

ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ  
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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ZH. K. KAIRBEKOV, E. A. AUBAKIROV, I. M. JELDYBAYEVA, E. T. YERMOLDINA

Al-Farabi Kazakh National University Republican State Enterprise  
Research Institute of New Chemical Technologies and Materials Affiliated State Enterprise,  
Almaty, Republic of Kazakhstan.

## THERMOLYSIS OF PETROLEUM PRODUCTS IN THE PRESENCE OF SHALE AND ZEOLITE

**Abstract.** This work presents the results of the process of thermolysis of straight-run fuel oil of the Pavlodar Oil Refinery using the Kendyrylk shale and zeolite of the Semey-tau deposit as an activating additive. By spectral analysis has been shown that there is a significant amount of elements which manifest catalytic properties ( $\text{Mo} = 6 \cdot 10^{-4} \%$ ,  $\text{Ni} = 2 \cdot 10^{-3} \%$ ,  $\text{Ti} = 1.8 \cdot 10^{-1} \%$ ,  $\text{Zn} = 50 \cdot 10^{-3} \%$ ) in zeolite treated at  $400^\circ\text{C}$ . The thermally treated zeolite was examined using thermogravimetric (DGA) and infrared spectroscopic analysis methods. It has been demonstrated that, the increase concentration of zeolite in the system from 1 to 5%, the yield of light petroleum products in the fractions increase and reach the values obtained in the use of combustible shale. Based on obtained data the effect of zeolites on the process of thermolysis of HOR (heavy oil residues), it can be said that the reaction of catalytic cracking of molecules of heavy materials occurs via the carbonium-ion mechanism both in the presence of an organo-mineral activator and of zeolite.

**Key words:** catalytic thermal treatment, activating additives, shale, fuel oil, zeolite.

**Introduction.** On the world market of raw materials, there are relatively high prices for the main energy carriers and mostly for oil. Economically developed countries, as well as countries such as China and Singapore, are forced to invest hundreds of millions of dollars in developing technologies for obtaining energy carriers from alternative renewable sources, the production of which is profitable only against expensive oil and gas.

In this regard, the problem of improving existing promising technologies for advanced oil processing and of developing the new ones is still a major concern for the domestic petroleum industry [1].

Together with "Institute of Fossil Fuels" FSUE we have developed an original process of thermochemical processing of heavy oil residues of native and destructive origin (fuel oil, tar, heavy tars of pyrolysis, cracked residues, used oils, etc.) in the presence of activating additives, which has no analogues abroad and is carried out in the range of pressure of 0.5-2 MPa, and temperature of 400-430  $^\circ\text{C}$  without hydrogen [2, 3].

Natural substances of sapropelite origin (combustible shales, peat, sapropelites, liptobiolites, bogheads, etc.) are used as activating additives. Their effect on oil residues has been studied by the example of the use of combustible shales.

Combustible shales actively promote the occurrence of hydrogenation reactions of unsaturated compounds formed during the cracking of oil residues and prevent intensive coke formation. On the other hand, the mineral part of

shales containing aluminosilicates, oxides of iron, molybdenum, cobalt, nickel and other catalytically active metals, also contributes to the intensification of the reaction of cracking and hydrogenation [4-5].

The process of thermal destruction of oil residues in the presence of organo-mineral activators (combustible shales) occurs via the carbonium-ion mechanism, and the mineral part of the shale plays the role of a coke pusher and to a certain extent has a catalytic effect, so we decided to intensify the process by using zeolites, which are acids of the Bronsted and Lewis.

## EXPERIMENT

This work presents the results of the process of thermolysis of straight-run fuel oil of the Pavlodar Oil Refinery using the Kendyrlyk shale and zeolite of the Semey-tau deposit as an activating additive. The experiments were carried out in a steel intensively agitated rotating reactor with a volume of 0.3 liters. The fractional composition of the raw materials and of reaction products was determined in accordance with GOST 2177. IR spectra of zeolites were recorded on a Perkin-Elmer-557 spectrophotometer. Samples of zeolites were ground, the powder was compressed in the form of tablets weighing 6-8 mg, which were placed in a special vacuum container, which allowed performing heat treatment of the sample and adsorption of various molecules from the gas phase. The vacuum system made it possible to reach a vacuum of  $10^{-6}$  Torr. The thermogravimetric studies were carried out with a MOM 1200 instrument. The linear temperature rise was carried out at a rate of 10 deg/min ( $\pm 1$  deg/min) from room temperature to 900 °C. Spectral analysis of the samples was recorded on Eplison X-ray fluorescence spectrometer.

