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EFFECT OF ULTRASOUND ON THE THERMOCHEMICAL DESTRUCTION OF FUEL OIL IN THE PRESENCE OF SHALE FROM THE KENDERLYK DEPOSIT

Abstract. In this article is represented the results of the influence of ultrasonic exposure on the process of thermochemical destruction of fuel oil in the presence of shale from the Kenderlyk deposit at different temperatures. A derivatographic analysis of suspensions was carried out before and after ultrasonic exposure for the selection of the working temperature range for the thermolysis of shale and fuel oil. It was established that the temperature of the onset of decomposition of the Kenderlyk shale and black oil organic mass is about 390-400 °C, and after ultrasonic treatment is 340 °C. Analysis of the results of the effect of temperature on the yield of thermolysis products shows that, under equal conditions, regardless of processing, with increasing process temperature, there is an increase in the yield of gas, gasoline fraction (initial boiling point is 180 °C), reaching maximum values in the temperature range of 415-425 °C. The yield of diesel fractions (180-360 °C) increases to a temperature of 415 °C, then begins to fall quite sharply to values lower than the yield of this fraction in the initial periods of the experiments (at temperatures of 395-415 °C). The yield of fractions boiling away at temperatures above 360 °C decreases with increasing temperature in the range of 395-435 °C. After ultrasonic exposure, the total yield of light distillates increases from 50.8 wt.% to 58.3 wt.%.

Key words: shale, fuel oil, hydrogenation, Kenderlyk, ultrasonic exposure, liquid yield, temperature.

Introduction. Due to numerous studies it was established that ultrasonic vibrations can disperse, emulsify substances, change their state of aggregation, and affect the rates of chemical reactions, diffusion in solutions, crystallization of substances from solutions and their dissolution. Flow cavitation hydrodynamic dispersers operating on the basis of the energy of fluid flow without using moving elements have found applications in various industries. Every year the number of publications devoted to the study of reactions that significantly change their speed or direction in the ultrasonic field increases. In relation to the effects of acoustic vibrations, the sound chemical reactions can be divided into two groups: some of them are accelerated in the ultrasonic field, but they can also occur in its absence, although at a lower speed, while other reactions do not occur at all without the influence of ultrasonic vibrations. For the implementation of both groups of reactions used high-frequency (2-10 MHz), mid-frequency (100 kHz) and low-frequency (10 Hz) vibrations. We have studied in the mid-frequency ultrasonic field the effect of ultrasound on the thermochemical destruction of fuel oil in the presence of shale in a different temperature range.

EXPERIMENTAL PROCEDURE

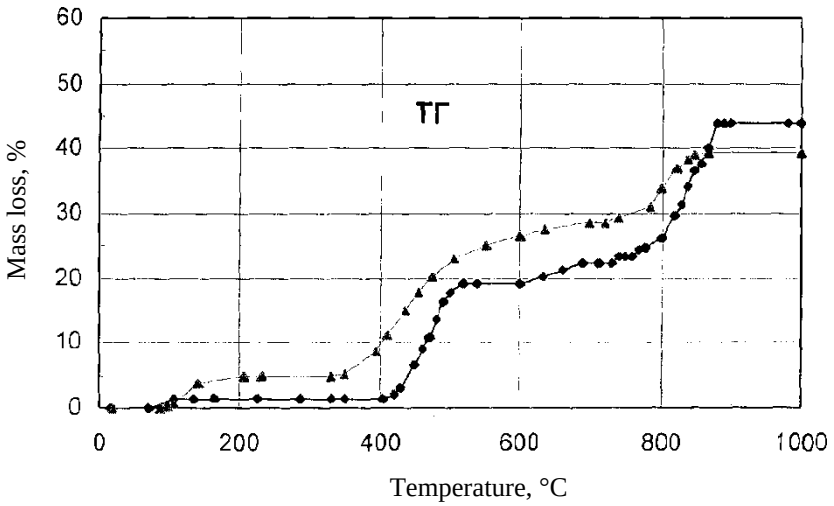
In order to study the process, the ultrasonic UZDN-2T disperser was used: frequency of 22 kHz, amplitude of vibration from the output of the transducer of 12 μm, from the tool end (acoustic waveguides with amplitude gain) – 20, 40 and 60 μm, acoustic power of 150 W at 80 °C .

Samples of suspensions before and after ultrasonic treatment were analyzed using modern methods [1-10].

