https://orcid.org/0000-0001-5405-4125
https://orcid.org/0000-0002-6097-3117
https://orcid.org/0000-0003-1182-7460

INFLUENCE OF TECHNOLOGICAL PARAMETERS ON THE COMPOSITION AND PROPERTIES OF PETROLEUM COKE

Y.A. AUBAKIROV,
Doctor of Chemical Sciences,
Professor,
miral.64@mail.ru

N. BUZAYEV,
1st-year doctoral student,
buzayev.n@gmail.com

K. TOSHTAY,
PhD., Senior Lecturer,
kainaubek.toshtay@gmail.com

AL-FARABI KAZAKH NATIONAL UNIVERSITY
Republic of Kazakhstan, Almaty, 050040, 71 al-Farabi Ave.

This study is devoted to studying the complex process of producing coke from heavy oil residues using previously developed experimental approaches and using analytical methods of analysis. The purpose of the study is to produce low-sulfur coke by thermal processing of heavy oil residues in the presence of waste motor oils. The resulting coke was analyzed by various physicochemical methods. The composition and structure of the resulting coke were studied using Raman spectroscopy methods. As a result of the analysis, the predominance of polyaromatic compounds and olefins in the coke composition was revealed. Electron microscopy techniques provided a visual representation of the microstructure and morphology of coke samples obtained both in the presence and absence of a recycling agent. Significant results were obtained by measuring the specific surface area of coke, which highlight the significant influence of temperature fluctuations on its characteristics of coke. It is noteworthy that the specific surface area of micropores varies significantly – from 16 to 600 m2/g. The results of the analysis of sulfur content showed the possibility of its thermal dehydration, which should lead to an improvement in the quality of coke. In addition, it has been shown that conducting the experiment in the presence of a recycling agent significantly increases the yield of coke and opens up prospects for more efficient use of heavy oil residues. Taken together, the results provide valuable insight into the intricacies of producing low-sulfur coke from heavy petroleum residues. In addition to industrial significance, this research also has environmental significance, since it proposes an approach that allows not only to maximize the use of secondary resources, but also to reduce the sulfur content in coke, which will help limit the environmental impact of industrial processes.
KEY WORDS: oil, petroleum mixture, coke, heavy oil residues, waste motor oils.

ВЛИЯНИЕ ТЕХНОЛОГИЧЕСКИХ ПАРАМЕТРОВ НА СОСТАВ И СВОЙСТВА НЕФТЯНОГО КОКСА

Е.А. АУБАКИРОВ, доктор химических наук, профессор, *miral.64@mail.ru*
Н. БУЗАЕВ, докторант 1 курса, *buzayev.n@gmail.com*
К. ТОШТАЙ, PhD., старший преподаватель, *kainaubek.toshtay@gmail.com*

КАЗАХСКИЙ НАЦИОНАЛЬНЫЙ УНИВЕРСИТЕТ ИМ. АЛЬ-ФАРАБИ
Республика Казахстан, Алматы, 050040, пр.аль-Фараби, 71

Данное исследование посвящено изучению сложного процесса получения кокса из тяжелых остатков нефти с привлечением разработанных ранее экспериментальных подходов и использованием аналитических методов анализа. Цель исследования - получение малосернистого кокса путем термической переработки тяжелых нефтяных остатков в присутствии отработанных моторных масел. Полученный кокс анализировали различными физико-химическими методами. Методом Рамановской спектроскопии исследованы состав и структура получаемого кокса. В результате анализа выявлена преобладание в составе кокса полиароматических соединений и олефинов. Методам электронной микроскопии было получено наглядное представление о микроструктуре и морфологии образцов кокса, полученных как в присутствии, так и в отсутствии рециклирующего агента. Существенные результаты получены путем измерения удельной поверхности кокса, которые подчеркивают существенное влияние температурных колебаний на его характеристики кокса. Примечательно, что удельная поверхность микропор имеет значительные колебания - от 16 до 600 м^2/г. Результаты анализа содержания серы показали возможность ее путем термического обезвоживания, что должно привести к улучшению качества кокса. Кроме того, показано, что проведение опыта в присутствии рециклирующего агента значительно увеличивает выход кокса и открывает перспективы для более эффективного использования остатков тяжелой нефти.

