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Original article

Thermal Destruction of Composite Raw Materials Based on Combustible Shale and Heavy Petroleum Products

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ABSTRACT
Background: The significance of this study stems from the necessity to broaden the hydrocarbon resource base as conventional oil reserves are steadily declining. Consequently, alternative sources like oil shale, which boast global reserves far exceeding those of traditional oil, have become a focal point of interest. Furthermore, incorporating fuel oil into composite feedstock's addresses the challenge of efficiently processing heavy oil residues, converting them into high-value motor fuel components.
Aim: Determining the effect of composite feedstock composition (shale/fuel oil) on thermal degradation parameters and investigating the physicochemical properties of the resulting products for their further application as motor fuel components.
Materials and Methods: The study objects included oil shale from the Kenderlyk deposit (East Kazakhstan Region, JSC "Quartz") and petroleum fuel oil from the Pavlodar refinery (Northeastern Kazakhstan). The hydrogenation process was studied using two types of equipment: in a rotating 2-liter autoclave and on a bench-scale flow-through unit (reactor volume 0.8 L). For the disposal of sludge (solid liquefaction residue), the pyrolysis method was used in a flow-through apparatus with a descending layer of solid heat carrier.
Results: Analysis of experimental data showed that increasing the hydrogenation temperature of oil shale from 410 to 440°C (at P = 8 MPa) intensifies gas formation from 10.2 to 12.2 wt.% and almost doubles hydrogen consumption to 1.6 wt.%, contributing to an increase in the yield of gasoline and diesel fractions. It was found that increasing the hydrogen pressure within the range of 4.0–8.0 MPa has a positive effect on the performance: the organic mass of shale (OMS) increases by 20%, while the yields of liquid products, gas, and water rise to 50.4, 10.5, and 7.7 wt.%, respectively. A further increase in pressure beyond 8.0 MPa is impractical, as it does not significantly affect the process. Optimization of the parameters of thermocatalytic processing of a mixture of fuel oil and shale made it possible to identify the best conditions: temperature 420°C, time 60 min, and concentration of shale as an activating additive 12 wt.%. In this mode, the total distillate yield reaches 59.2% by mass.
Conclusion: The fundamental feasibility and high efficiency of the co-processing of oil shale and heavy petroleum residues have been proven. The resulting liquid degradation products possess optimal physicochemical properties for the subsequent compounded processing of solid fossil fuels. They serve as a direct alternative to the scarce components of highly marketable motor fuels.
Keywords: *oil shale; fuel oil; thermal processing; liquid fuel; motor fuels.*

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Оригинальное исследование

Термическая деструкция композиционного сырья на основе горючих сланцев и тяжёлых нефтепродуктов

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АННОТАЦИЯ

Обоснование. Актуальность исследования обусловлена необходимостью расширения ресурсной базы углеводородного сырья на фоне постепенного истощения запасов легко добываемой нефти. В связи с этим особое внимание привлекают альтернативные источники, такие как горючие сланцы, мировые запасы которых многократно превышают запасы традиционной нефти. Использование мазута в качестве компонента композиционного сырья решает задачу квалифицированной утилизации тяжёлых нефтяных остатков, превращая их в высоколиквидные компоненты моторных топлив.

Цель. Установление влияния состава композиционного сырья (сланец / мазут) на показатели процесса термической деструкции и изучение физико-химических свойств полученных продуктов для их дальнейшего использования в качестве компонентов моторных топлив.

Материалы и методы. Объектами исследования послужили горючий сланец месторождения Кендерлык (Восточно-Казахстанская область, Казахстан, АО «Кварц») и нефтяной мазут Павлодарского нефтеперерабатывающего завода (Северо-Восточный Казахстан). Процесс гидрогенизации изучался на двух типах оборудования: во вращающемся двухлитровом автоклаве и на стендовой проточной установке (объём реактора 0,8 л). Для утилизации шлама (твёрдого остатка ожижения) применялся метод пиролиза в проточном аппарате с нисходящим слоем твёрдого теплоносителя.