RESULTS AND DISCUSSION

It is known that the main factors affecting the thermal cracking of black oil are the thermal stability of the feedstock, temperature, concentration, duration of the process, and pressure. Temperature plays a decisive role taking into account all the above-mentioned factors. Therefore, the effect of temperature on the process of thermochemical processing of fuel oil was initially studied. A derivatographic analysis of suspensions was carried out before and after ultrasonic exposure for the selection of the working temperature range for the thermolysis of shale and fuel oil (figures 1, 2) and it was established that the temperature of the onset of decomposition of the Kenderlyk shale and black oil organic mass is 390-400 °C, and ultrasonic treatment is 340 °C [1-10].

From the analysis of these data, it was found that the integral and differential mass loss curves for shale of different fractional composition can be divided into three main temperature ranges of decomposition for shale and fuel oil before ultrasonic exposure and two temperature ranges for exposed suspension. For



♦ – suspension before ultrasonic exposure; ▲ – suspension after ultrasonic exposure

Figure 1 – Integral mass loss curves for shale and fuel oil samples

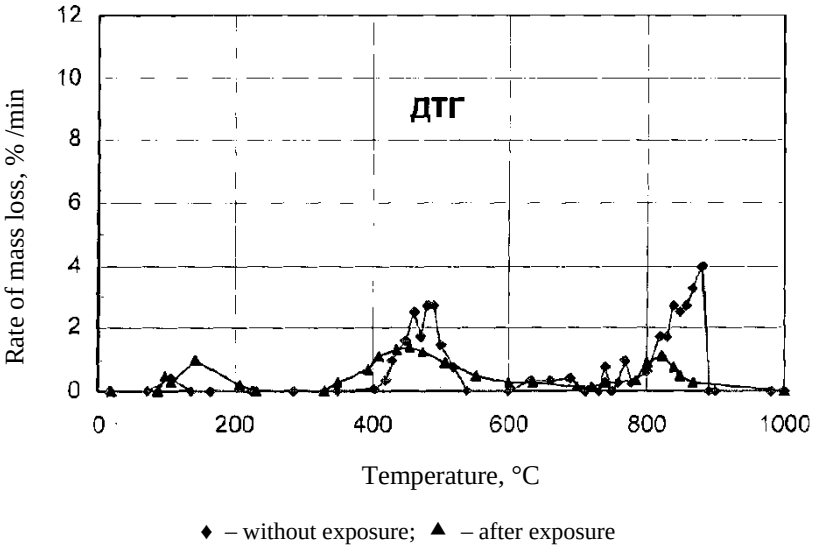


Figure 2 – Differential mass loss curves for shale samples

example, the decomposition of oil shale without ultrasonic exposure begins at a temperature of 380-400 °C. Intensive destruction of the organic component occurs regardless of the shale particle size in the range of up to 500 °C with a maximum speed at 460 °C (I interval). The interval of 600-700 °C is characteristic of the decomposition of carbonates. In the III interval from 780-795 to 880 °C, the mineral component of the shale is further decomposed [2-6].

There are differences in the magnitude of the mass loss in each of the temperature ranges Depending on the particle size distribution.

The smallest amount of the organic component, the destruction of which occurs in the I interval in the shale with a particle size of 0-0.1 and 0-0.063 mm. The mass loss of these shale fractions in this temperature range is 13-17.5 %. The greatest mass loss in this temperature range of 19-19.5% is typical for shale with a particle size of 0.063-0.1 and 0-0.2 mm [7-10].

On the other hand, a comparison of the samples under study makes it possible to reveal some regularities related to their mineral composition. Based on the above-mentioned data, it can be concluded that during shale grinding, the mineral phase is concentrated in small fractions of 0-0.063 and 0-0.1 mm, with the exception of calcium and magnesium carbonates, which, on the contrary, are concentrated in larger shale particles [7-10].

Therefore, studies of thermochemical processing of fuel oil in a mixture with shale were carried out in the temperature range of 395-435 °C at a concentration of shale in a mixture of 9 wt. % Shale concentration of 9 wt. % is selected according to the results of previous studies on the thermal cracking of a mixture of shale and fuel oil [11]. Isothermal time was 60 minutes. The shale particle size

distribution was 0-0.2 mm, which is also taken from literature data, where the particle size distribution ranged between 0-0.2, 0-0.3, and 0-0.5 mm.