Полученные результаты в совокупности дают ценное представление о тонкостях получения малосернистого кокса из тяжелых нефтяных остатков. Помимо промышленного значения, данное исследование имеет и экологическое значение, поскольку предлагает подход, позволяющий не только максимально использовать вторичные ресурсы, но и снизить содержание серы в коксе, что будет способствовать ограничению влияния на экологию промышленных процессов.

КЛЮЧЕВЫЕ СЛОВА: *нефть, нефтяная смесь, кокс, тяжелых остатков нефти, отработанных моторных масел.*

ТЕХНОЛОГИЯЛЫҚ ПАРАМЕТРЛЕРДІҢ МҰНАЙ КОКСЫНЫҢ ҚҰРАМЫ МЕН ҚАСИЕТТЕРІНЕ ӘСЕРІ

Е.А. АУБАКИРОВ, Химия ғылымдарының докторы, профессор, *miral.64@mail.ru*
Н. БУЗАЕВ, 1 курс докторанты, *buzayev.n@gmail.com*
Қ. ТОШТАЙ, PhD., аға оқытушы, *kainaubek.toshtay@gmail.com*

ӘЛ-ФАРАБИ АТЫНДАҒЫ ҚАЗАҚ ҰЛТТЫҚ УНИВЕРСИТЕТІ,
Қазақстан Республикасы, 050040, Алматы, әл-Фараби даңғылы, 71

Бұл зерттеу бұрын әзірленген тәжірибелік тәсілдерді және талдаудың аналитикалық әдістерін қолдану арқылы ауыр мұнай қалдықтарынан кокс алудың күрделі процесін зерттеуге арналған. Зерттеудің мақсаты – мотор майларының қалдықтары болған жағдайда ауыр мұнай қалдықтарын термиялық өңдеу арқылы күкіртті аз кокс алу. Алынған кокс

әртүрлі физика-химиялық әдістермен талданды. Алынған кокстың құрамы мен құрылымы Раман спектроскопиялық әдістерімен зерттелді. Талдау нәтижесінде кокс құрамында полиароматты қосылыстар мен олефиндердің басым екені анықталды. Электрондық микроскопия әдістері рециклинг агенті бар да, жоқ та алынған кокс үлгілерінің микроқұрылымы мен морфологиясының көрнекі көрінісін қамтамасыз етті. Маңызды нәтижелер кокстың меншікті бетінің ауданын өлшеу арқылы алынды, бұл оның кокс сипаттамаларына температура ауытқуларының елеулі әсерін көрсетеді. Бір қызығы, микрокеуектердің меншікті бетінің ауданы айтарлықтай ауытқуларға ие - 16-дан 600 м²/г дейін. Күкірт құрамын талдау нәтижелері оның термиялық сусыздану мүмкіндігін көрсетті, бұл кокс сапасының жақсаруына әкелуі керек. Сонымен қатар, тәжірибені қайта өңдеу агентінің қатысуымен жүргізу кокстың шығымдылығын айтарлықтай арттыратыны және ауыр мұнай қалдықтарын тиімдірек пайдалану перспективаларын ашатыны көрсетілген. Біріктірілген нәтижелер ауыр мұнай қалдықтарынан төмен күкіртті кокс өндіру үшін құнды түсінік береді. Өнеркәсіптік маңыздылығынан басқа, бұл зерттеудің экологиялық мәні де бар, өйткені ол қайталама ресурстарды барынша пайдалануды ғана емес, сонымен қатар кокстағы күкірттің мөлшерін азайтуға мүмкіндік беретін тәсілді ұсынады, бұл өндірістік процестердің қоршаған ортаға әсерін шектеуге көмектеседі.

ТҮЙІН СӨЗДЕР: *мұнай, мұнай қоспасы, кокс, ауыр мұнай қалдықтары, мотор майларының қалдықтары.*

Introduction. The impressive capacity for processing oil coking waste, which currently stands at an impressive 252.9 million tonnes annually, characterizes the oil and gas industry's current landscape. This capability demonstrates the sector's steadfast dedication to addressing oil refining's primary goal: the creation of high-octane, environmentally friendly gasoline and diesel fuels [1,2].