Результаты. Анализ экспериментальных данных показал, что повышение температуры гидрогенизации горючего сланца с 410°C до 440°C (при давлении 8 МПа) интенсифицирует газообразование с 10,2 до 12,2%масс. и увеличивает расход водорода почти вдвое – до 1,6%масс., способствуя росту выхода бензиновых и дизельных фракций. Установлено, что рост давления водорода в интервале 4–8 МПа положительно влияет на показатели: степень превращения органической массы сланца возрастает на 20%, а выход жидких продуктов, газа и воды увеличивается до 50,4, 10,5 и 7,7%масс. соответственно. Дальнейшее повышение давления свыше 8 МПа оказывается нецелесообразным, т.к. не оказывает существенного влияния на ход процесса. Оптимизация параметров термокаталитической переработки смеси мазута и сланца позволила выявить наилучшие условия: температура 420°C, продолжительность – 60 мин, концентрация сланца как активирующей добавки – 12%масс. В данном режиме суммарный выход дистиллятов достигает 59,2%масс.

Заключение. В работе доказана принципиальная возможность и высокая эффективность совместной переработки горючих сланцев и тяжёлых нефтяных остатков. Полученные жидкие продукты деструкции обладают оптимальными физико-химическими свойствами для дальнейшей компаундированной переработки твердых горючих ископаемых. Они служат прямой альтернативой дефицитным компонентам высоколиквидных моторных.

Ключевые слова: *сланец, мазут, термическая переработка, жидкое топливо, моторные топлива.*

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Түпнұсқа зерттеу

Жанғыш тақтатастар мен ауыр мұнай өнімдеріне негізделген композициялық шикізаттың термиялық жойылуы

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АҢДАТПА

Негіздеу. Зерттеудің өзектілігі оңай өндірілетін мұнай қорларының біртіндеп сарқылуы аясында көмірсутек шикізатының ресурстық базасын кеңейту қажеттілігіне байланысты туындап отыр. Осыған байланысты әлемдік қорлары дәстүрлі мұнай қорларынан бірнеше есе асып түсетін жанғыш тақтатастар сияқты балама көздерге ерекше назар аударылады. Мазутты композициялық шикізаттың құрамдас бөлігі ретінде пайдалану ауыр мұнай қалдықтарын мотор отынының жоғары өтімді компоненттеріне айналдыру арқылы білікті түрде кәдеге жарату мәселесін шешеді.

Мақсаты. Композициялық шикізат құрамының (тақтатас / мазут) термиялық ыдырау процесінің көрсеткіштеріне әсерін белгілеу және оларды мотор отындарының компоненттері ретінде одан әрі пайдалану үшін алынған өнімдердің физикалық-химиялық қасиеттерін зерттеу.

Материалдар мен әдістер. Зерттеу нысандары Кендірлік кен орнының жанғыш тақтатасы (Шығыс Қазақстан облысы, Қазақстан, «Кварц» АҚ) және Павлодар мұнайды қайта өңдеу зауытының мұнай мазуты (Солтүстік-Шығыс Қазақстан) болды. Гидрогенизация процесі жабдықтың екі түрінде зерттелді: айналмалы екі литрлік автоклавта және стендтік ағынды қондырғыда (реактордың көлемі 0,8 л). Шламды (сұйылтудың қатты қалдығы) кәдеге жарату үшін қатты салқындатқыштың төменгі қабаты бар ағынды аппаратта пиролиз әдісі қолданылды.