The increase in the yield of light distillates (initial boiling point is 360 °C) demonstrates the difference between the number of light distillates originally contained in fuel oil and shale before ultrasonic exposure, and the number of light distillates obtained after carrying out the process of thermochemical processing of fuel oil containing shale additives after exposure.

The results of the experiments are shown in table 1, 2, and in figure 3.

Table 1 – The effect of temperature on the thermochemical processing of fuel oil with Kenderlyk shale. Conditions of 60 min., 9% shale, 5 MPa, without ultrasonic exposure

Thermolysis product, wt.%	Temperature, °C				
	395	405	415	425	435
Gas	3.0	4.4	5.5	7.1	9.1
Fraction of initial boiling point 180 °C	6.2	11.9	13.5	17.6	21.2
Fraction of 180-360 °C	30.8	34.9	37.3	31.0	23.2
Fraction of >360 °C including coke	60.0 5.0	48.8 5.5	43.3 5.3	44.3 4.8	46.5 5.0
Total yield of distillates	37.0	46.8	50.8	48.6	44.4

Table 2 – The effect of temperature on the thermochemical processing of fuel oil with Kenderlyk shale. Ultrasonic exposure conditions: T = 80 °C, frequency – 22 kHz, t = 60 min

Thermolysis product, wt.%	Temperature, °C				
	395	405	415	425	435
Gas	8.0	8.2	8.0	7.8	8.0
Fraction of initial boiling point 180 °C	7.6	11.3	17.5	25.8	29.0
Fraction of 180-360 °C	32.5	34.5	36.0	32.5	26.7
Fraction of >360 °C including coke	51.9 5.0	46.0 5.5	39.0 5.3	33.9 5.0	36.1 4.8
Total yield of distillates	40.1	45.8	53.0	58.3	55.9

According to table 2, a graph of the dependence of the total yield of light distillates on the process temperature (figure 3) is plotted. The figure shows that the yield of light distillates has a polynomial dependence on temperature (R = 0.9623).

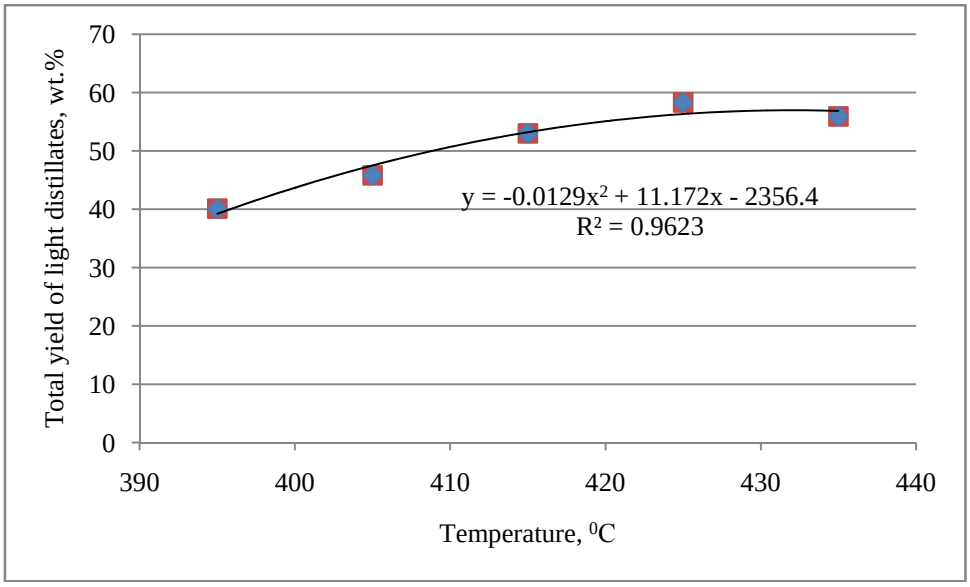


Figure 3 – The effect of temperature on the thermochemical processing of fuel oil with Kenderlyk shale (9 wt.% of shale), subjected to ultrasound exposure

The function describing the total yield of light distillates G (x, y) from temperature x and the yield of fractions >360°C y is as follows:

$$G(x, y) = 0.2239*x + 1.148*y - 0.005254*x*y . \quad (1)$$

The reproducibility of the function is shown in table 3, and its graph in the three-dimensional coordinate system is in figure 4.

