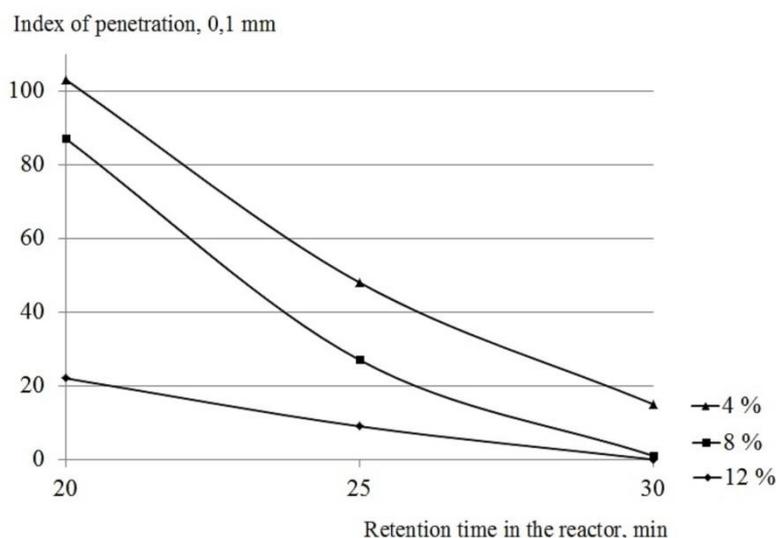


Figure 8. Dependence of the penetration index in the residue of thermal-oxidative cracking at 250C on the retention time in the reactor with a diverse inputs of the initiator

It should be noted that in addition to deterioration of the heavy residue in the hard conditions (an increased amount of the initiator, high retention time, high temperature) the beginning of coke formation were seen, what is unacceptable in the industry installations. However under less stringent conditions, coke formation is not observed. The averaged values of the parameters of various factions formed in the process of initiated cracking are presented in Table 4 and Table 5.

Table 4. The properties of the gasoline fraction (< 180°C)

Density, kg / m ³	690 - 720
Iodine number, g I ₂ /100 g fraction	65 - 70
Mass fraction of unsaturated hydrocarbons	30 - 32
Sulfur content, wt. %	0,8 - 1,0

Table 5. The properties of the diesel fraction (> 180°C)

Density, kg / m ³	840 - 860
Iodine number, g I ₂ /100 g fraction	35 - 38



Mass fraction of unsaturated hydrocarbons	27 - 30
Sulfur content, wt. %	1,6 - 1,8

**the viscosity of fraction >360 °C at 100 °C - 6,5 sq.mm/sec.*

The research showed a possibility in principle of using the initiated thermal cracking for increasing the yield of light fractions in the processing of black oil fuel. The performance is improved due to the formation of peroxide compounds under the influence of ambient oxygen. These compounds initiate radical reactions, which enhances cracking of fuel oil. Owing to a relatively low temperature of the process and the short retention time of the reaction mass in the reaction zone, there is almost no coke formed.

The yield of light fractions may reach more than 70% wt, and when the still bottoms correspond to the viscosity of the fuel oil, this yield may reach approximately 50-60% wt.(depending on feedstock), which considerably surpasses the results of visbreaking (16-22%). An optimal time of the process (about 20 minutes) and quantity of initiator (about 8%) can be connected with kinetics of the process of formation of peroxide compounds.

The small quantity of the initiator supplied makes the work of the plant safe, since it operates above the upper limit of the explosive range. The technology requires no expensive catalysts or complex equipment and can be implemented quickly by means of updating units for thermal cracking or visbreaking. The latter factor coupled with good performance indicators make this technology competitive. The obtained results can be reproduced industrially.

Implications and Recommendations

1. This technology of induced cracking may considerably increase the depth of oil refining given reasonable investment. The yield of light fraction (atmospheric distillate) can be increased up to 50-70 % versus 30-45 % during thermal cracking process without initiator.

2. Optimum conditions of induced cracking of fuel oil were found. The highest rate of yield of light fraction was measured at a temperature 450 °C and input of initiator of 12 %.

3. The yield of light fractions is compatible with the yield on expensive manufacturing units.

4. The lack of a heterogenous catalyst and, hence, centers of coke formation allows to increase effective production time.

5. The unit is capable of working on both light duty of processing, during which fuel oil and additional light fractions are produced, and heavy duty, during which bitumen is produced.

Acknowledgments

The research was conducted with financial support of the Ministry of Education and Science of the Russian Federation, project № RFMEFI57714X0107.

Disclosure statement

No potential conflict of interest was reported by the authors.

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