Straight-run fuel oil of Pavlodar Oil Refinery with the following physical and chemical characteristics was used as raw material: density of 937 kg/m<sup>3</sup>, viscosity at 80°C 10.5 °E, content of asphaltenes 1.9 and of sulfur 2.2% wt.

Zeolite of the Semey-tau deposit was chosen as a catalyst. Physical and chemical characteristics of the zeolite of the Semey-tau deposit are as follows: color - reddish, gray; chemical composition: SiO<sub>2</sub> - 72.80%; Al<sub>2</sub>O<sub>3</sub> - 10.61%; Fe<sub>2</sub>O<sub>3</sub> - 1.50%; K<sub>2</sub>O - 5.04% and other metal oxides in small quantities. Ordinary shale of Kendyrlyk (W<sup>a</sup> - 0.8%, A<sup>d</sup> - 46.5%, CO<sub>2</sub> - 14%, H<sup>daf</sup> - 9.43%, S<sup>f</sup> - 1.51%, N<sup>daf</sup> - 0.26%) with particle size < 200 µm was used as an organo-mineral activator.

## RESULTS AND DISCUSSION

In order to optimize the thermolysis conditions, a study has been performed using shale and zeolite as an activating additive (table 1).

As is seen from table 1, when using zeolite of Semey-tau deposit as an additive in the amount of 5.0 % wt, the yield of light distillate fractions reaches the values obtained with 10.0% of combustible shale additive.

Table 1 – Catalytic processing of fuel oil in the presence of activating additives (688 K, processing time 60 minutes)

Additive	Additive quantity, % wt	Product yield, % wt				
		gas	up to 180 °C	180 to 360 °C	higher than 360 °C	coke
–	–	8.1	15.2	14.2	57.4	5.1
Shale	10	5.8	14.2	42.0	34.5	3.5
Shale-Semey-tau	5	3.0	12.3	33.4	51.5	1.8

Natural zeolite of Semey-tau deposit is classified as the type of minerals of clinoptilolite with the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.84$ . Such properties of natural zeolite as sorption, catalytic and molecular stability are observed only in its dehydrated state. Therefore, natural zeolite was heated at various temperatures at an interval of 473-1073 K.

Catalytic thermal treatment of fuel oil was studied on zeolites heated at various temperatures. The results are represented in table 2.

Table 2 – Influence of heat treatment on the catalytic properties zeolite and its concentrations at the thermolysis of fuel oil (688 K, processing time 60 min)

Temperature of heat treatment, °C	BET surface area, $\text{m}^2/\text{g}$	Additive quantity, % wt	Product yield, % wt				
			gas	up to 80 °C	180 to 360 °C	>360°C	$\Sigma_{\text{IRR}}$
200	40.2	1	3.0	13.8	30.1	53.1	43.9
		3	3.5	15.0	37.5	44.0	52.5
		5	4.2	16.2	39.5	40.1	55.7
400	62.5	1	4.0	12.1	34.5	49.4	46.6
		3	3.5	15.6	36.1	44.8	51.7
		5	2.5	18.2	40.5	38.8	58.7
600	56.1	1	4.1	11.3	30.1	54.5	41.4
		3	3.9	11.6	32.3	52.2	43.9
		5	3.6	13.2	34.6	48.6	47.8
800	28.5	1	4.5	10.6	29.6	55.3	40.2
		3	4.2	11.0	31.8	53.0	42.8
		5	4.0	12.8	35.1	48.1	47.9

As is seen from the table, the yield of products has increased by 12 % wt with the use of zeolite treated at 400 °C. The yield of the gasoline fraction has increased to 6 % wt, and the yield of the third fraction and of gas has decreased. This can be explained by the changes observed in zeolite treated at 400 °C. The processed zeolite is also characterized by a large specific surface (table 2). Based

on this, a zeolite treated at  $T = 400\text{ }^{\circ}\text{C}$  was used to determine the optimal conditions for the hydrogenation of coal.