Several major difficulties are brought to the fore in this dynamic environment. These issues center on how heteroatom compounds affect catalyst activity, product quality, and their broader environmental effects [3,4].

According to global production statistics, low-temperature fuel coke makes up 80% of the output, and electrode coke makes up the remaining 20%. This pattern highlights the increasing number of slow coking plants, a phenomenon fueled by a variety of factors [1–5]. These include their exceptional productivity, their capacity to produce both petroleum coke and distillate products, which are essential to the majority of industrial processes, as well as their ability to process different raw materials effectively. For the production of valuable distillate products, coking heavy oil residues does indeed prove to be a financially responsible strategy.

Improvements in technical and technological efficiency, environmental optimization, and raising of product quality standards are the main areas of focus in the never-ending quest to improve the slow coking process [7-12]. In order to shed light on the ongoing evolution of coke production from oil reserves within the oil and gas industry, this paper delves into these crucial dimensions.

Coke production and the production of light petroleum products are the two main goals of the coking process, especially in international contexts. The type of coke that is produced depends on the raw materials used and the specifics of the chosen process, and possible results include fuel coke, anode coke, or needle coke.

However, the significant problem posed by the disposal of the pulverized coke left over from the "fluid" process must be addressed. With over 50 Lummus units and more than

85 Fost Wheeler units already operational in the United States [13–16], the Lummus and Fost Wheeler versions of slow coking units are currently in high demand. This represents a significant advancement in the industry's efforts to maximize the production of coke from oil reserves. The aim of this study is to investigate the complex process of coke production from heavy oil waste using previously developed experimental approaches and analytical methods of analysis.

Experimental part. The procedure starts with the addition of the raw material into the reactor in the experimental stage of the coking process to obtain coke from oil reserves. We used 8 grams of leftover oil and 12 grams of tar as our raw materials, specifically. Following the loading of the raw material, the reactor is sealed with specialized bolts. We introduce nitrogen gas into the reactor to ensure that the coking process occurs in an inert environment. Once the reactor has the desired inert atmosphere, the pressure is carefully adjusted to 0.4 MPa. Before starting the process, we run a pressure check to make sure the system is intact. The furnace is then heated by applying the necessary current with the help of a lab autotransformer. The pressure is kept at 0.4 MPa using a pressure regulation valve. The valve releases any extra pressure if the pressure rises above this limit. The current from the autotransformer raises the temperature of the system, and thermocouples continuously record this temperature. The moment the system temperature reaches 365°C is noted.

The process continues for another hour under process pressure three hours after this temperature milestone is reached. In this phase, the temperature ranges between 480 and 520 °C. In order to collect the liquid product, the coking process's released vapors are condensed using a reverse refrigerator and directed into a receiving flask. Additionally, a gasometer is used to collect the extracted gas. We turned off the furnaces, the laboratory autotransformer, and the refrigerator when the procedure was finished. We start by cleaning the coke residues out of the reactor after allowing it to cool.

Results and discussion. *Table 1* shows the results of chromatographic analysis for the fractions obtained through atmospheric distillation of distillates during the coking of heavy oil waste with the addition of a recycling agent.

The composition of coke comprises numerous chemical compounds, with particular emphasis on the significance of C-C and aromatic bonds in coke formation. Additionally, the presence of graphite enhances the structural rigidity of coke. These chemical bonds and compounds exert a substantial influence on coke's overall structure.

Distinct variations in coke composition and structure, whether identical or diverse, can be effectively discerned through the analysis of their vibrational patterns in Raman spectra. This underscores the utility of Raman spectroscopy for characterizing coke composition and structure (*Figure 1*). Raman spectroscopy was employed to ascertain the group composition of coke generated during the coking process, as illustrated in *Figure 1*. Within the resulting spectra, three primary peaks are discerned, exhibiting remarkable similarity to literature data (*Table 2*). Notably, the presence of a peak at 1347 and 1350 cm^{-1} in the Raman spectrum signifies the vibrational characteristics of C-NO$_2$ compounds. Furthermore, secondary peaks in Raman scattering at 1165 cm^{-1} correspond to CC aromatic and C=C regions, indicative of a notably high crystalline nature within the coke structure. Additional evidence is found in the Raman spectrum, which reveals bands at 3173 cm^{-1}