Нәтижелері. Эксперименттік деректерді талдау жанғыш тақтатастың гидрогенизация температурасының 410°С-тан 440°С-қа дейін көтерілуі (8 МПа қысымда) газ түзілуін 10,2-ден 12,2%масс.-ға дейін күшейтетінін көрсетті, және сутегі шығынын екі есе дерлік арттырады – 1,6%масс. дейін, бензин мен дизель фракцияларының шығымдылығының өсуіне ықпал етеді. 4–8 МПа аралығындағы сутегі қысымының жоғарылауы көрсеткіштерге оң әсер ететіні анықталды: тақтатастың органикалық массасының өзгеру дәрежесі 20%-ға артады, ал сұйық өнімдердің, газдың және судың шығымы сәйкесінше 50,4, 10,5 және 7,7%масс.-ға дейін артады. 8 МПа-дан жоғары қысымның одан әрі көтерілуі мүмкін емес, өйткені бұл процестің барысына айтарлықтай әсер етпейді. Мазут пен шифер қоспасын термокаталитикалық қайта өңдеу параметрлерін оңтайландыру ең жақсы жағдайларды анықтауға мүмкіндік берді: температура 420°С, ұзақтығы – 60 мин, шифер концентрациясы активтендіретін қоспа ретінде – 12%масс. Бұл режимде дистилляттардың жалпы шығымы 59,2%масс.-ға жетеді.

Қорытынды. Жұмыста жанғыш тақтатастар мен ауыр мұнай қалдықтарын бірлесіп қайта өңдеудің принципті мүмкіндігі мен жоғары тиімділігі дәлелденді. Алынған сұйық деструкция өнімдері қатты жанғыш қазбаларды одан әрі компаундталған қайта өңдеу үшін оңтайлы физикалық-химиялық қасиеттерге ие. Олар жоғары өтімді мотор отындарының тапшы компоненттеріне тікелей балама болып табылады.

Негізгі сөздер: *тақтатас, мазут, термиялық қайта өңдеу, сұйық отыны, мотор отындары.*

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Introduction

The current state of the global energy sector is characterized by a decline in traditional oil reserves (not exceeding 90 billion tons) against the backdrop of the enormous resource potential of combustible shale concentrated in Russia, Kazakhstan, and Estonia. In these conditions, the search for effective methods of chemical processing of solid caustic biolites is of strategic importance for replenishing the deficit of hydrocarbon raw materials [1–3].

Previous studies (in particular, on the processing of Gdov and Volga shales) were based on the use of ultra-high pressures (up to 30 MPa). This technology is associated with critical wear and intensive erosion of equipment, and high cost of end products [3–4].

There is an urgent need to develop processes that operate under milder conditions. The transition to the use of moderate pressure while maintaining a high degree of conversion of organic mass of shale (OMS) is a priority task.

Joint processing of high-ash shale with oil residues not only expands the raw material base, but also significantly improves economic performance by reducing capital costs for high-pressure equipment.

Interest in combustible shale as a component of raw material mixtures for the production of motor fuels is due to its unique physical and chemical properties, which distinguish it favorably from traditional solid fuels (coal). The relevance of research in this area is based on the following key aspects:

Features of molecular structure: Organic mass of shale (OMS) is considered a self-associated multimer stabilized by weak electron donor-acceptor (EDA) interactions. Unlike highly metamorphosed coals, this structure allows up to 80% of OMS to be converted into low-molecular-weight liquid products under moderate thermal exposure (350–380°C), which opens up opportunities for the creation of energy-efficient technologies [5–6].

High reactivity: The predominance of naphthenic cycles and aliphatic chains, as well as the presence of labile oxygen-containing bonds, ensure high rates of OMS destruction. This enables the hydrogenation process to proceed under more moderate conditions than those required by traditional heavy oil processing techniques.

Resource efficiency and economics: The high hydrogen content in OMS (over 9%) significantly reduces its external consumption during the hydrogenation process. This key advantage makes shale processing more economically attractive compared to coal chemical processes [7–9].

Innovative potential of mixed raw materials: Using OMS as an activating additive (10–20%) to heavy oil residues (HOR) or coal allows the destruction of the latter to be initiated due to the high reactivity of shale. This approach is in line with global trends in petrochemistry, which are being actively developed in leading scientific and technological centers (Russia, Germany, USA, Japan) [10–12].

Thus, the scientific rationale for the joint processing of shale and fuel oil not only expands the resource base, but also significantly reduces the technological barriers (pressure, temperature, hydrogen consumption) that exist in modern oil refining.