By spectral analysis, it has been demonstrated that there is a significant amount of elements that are hydrogenation catalysts ( $\text{Mo} = 6 \cdot 10^{-4}\%$ ,  $\text{Ni} = 2 \cdot 10^{-3}\%$ ,  $\text{Ti} = 1.8 \cdot 10^{-1}\%$ ,  $\text{Zn} = 50 \cdot 10^{-3}\%$ ) in zeolite treated at  $400\text{ }^{\circ}\text{C}$ . These elements contribute to increasing the catalytic activity of the natural zeolite in the process of coal hydrogenation.

The thermally treated zeolite was examined using thermogravimetric (DGA) and infrared spectroscopic analysis methods. The results of DGA have shown that the process of dehydration of zeolite begins at the lowest temperatures, from about  $60\text{ }^{\circ}\text{C}$ , and proceeds continuously over a wide temperature range up to  $400\text{ }^{\circ}\text{C}$ , at the same time, the effect reaches its maximum between  $150$  and  $180\text{ }^{\circ}\text{C}$ . The water is discharged continuously and smoothly, which does not correspond to the character of the weight loss curve. This distinguishes clinoptilolite from other zeolites, in which the process of dehydration occurs in stages. Within the range of  $400$ - $500\text{ }^{\circ}\text{C}$ , the observed low endoeffects are caused by an addition of clay mineral, and the higher-temperature endoeffect at  $780$ - $850\text{ }^{\circ}\text{C}$  is caused by an addition of carbonate substance, the dissociation of which is recorded on the curves of DTA, DTG and TG.

In the IR spectra of zeolite, there are absorption bands in the wavelength range of  $3691$ - $3264\text{ cm}^{-1}$  corresponding to OH-groups in the range of  $1645\text{ cm}^{-1}$ , corresponding to hydroxonium ions  $[\text{H}_3\text{O}]^+$ , oscillations in the range of  $1219$ - $1043\text{ cm}^{-1}$  corresponding to the frame of Al,  $\text{SiO}_4$  ( $\text{TO}_4$ ). In zeolite treated at  $673\text{ K}$ , in the wavelength range of  $1423\text{ cm}^{-1}$ , OH-groups were found, which were not observed at other temperatures and are associated with Lewis aprotic centers. These changes can be explained by the restructuring of the zeolite frame due to the dehydration reaction.

It is shown (table 2) that, with the increase in the concentration of zeolite from 1 to 5%, the yield of light petroleum products fractions increases and reaches the values obtained in the use of combustible shale. The process occurs without pellet formation.

Table 3 – Effect of the shall: zeolite ratio on the thermolysis of fuel oil ( $415\text{ }^{\circ}\text{C}$ , 60 min)

Zeolite	Additive concentration, % wt.		Product yield, % wt					$\Sigma_{\text{IRR}}$	coke
	shale	zeolite	gas	up to $180^{\circ}\text{C}$	180 to $360^{\circ}\text{C}$	$>360^{\circ}\text{C}$			
400 $^{\circ}\text{C}$	9	1	5.7	15.2	38.6	38.3	53.8	2.2	
	5	3	5.4	13.1	38.6	39.8	51.7	3.1	
	3	3	5.2	14.2	38.8	39.3	53.0	2.5	
	1	3	4.8	15.1	38.6	38.8	53.7	2.7	
	5	5	5.0	13.8	41.5	37.1	55.3	2.6	
	3	5	4.9	14.3	42.2	36.4	56.5	2.2	
	1	5	5.5	17.6	45.2	27.9	62.8	3.8	

Cracking capability of zeolites, which are characterized by Lewis acidity, makes it possible to conduct thermolysis of fuel oil with the replacement of most of the combustible shale (table 3). With the ratio of shale: zeolite 1 : 3 (i.e., the total number of activators is 4%), the yield of light petroleum products during thermolysis of fuel oil reaches 57-59% with low coke formation (3 to 5 % wt). At the same time, the whole coke is deposited on the zeolite and is taken out with it from the reactor.