Table 1 - **Chemical composition of distillates obtained by coking heavy oil waste in the presence of a recycling agent**

№	Group chemical composition of hydrocarbons	Gasoline fraction, 0-180 ºC	Light gas oil fraction, 180-240 ºC	Heavy gas oil fraction, 240-320 ºC
1	Alkanes	15.53	17.82	19.14
2	Isoalkanes	3.57	1.36	0.98
3	Alkers	7.44	2.56	4.53
4	Cycloalkane	2.19	2.25	1.24
5	Aromatic hydrocarbon	25.83	9.84	11.35

and 3197 cm⁻¹, corresponding to the O-H functional group area, further confirming the prevalence of polyaromatic compounds and olefins in the structure of the cokes analyzed during our experimental investigations.

Table 2 - **Literature data of Raman spectroscopy**

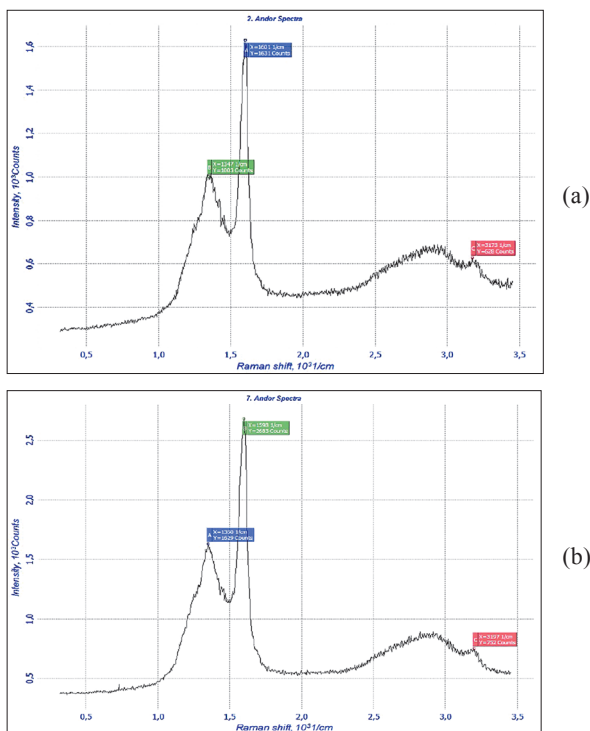| Functional group/ Vibration	Region, cm⁻¹	Raman
$\upsilon(C-(NO_2))$	1340 – 1380	strong
$\upsilon(CC)$ aromatic ring chain vibrations	1580, 1600	strong
$\upsilon(C=C)$	1500 – 1900	strong
$\upsilon(O-H)$	3100 – 3650	weak

(a)

(b)

Figure 1 – **Raman spectroscopy of coke (a) at 510ºC b) at 520ºC**

To investigate the microstructural characteristics of the coke produced through the coking process, electron microscopy was utilized to capture images. *Figures 2* depict illustrations of microstructures of varying sizes of coke, obtained both in the presence and absence of a recycling agent.
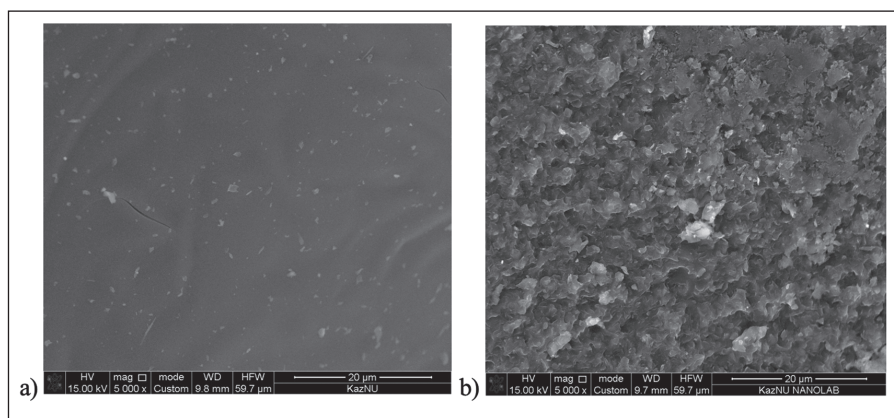

Figure 2 – **SEM micrographs of coke obtained a) without recycling agent; b) with recycling agent at 510ºC.**

Several chemical and physical-chemical attributes crucial to assessing the quality of coke are linked to its surface structure and porosity. For instance, the reactivity of coke is substantially influenced by the extent of its internal specific surface area. Techniques employed to determine the specific surface area of coke simultaneously provide highly accurate insights into its internal specific surface characteristics.