Materials and methods

This paper presents the results of research on the hydrogenation of Kenderlyk oil shale, as well as its blends with fuel oil, aimed at producing motor fuel components; it also evaluates the current state and prospects of using low-pressure hydrogenation to address this challenge.

The raw material employed in the hydrogenation process consisted of combustible shale specimens sourced from the Kenderlyk deposit.

The shale concentrates had a particle size of less than 0.1–0.2 mm and contained (wt.%): W^a – 1.2–1.3; A^d – 18–22 (including carbon dioxide 2.4–2.5); S^d – 1.7–1.8. The elemental analysis of the samples yielded the following results (%daf): C – 74.2–74.7; H – 8.9–9.0; S – 1.2–1.4; N – 0.4–0.5; and O – 14.5–15.0. The gross calorific value (Q^{daf}) of the oil shale ranged from 31.5 to 33.4 MJ/kg. The composition of the mineral part, %: SiO_2 – 58.2; Al_2O_3+TiO_2 – 17.2; Fe_2O_3 – 7.3; CaO – 2.3; MgO – 1.0; SO_3 – 3.4; Na_2O+K_2O – 10.3 [13–14].

The composition of the hydrogenation off-gases was determined using a CHROM-5 chromatograph (a 3.5 m stainless steel column with a 3 mm internal diameter packed with CHN). The carrier gas (helium) flow rate was 5 L/h. The catharometer cells operated at 430 K with a current of 125 mA. The analysis of the gasoline fraction of synthetic oil was performed on a CHROM-5 chromatograph equipped with a capillary column and a flame ionization detector. Squalane, an individual triterpene hydrocarbon, was used as the stationary phase. The column length was 100 m. Argon was used as the carrier gas, while hydrogen served as an auxiliary carrier gas.

An oil shale paste was prepared by mixing 40 wt.% oil shale with 60 wt.% liquid oil shale products with a boiling point above 400–440°C obtained from the process itself and from pyrolysis of the liquefaction residue, was subjected to hydrogenation. The paste was added with 0.5–3.0 wt.% of catalysts, represented by appropriate polymetallic ores containing Fe.

The hydrogenation process was studied using two types of equipment: in a rotating 2-liter autoclave and on a bench-scale flow-through unit (reactor volume 0.8 L). For the disposal of sludge (solid liquefaction residue), the pyrolysis method was used in a flow-through apparatus with a descending layer of solid heat carrier.

Results and Discussion

1. Shale Hydrogenation

Autoclave testing demonstrated that an 82–84% conversion of the organic matter of shale (OMS) into liquid and gaseous products is achievable at 420°C and 8 MPa over a 60-minute period using iron-based catalysts. Temperature serves as a crit-

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ical factor influencing both the liquefaction degree of the OMS and the overall product yields (Tab. 1). Elevating the temperature from 410°C to 440°C leads to a rise in gas formation (from 10.2 to 12.2 wt.%) and hydrogen consumption (from 0.9 to 1.6 wt.%), stemming from the cracking of fractions boiling above 320°C. Consequently, the concentration of these heavy fractions in the hydrogenate drops from 22.6 to 16.9 wt.%, whereas the yield of gasoline and diesel fractions significantly improves. Extending the reaction time to 30–45 min exerts a comparable influence on the process dynamics.

Table 1. The effect of temperature on the hydrogenation outcomes of Kenderlyk oil shale

№	Indicator	Temperature, °C		
		410	420	440
1	Degree of OMS transformation, wt.%	83.3	84.6	82.3
2	Hydrogen for reaction, wt.%	0.9	1.3	1.6
3	Yield of liquid products, wt.%:			
	TOTAL	49.6	50.4	46.3
	with boiling point up to 320°C	27.0	28.6	29.4
	with boiling point above 320°C	22.6	21.8	16.9
4	Gas, wt.%	10.2	10.5	12.2
5	Water, wt.%	7.7	7.7	8.1
6	Coke on mineral part of oil shale, wt.%	2.6	2.8	3.5