Analysis of the results of the effect of temperature on the yield of thermo-lysis products shows that under equal conditions, regardless of processing, with increasing process temperature, there is an increase in the yield of gas, gasoline fraction (initial boiling point is 180 °C), reaching maximum values in the temperature range of 415-425 °C The yield of diesel fractions (180-360 °C) increases to a temperature of 415 °C, then rather sharply (compared to the left branch of the

Table 3 – Comparison of experimental and calculated data on the total yield of light products from temperature and fractions >360°C

The total yield of light products		Δ=(exp.-calc.)	100*Δ/calc., %
experiment	calculation		
40,1	40,3	-0,2	-0,4988
45,8	45,62	0,18	0,3930
53,0	52,69	0,31	0,5849
58,3	58,39	-0,09	-0,1544
55,9	56,31	-0,41	-0,7335

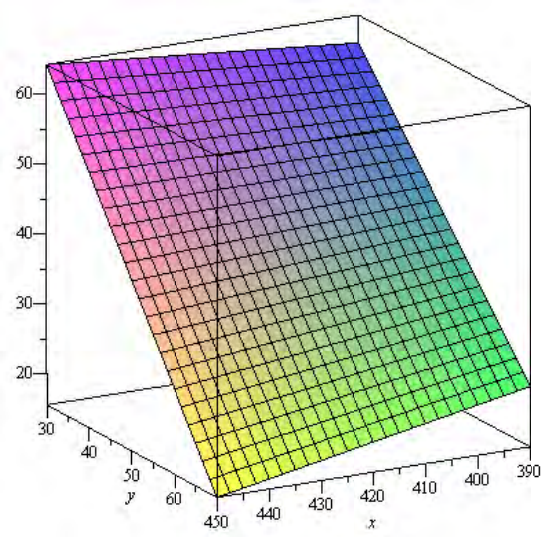
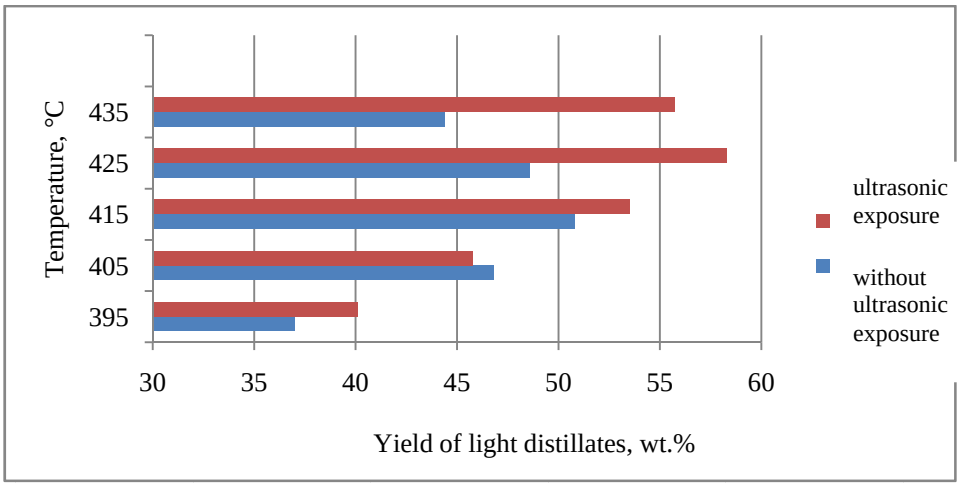


Figure 4 – Function graph G (x, y)

dependence curve) begins to fall to values lower than the yield of this fraction in the initial periods of the experiments (at temperatures of 395-415 °C). The yield of fractions of boiling away at temperatures above 360 °C decreases with increasing temperature in the range of 395-435 °C.

Thus, when considering the effect of ultrasound exposure on the thermolysis of shale-fuel oil paste, it has been found that the ultrasound exposure of feedstock reduces its thermal stability and increases the yield of light distillate fractions.



9 wt. % of shale, 425 °C, 60 min

Figure 5 – The yield of light fractions during thermochemical processing of fuel oil with shale

Comparison of the effect on the thermochemical processing of fuel oil in the presence of Kenderlyk shale without exposure and with ultrasonic exposure shows that the increase in light distillates at temperatures of 415-425 °C is noticeably greater when using ultrasound (figure 5). This, apparently, can be explained by the fact that the organic mass of shale after ultrasonic exposure (according to derivatography) begins to undergo thermolysis at lower temperatures than the organic mass of combustible shale without exposure.