According to existing literature, the specific surface area of micropores varies significantly among different cokes, spanning a range of 16 to 600 m^2/g, depending on the degree of burnup. *Table 3* presents the outcomes of two experiments; initially, coke exhibited a specific surface area of 67.6 m^2/g, which decreased as the temperature increased.

Table 3 - **Specific surface area of coke by Sorbtometer M**

Experiments	At 510ºC	At 520ºC
Specific surface area, m^2/g	67.6	13.1

Coke is comprised of an extensive array of chemical compounds, and its structural rigidity is notably enhanced by the presence of graphite. The configuration and properties of coke are significantly impacted by the presence of various chemical bonds and compounds.

Table 4 presents data regarding the sulfur content found in both coke and liquid products resulting from the coking of heavy oil waste in the presence of a recycling agent.

Table 4 - **The content of sulfur in products formed during coking, mass. %**

Components	Gasoline	Gasoline	Gasoline	Coke
Sulfur content, %	0.132	0.802	0.432	0.930

Sulfur content in the resulting coke can be decreased through a process of thermal dehydration. Elevating both temperature and pressure facilitates a reduction in sulfur content to levels below 2.5%, resulting in an overall improvement in coke quality. Importantly, the incorporation of a recycling agent has been found to increase the yield of coke obtained from heavy oil waste.

Table 5 illustrates the material balance for the procedure involved in producing low-sulfur coke with the inclusion of a recycling agent.

Table 5 - **Material balance of the process**

Input	m, g	mass. %	Output	m, g	mass. %
Tar residue oil	10 10	50 50	Coke Distillates Gas Loss	4.53 14.00 1.00 0.47	22.65 70.00 5.00 2.35
Overall	20	100	Overall	20	100

Through the coking process in the presence of a recycling agent, the primary product, coke, was separated from liquid distillates and gas. A total of 4.53 grams of coke was produced during the coking process, constituting 70% of the total liquid product obtained. The release of gaseous products was 1 g (5%) while the loss reached 2.35% (0.47 g)

Conclusion. In conclusion, our research demonstrates the effectiveness of Raman spectroscopy in characterizing the composition and structure of coke. Through vibrational analysis, we successfully differentiated coke with varying structures and component ratios. The presence of specific peaks in the Raman spectrum provided valuable insights into the composition and crystallinity of the coke. Furthermore, electron microscopy revealed microstructural variations in coke, influenced by the use of a recycling agent. Notably, the quality of coke was found to be strongly linked to its surface structure and porosity, which impact reactivity. Additionally, our findings highlight the potential for reducing sulfur content in coke through thermal dehydration, leading to improved coke quality, particularly when a recycling agent is introduced, which also enhances coke yield during the coking of heavy oil waste.

REFERENCES

1   Beibei C., Yanfeng S., Jiang G., Xin J., Meijun W., Wei X., Liping C. A study of coking mechanism based on the transformation of coal structure // Fuel. – 2022. – №328. –P. 125360.

2   Lili W., Yuanshun X., Zehua Z., Dapeng Z., Xiaochen L., Bing M., Houhu Z. Analysis of Pyrolysis Characteristics of Oily Sludge in Different Regions and Environmental Risk Assessment of Heavy Metals in Pyrolysis Residue // ACS Omega. – 2022. – №7 (30). – P. 26265–26274.