Process conditions: ratio of shale to paste former – 1:1.5; pressure – 8 MPa; duration of the experiment – 60 min; a mixture of water-soluble salts of divalent and trivalent iron was used as a catalyst

Table 2. Characteristics of Kenderlyk oil shale hydrogenolysis as a function of process pressure

Process parameters	Hydrogen pressure in the reactor volume, MPa				
	4.0	6.0	8.0	9.0	10.0
Degree of OMOS transformation, wt.%	64.2	76.2	84.6	84.2	83.2
Hydrogen for reaction, wt.%	0.5	0.7	1.3	1.2	1.1
Yield of liquid products, wt.%	40.1	46.9	50.4	50.0	49.6
With boiling point up to 320°C	18.2	19.0	28.6	27.0	26.5
Residue with boiling point above 320°C	21.9	27.9	21.8	23.0	23.1
Gas, wt.%	6.7	8.8	10.5	11.1	10.6
Water, wt.%	5.5	6.9	7.7	7.7	7.7
Coke on mineral part, wt.%	1.9	2.2	2.8	2.4	2.6

Conditions: 1:1.5 shale-to-slurry oil ratio; temperature: 420°C; reaction time: 60 min; catalyst: a mixture of water-soluble Fe(II) and Fe(III) salts

The influence of pressure on the process of hydrogenolysis of oil shale was studied at temperature of 420°C and pressure within the interval from 4.0 to 10.0 MPa (Tab. 2).

Elevating the hydrogen pressure from 4.0 to 8.0 MPa results in an approximately 20% increase in the organic matter conversion of the shale, while the amount of hydrogen consumed in the reaction doubles. Concurrently, the yield of liquid products rises from 40.1 to 50.4 wt.%, while gas and water yields increase from 6.7 to 10.5 wt.% and 5.5 to 7.7 wt.%, respectively.

These trends demonstrate an intensification of Kenderlyk shale hydrogenolysis and an enhanced proportion of gasoline and diesel fractions. Notably, no significant improvements in process performance are observed at pressures exceeding 8 MPa.

The gasoline fractions (IBP – 180°C) are composed of 1.0–1.6% phenols, 34–38% neutral oxygen-containing compounds, 35–38% unsaturated, 15–17% aromatic, and 43–46% paraffin-naphthenic hydrocarbons. –Additionally, the mixture contains organic acid and pyridine base impurities, with a total sulfur content ranging from 0.5% to 0.7% (Tab. 3).

Diesel fuel fractions boiling between 180 and 320°C contain up to 8% C_6–C_8 phenols, with approximately 3% consisting of phenol, cresols, and xylenols. Additionally, they comprise 9% neutral oxygenates, 20–26% aromatic, and 30–33% unsaturated hydrocarbons, along with minor impurities (<1.3%) of organic acids and pyridine bases. These distillates serve as viable feedstocks for chemical production or, following hydrotreatment, as motor fuel components. The process water, enriched with water-soluble phenols (including dihydric and trihydric types), is also suitable for subsequent phenol extraction (Tab. 3).

Table 3. Characteristics of distillate products

Indicator	Fractions with boiling point, °C	
	up to 180°C	180–320°C
Content, vol.%:		
phenols	1.0–1.6	up to 8
neutral oxygen compounds	34–38	9
pyridine compounds	0.5–0.7	less than 1.3
Hydrocarbon group composition, wt.%:		
unsaturated	35–38	30–33
aromatic	15–17	20–26
paraffinonaphthenic	43–46	-

Conditions: ratio of oil shale: paste-former 1:1.5; pressure – 8 MPa; temperature – 420°C; experiment duration – 60 min; catalyst-mixture of water-soluble salts of two and trivalent Fe

Since the shale liquefaction products contain mineral ash and catalyst components, the residue remaining after partial liquid separation via centrifugation was subjected to pyrolysis at 440°C using a moving solid heat carrier. The generated coke was subsequently utilized to heat the heat carrier.