When using combustible shale of the Kenderlyk deposit without ultrasonic exposure, preference should be given to a temperature of 415 °C. At this temperature, the yield of light distillates reached 50.8 wt. % When using exposed shale, the optimal process temperature is 425 °C and the yield of light distillates increases by 7.5 wt.%, i.e. is equal to 58.3 wt.%. These optimum temperature values confirm the assumption that the organic mass of the irradiated shale is less thermally stable.

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Резюме

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КЕНДЕРЛІК КЕН ОРНЫ ТАҚТАТАСЫ ҚАТЫСЫНДА
МАЗУТТЫҢ ТЕРМИЯЛЫҚ ЫДЫРАУЫНА
УЛЬТРАДЫБЫСТЫҢ ӘСЕРІ

Мақалада әртүрлі температуралық аралықта Кендірлік кен орнының тақтатасы қатысында мазуттың термохимиялық ыдырау үрдісіне ультрадыбыстық (УДӨ) өңдеудің нәтижелері келтірілген. Тақтатас пен мазут термолизінің жұмыс температурасының диапазонын таңдау үшін, суспензияларды ультрадыбыстық зерттеуге дейінгі және кейінгі үлгілеріне дериватографиялық талдау жүргізілді. Кендерлік тақтатастың және мазуттың органикалық массасының ыдырауының бастапқы температурасы 390-400 °С, ал ультрадыбыстық зерттеуден кейінгі температурасы - 340 °С болғаны анықталды. Термолиз өнімдерінің шығымына температураның әсер ету нәтижелерін талдау, барлық жағдайларда, технологиялық үрдіске қарамастан, өңдеу температурасының жоғарылауы газдың және бензин фракциясының жоғарылауына (б.қ.н. - 180 °С) 415-425°С максималды температуралық аралықта жетеді. Дизель фракцияларының шығымы (180-360 °С) алдымен 415 °С температураға дейін артады, содан кейін өте қарқынды түрде төмен құлдырап, осы фракцияның бастапқы зерттеулеріндегі мәннен де төмендейді (395-415 °С температурасында). 360 °С-тан жоғары температурада қайнайтын фракцияның шығымы 395-435 °С аралығындағы температураға дейін жоғарылап қайта азаяды. УДӨ-ден кейін жарық дистилляттар шығымы 50,8 масс.% -дан 58,3 масс.% -ға дейін артады.

Түйін сөздер: тақтатас, мазут, гидрогендеу, Кендерлік, ультрадыбыстық өңдеу, сұйық өнімдердің шығымы, температура.

Резюме

Ж. К. Каирбеков, И. М. Джелдыбаева

ВЛИЯНИЕ УЛЬТРАЗВУКА
НА ТЕРМОХИМИЧЕСКУЮ ДЕСТРУКЦИЮ МАЗУТА
В ПРИСУТСТВИИ КЕНДЕРЛЫКСКОГО СЛАНЦА

В статье приведены результаты влияния ультразвукового воздействия (УЗВ) на процесс термохимической деструкции мазута в присутствии сланца месторождения Кендерлык при различном интервале температур. Для подбора рабочего интервала

температур осуществления термолиза сланца и мазута был проведен дериватографический анализ суспензий до и после ультразвукового воздействия. Установлено, что температура начала разложения органической массы Кендерлыкского сланца и мазута 390-400 °С, а после ультразвуковой обработки – 340 °С. Анализ результатов влияния температуры на выход продуктов термолиза показывает, что в равных условиях, независимо от обработки, с ростом температуры процесса наблюдается увеличение выхода газа, бензиновой фракции (н.к. – 180°С), достигая максимальных значений в диапазоне температур 415-425 °С. Выход дизельных фракций (180-360 °С) сначала до температуры 415 °С возрастает, затем довольно резко начинает падать до значений более низких, чем выход этой фракции в начальные периоды экспериментов (при температурах 395-415 °С). Выход фракций, выкипающих при температурах более 360°С, уменьшается с ростом температуры в диапазоне 395-435 °С. После УЗВ суммарный выход светлых дистиллятов возрастает от 50,8 до 58,3 масс.%.

Ключевые слова: сланец, мазут, гидрогенизация, Кендерлык, ультразвуковое воздействие, выход жидких продуктов, температура.