**Conclusion.** Based on the obtained data on the effect of zeolites on the process of thermolysis of HOR (heavy oil residues), it can be said that the reaction of catalytic cracking of molecules of heavy materials occurs via the carbonium-ion mechanism both in the presence of an organo-mineral activator and of zeolite.

Activating additives play the role of both a catalyst and a reservoir of coke deposits. Rich with coke solid phase of zeolite particles or of the mineral part of the combustible shale together with the unreacted residue can be used to obtain high-quality road bitumen. Thus, the results obtained indirectly indicate that combustible shales and, in particular, their mineral part are a catalyst for cracking fuel oil the same as natural and artificial zeolites.

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#### Резюме

*Ж. Қ. Қайырбеков, Е. А. Әубәкіров, И. М. Джелдыбаева, Э. Т. Ермолдина*

#### МҰНАЙ ӨНІМДЕРІН ТЕРМИЯЛЫҚ ӨҢДЕУ КЕЗІНДЕ ТАҚТАТАС ПЕН ЦЕОЛИТТИ ПАЙДАЛАНУ

Берілген жұмыста Павлодар МӨЗ тура айдап алынған мазутқа белсендіруші қоспа ретінде Кендерлік кен орны тақтатасы мен «Семей-тау» кен орны цеолитін қосу арқылы термоөңдеу үрдісі жүргізілген және оның нәтижелері көрсетілген. Спектральді талдау әдісі көмегімен 400°C дейін өңделген цеолит құрамында каталлизаторлық қасиет таниатын элементтер бар екендігі анықталды ( $Mo = 6 \cdot 10^{-4} \%$ ,  $Ni = 2 \cdot 10^{-3} \%$ ,  $Ti = 1.8 \cdot 10^{-1} \%$ ,  $Zn = 50 \cdot 10^{-3} \%$ ). Термиялық өңделген цеолит термо-

гравиметриялық (ДНА) және ИҚ-спектрлік талдау әдістерімен зерттелінді. Цеолит концентрациясының 1-ден 5%-ға дейін артырғанды мұнай өнімдерінің жеңіл фракцияларының өнімділігі артып, жанғыш тақтатас көмегімен алынған мәндерге жетеді. Цеолиттердің мұнайдың ауыр қалдықтарын термоөңдеу үрдісіне әсер етуі туралы алынған деректер негізінде, орғано-минералды активатор мен цеолиттің қатысуында ауыр шикізаттың молекулаларының каталитикалық крекинг реакциясы карбоний-иондық механизмі арқылы жүзеге асырылады деп айтуға болады.

**Түйін сөздер:** термокаталитикалық өңдеу, белсендіруші қоспалар, тақтатас, мазут, цеолит.

### Резюме

*Ж. К. Каирбеков, Е. А. Аубакиров, И. М. Джелдыбаева, Э. Т. Ермолдина*

#### ИСПОЛЬЗОВАНИЕ СЛАНЦА И ЦЕОЛИТА ПРИ ТЕРМОЛИЗЕ НЕФТЕПРОДУКТОВ

Приведены результаты процесса термолиза прямогонного мазута Павлодарского НПЗ с использованием в качестве активирующей добавки кендырлыкского сланца и цеолита месторождения «Семей-тау». С помощью спектрального метода анализа было показано, что в цеолите, обработанном при 400 °С, присутствует значительное количество элементов, являющихся катализаторами различных процессов ( $Mo = 6 \cdot 10^{-4} \%$ ,  $Ni = 2 \cdot 10^{-3} \%$ ,  $Ti = 1,8 \cdot 10^{-1} \%$ ,  $Zn = 50 \cdot 10^{-3} \%$ ). Термически обработанный цеолит был исследован с помощью термогравиметрического (ДГА) и ИК-спектрального методов анализа. Показано, что с увеличением концентрации цеолита от 1 до 5 % выход фракций светлых нефтепродуктов растет и достигает значений, получаемых при использовании горючего сланца. На основании полученных данных по влиянию цеолитов на процесс термолиза ТНО можно утверждать, что в присутствии как органоминерального активатора, так и цеолита протекает реакция каталитического крекинга молекул тяжелого сырья по карбоний-ионному механизму.

**Ключевые слова:** термокаталитическая переработка, активирующие добавки, сланец, мазут, цеолит.