2. Thermocatalytic destruction of Kenderlyk oil shale and fuel oil

In recent years, the world market of raw materials has seen relatively high prices for major energy carriers and, above all, for oil. In this regard, the task of improving existing and creating new promising technologies for deep oil processing remains relevant for the domestic oil industry.

Improving deep oil refining processes is important for the environment and resources. Despite the availability of foreign solutions from companies such as Shell and Axens, their high capital intensity limits their implementation at domestic enterprises. This creates an urgent need to develop affordable domestic technologies that can compete with global engineering solutions [15–16].

A thermochemical process has been developed for the treatment of heavy oil residues of both native and destructive origin (such as fuel oil, tar, and heavy pyrolysis resins) in the presence of Kenderlyk shale as an activating additive. This unique technology, which has no foreign counterparts, is implemented without external hydrogen at temperatures

of 400–430°C and pressures ranging from 0.5 to 8 MPa [13–14, 17–20].

It was demonstrated that both the organic and mineral constituents of oil shales exert an activating effect on the thermal conversion of heavy petroleum fractions. Within the 370–420°C temperature range, the decomposition of the shale organic matter (kerogen) yields compounds that exhibit strong hydrogen-donor properties. They intensify the hydrogenation reactions of unsaturated compounds that occur during the cracking of petroleum residues (fuel oil) and at the same time reduce the system's tendency to form coke intensively.

The shale's mineral fraction, rich in aluminosilicates and transition metal oxides (Fe, Mo, Co), also promotes cracking and hydrogenation. Incorporating 5–25% oil shale as an activator allows for precise control over the thermal cracking of heavy residues at 390–450°C, yielding up to 70% light products with minimal carbonaceous deposits (under 5%). This process operates via a carbon-ion mechanism, with the mineral phase facilitating coke removal and providing auxiliary catalytic activity. In this regard, it was decided to enhance the process with zeolites, which act as Bronsted strong acids.

Table 4. Physical and chemical properties of fuel oils

Fuel oil type	Density, kg/m³	Fractional composition, vol.%			Conditional viscosity at 80°C, °E	Content, wt.%			
		Initial boiling point, °C	Initial boiling point, 360°C	boils out before reaching 450°C		waters	asphaltenens	sulphur	mechanical impurities
Straight fuel oil from Pavlodar refinery	938	251	12.5	45.9	10.4	0	1.8	2.3	0

Table 5. Dependence of product yields from thermocatalytic processing of fuel oil and shale mixtures on process parameters: temperature, time, and additive concentration

Thermolysis product	Amount of oil shale, wt.% (420°C, 60 min)						Temperature, °C (12% oil shale, 60 min)					Thermolysis time, min (420°C, 12% oil shale)				
	0	3	5	8	10	12	300	400	420	430	440	10	20	30	45	Q60
Gas	8.2	4.7	5.3	5.5	5.9	8.7	3.3	4.6	8.7	7.5	9.1	2.1	2.7	3.6	5.3	8.7
Fraction <180°C	15.3	6.8	7.6	11.5	14.1	17.3	8.1	12.2	17.3	16.7	16.0	7.6	8.8	10.6	13.4	17.3
Fraction 180–360°C	14.4	28.1	29.8	36.4	42.2	41.9	37.0	38.8	41.9	38.4	38.9	22.7	28.4	33.2	36.8	41.9
Fraction > 360°C	62.1	60.4	57.3	46.6	37.8	32.1	51.6	44.4	32.1	37.4	36.0	67.6	60.1	52.6	44.5	32.1
Coke on solid phase	8.2	4.8	5.3	5.5	5.9	6.7	3.2	4.4	6.7	7.1	9.1	2.3	2.9	3.8	5.3	6.7
Total yield of light distillates	29.7	34.9	37.4	47.9	56.3	59.2	45.1	51.0	59.2	55.1	54.9	30.3	37.3	43.8	50.2	59.2

No formation of pellets was observed

Straight-run fuel oil from the Pavlodar refinery was used as the starting raw material.