3   Zhijian Wan, Gang Kevin Li, Chuanfu Wang, Hong Yang, Dongke Zhang Relating coke formation and characteristics to deactivation of ZSM-5 zeolite in methanol to gasoline conversion // Applied Catalysis. – 2018. – Vol. 549. – P. 141-151. https://doi.org/10.1016/j.apcata.2017.09.035

4 Современное состояние и важнейшие достижения мировой нефтепереработки в развитии технологии коксования остаточных нефтепродуктов для углубления переработки нефти и увеличения производства- моторных топлив и нефтяных коксов. Аналитический материал. – М.: ЦНИИТЭнефтехим, 2005. - 48 с. [Sovremennoe sostoyanye I vazhneishye dostizheniya mirovoi neftepererabotki v razvitii tehnoligii koksovaniya nefteproduktov dlya uglubleniya pererabotki nefti I uvelicheniya proizvodstva-motornyh topliv i neftyanyh koksov. Analiticheskiy material. – M: TsNIITEneftehim, 2005. - 48 s.]

5 Копытов М.А., Головко А.К., Кирик Н.П., Аншиц А.Г. Название статьи!!1 // Нефтехимия. –2013. – Т. 53. – №1. – С.16. [Kopytov M.A., Golovko A.K., Kirik N.P., Anship A.G. Название статьи!!1 // Neftehimiya. -2013. V. 53. – №1. – S.16.   ]

6 Ахметов С. А. Технология глубокой переработки нефти и газа: Учебное пособие для вузов. – Уфа: Гилем, 2002. – 672 с. [Akhmetov S.A. Tehnologiya glubokoi pererabotki nefti i gaza: Uchebnoe posobie dlya vuzov. – Ufa: Gilem, 2002. – 672 s.].

7 Yuming Zhang, Lei Huang, Xiaoying Xi, Wangliang Li, Guogang Sun, Shiqiu Gao, Shu Zhang Deep Conversion of Venezuela Heavy Oil via Integrated Cracking and Coke Gasification−Combustion Process // Energy Fuels. – 2017. – N 31. – P. 9915-9922. https://doi.org/10.1021/acs.energyfuels.7b01606

8 Aitor Ochoa, Javier Bilbao, Ana G.Gayubo, Pedro Castano Coke formation and deactivation during catalytic reforming of biomass and waste pyrolysis products: A review // Renewable and Sustainable Energy Reviews, 2019. https://doi.org/10.1016/j.rser.2019.109600

9 Капустин В. М. Технология переработки нефти. Часть II. Физико-химические процессы. – М.: Нефть и газ» РГУ нефти и газа имени И. М. Губкина, 2013. – 418 с. [Kapustin V.M. Tehnologiya pererabotki nefti. Chast II. Fiziko-himicheskie protsessy. Pererabotannoe i dopolnennoe. – M.: Neft i gaz RGU nefti I gaza imeni I.M. Gubkina, 2013. – 418 s.].

10 Speight J.G. Heavy hydrocarbon gasification for synthetic fuel production Gasification for Synthetic // Fuel. – 2015. – P. 221-239. https://doi.org/10.1016/B978-0-85709-802-3.00010-2

11 Zhang Y., Yao M., Gao S., Sun G., Xu G. Reactivity and kinetics for steam gasification of petroleum coke blended with black liquor in a micro fluidized bed // Applied Energy. – 2015. – N 160. – P. 820–828. doi:10.1016/j.apenergy.2015.01.009

12 Gomez A., Mahinpey N. A new model to estimate CO2 coal gasification kinetics based only on parent coal characterization properties // Appl Energy. – 2015. – N 137. – P. 126–33.

13 Hayashizaki H., Kanehashi K., Uebo K., Nomura S., Saito Y., Matsushita Y., Aoki H. Effects of Hydrocarbon Addition on Increase in Dilatation of Coal // ISIJ International. – 2019. –№59. – P. 1404–1412.

14 Kondrasheva N. K., Rudko V. A., Nazarenko M. Yu. Influence of Pressure in the Coking of Heavy Oil Tar and Asphalt on the Coke Properties and Structure // Coke and Chemistry. – 2018. – 61. – P. 483–488.

15 Chesnokov V. V., Chichkan A. S., Moseenkov S. I., Parmon V. N. Influence of Carbon Nanotubes on the Properties of Coke Derived from Heavy Tar // Coke and Chemistry. – 2021. – №64. – P. 522–526.

16 Lee S., Yu J., Mahoney M., Tahmasebi A., Stanger R., Wall T., Lucas J.. In situ study of plastic layers during coking of six Australian coking coals using a lab-scale coke oven // Fuel Processing Technology. – 2019. – №188. – P. 51–59.