Natural zeolite of clinoptilolite structure of Shankanai deposit of Kazakhstan (W^a – 4.3%, A^d – 81.2%, SiO_2/Al_2O_3 = 7,5, density – 2500 kg/m³, clinoptilolite content 65%, SiO_2 – 67.5%, Al_2O_3 – 15.8%, Fe_2O_3 – 4.6%) was studied as a catalyst [17–18].

To find the optimal conditions for fuel oil thermolysis, the use of ordinary shale from the Kenderlyk field as an activating additive was considered. The dependence of the yield of processing products on temperature, process duration, and shale content in the mixture was analyzed (Tab. 5).

To find the optimal conditions for fuel oil thermolysis, the use of ordinary shale from the Kenderlyk field as an activating additive was considered. The dependence of the yield of processing products on temperature, process duration, and shale content in the mixture was analyzed (Tab. 5).

An evaluation of the shale additive's impact on fuel oil thermal cracking demonstrated a clear correlation: higher shale concentrations lead to increased yields of gasoline (from 6.8% to 17.3%) and diesel (from 28.1% to 41.9%) fractions, while concurrently decreasing the proportion of middle distillates from 60.4% to 32.1%. The total yield of light petroleum products increases from 34.9% to 59.2%. It is important to emphasize that the use of shale in optimal proportions reduces coking compared to pure fuel oil.

From the data of Tab. 5 it follows that dependence of fuel oil the yield of light distillate fractions on the temperature of thermal cracking is 45.1–59.2 wt.%. In this case, the yield of the gasoline fraction (IBP – 180°C) rises from 8.1 wt.% at 300°C to 17.3 wt.% at 420°C, while the diesel fraction(180–320°C) yield ranges between 37.0 and 41.9 wt.%. At the temperature above 320°C, the coke formation is 3.1–6.7 wt.%.

Data from Tab. 5 indicate that increasing the residence time from 10 to 60 min enhances the output of gasoline and diesel distillates, reaching 17.3% and 41.9%, respectively. At the same time, there is a regular decrease in the share of middle distillates – from 67.6% to 32.1%.

The optimal process parameters ensuring maximum yield of distillate fractions (59.2 wt.%) are as follows: temperature 420°C, reaction time 60 min, and shale additive content in the range of 12 wt.%.

Conclusion

Thus, the paper shows the possibility of obtaining synthetic oil from oil shale by means of hydrogenation processing. In this case it is possible to extract more than 90% of the organic matter of oil shale. According to the obtained results, increasing the temperature of oil shale hydrogenation from 410°C to 440°C at a pressure of 8.0 MPa leads to increase in gas formation from 10.2 to 12.2 wt.%

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and hydrogen consumption from 0.9 to 1.6 wt.%, and connection of gasoline and diesel fuel fractions. As the hydrogen pressure increaseswithin the 4.0–8.0 MPa range, the conversion degree of the shale's organic mass grows by 20%. Concurrently, the yields of liquid fractions, gas, and water reach 50.4, 10.5, and 7.7 wt.%, respectively, up from their initial values. Hydrogen pressure above 8.0 MPa has no effect on the process parameters.

Experimental data confirm that single-stage processing under moderate conditions (8 MPa, 425 °C, 1.0 h^{-1}) ensures deep feedstock conversion, yielding 17.2% of the gasoline fraction, 41.8% of diesel distillates, and 51.7% of the fraction heavier than 360 °C, suitable for catalytic cracking. The resulting coke-like products, along with the V and Ni present in the feedstock, are deposited on the mineral part of the shale and removed from the reaction zone with the liquid process products.

A scientifically grounded approach has been developed for the co-processing of oil shale and fuel oil under mild conditions. It is shown that the specific structure of the shale organic matter allows for a high degree of conversion without the use of ultra-high pressure, achieved by optimizing contact time and the concentration of the catalytically active shale additive.

ADDITIONAL INFORMATION

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