

S.V. Kim¹, V.A. Kim¹, O.R. Sariev², S.Kh. Kudarinov¹,
O.A. Bogoyavlenskaya¹, A.S. Orlov¹, V.V. Orlova¹, A.V. Zhdanov³

¹Zh.N. Abishev Chemical-Metallurgical Institute, Karaganda, Kazakhstan;

²K. Zhubanov Aktobe Regional State University, Kazakhstan;

³Ural Federal University named after the first President of Russia B.N. Yeltsin, Yekaterinburg, Russia

(E-mail: o-bogoyavlenskay@mail.ru)

Influence of coal heat treatment parameters on physical-chemical properties of smokeless fuel

A series of experiments on coking long-flame coals by high-speed thermooxidative pyrolysis was carried out as a part of smokeless fuel technology development from domestic energy coals. The objective of experiments was to determine the influence of basic technological parameters of the coking process (heating rate, coking temperature) on the final physical-chemical properties of the semi-coke, which is an initial material for briquetted smokeless fuel manufacture. The experiments were carried out in a Tamman resistance furnace at 600–1100 °C imitating the coking process in industrial shaft furnace. The rate of heating and the final temperature of coking were found the most important control factors ensuring the production of lump coke with sufficient strength. In the mentioned temperature interval, the reactivity of semi-coke changes by a complicated pattern varying from 3.5 to 9.7 ml/g·s. Along with coking temperature and heating rate, the structural strength of semi-coke grows monotonically, reaching 80 % at heating rate of 90 degrees per minute and a temperature of 1100 °C. Thus, the results of this work allow us to conclude that the most rational temperature range for smokeless fuel production by means of high-speed pyrolysis of young high-volatile coal is found within 600–700 °C (the temperature interval of semi-coking). To ensure sufficient structural strength of semi-coke the rate of coal heating should be at least 30 °C/min. A highly active material with a reactivity of over 9 ml/g·s and a sufficiently high strength and a residual volatiles content of about 8–11 % can be obtained using this method.

Keywords: smokeless fuel, thermo-oxidative pyrolysis, energy coals, semi-coke, coking temperature, structural strength, reactivity, volatile substances.

Long flame coal from the Shubarkol coal field was used as a raw material for smokeless fuel making. Shubarkol deposit with overall reserves of over 1.8 billion tons [1, 2] is located in Tengiz area of Karaganda region. The coal is related to long flame (free-burning) coal type, is petrographically homogeneous and vitrinitized. By reflectance, the coal is related to grade D (candle type) [3]. Coals are low-ash, low-sulfur with low phosphorus content, easy and medium-enriching. The content of vitrinite is over 80 % of the organic mass. The reflection is 0.6 %. The quality of coals according to exploration data is as follows: W^p — 15 %; A^d — 5÷15 %; V^{daf} — 40 %; S_t^d — 0.5 %; C^{daf} — 76 %; H^{daf} — 5.5 %; Q_s^{daf} — 26 MJ/kg; Q_i^r — 22 MJ/kg. It can be seen that for Shubarkol coal has distinctively low ash content. In separate parts of the coal bed, the ash level has extreme values of 1.4 and 31.0 %. At the same time, the bulk of coal contains 6.0 % ash and below.

The method of high-speed thermooxidizing coking was used to obtain durable lump material from sieved Shubarkol coal based on the rapid heating of coal particles by heat released during the combustion of volatile products of thermal destruction [4–6]. In this process, the formation of the coke structure goes through a series of reactions of coal matter decomposition and the synthesis of new compounds with the formation of semi-coke. Further transformations of the latter lead to the formation of a carburized coke material [7].

To simulate coal heating conditions of high-speed thermooxidizing coking, we used the Tamman resistance furnace, into which a crucible of heat-resistant steel with a coal sample inside was introduced. The crucible has high walls to provide access of air oxygen into the reaction zone. The electric supply of the heater is provided by a power transformer of 80 kVA with thyristor regulation of voltage and current, which allows maintaining the set temperature with an accuracy of 10 °C. A portion of the coal charge was prepared from the 10–20 mm Shubarkol coal. The temperature in the furnace and in the coal layer was constantly measured during the experiment. After the experiment, the residue was weighted to determine the mass loss.

The studies were carried out at a strictly fixed temperature, which was varied from 600 to 1100 °C with the interval of 100 °C. A sample of coal in a heat-resistant steel reactor was loaded into a preheated furnace. During the experiment, a continuous measurement of the temperature in the coal bed was made and, after

reaching a predetermined level of heating, an exposure was held for 5 minutes. After that, the reactor was removed from the furnace and cooled in a sealed container to room temperature. The coking gas evolved in the process of pyrolysis was burned down outside the furnace.

In order to eliminate the influence of heat loss by moisture evaporation, the beginning of recording the temperature in the layer is attributed to the dry state of the material. The zero test time corresponds to coal sample temperature of 180–250 °C, at which point the physical moisture is completely removed from the sample (Fig. 1).

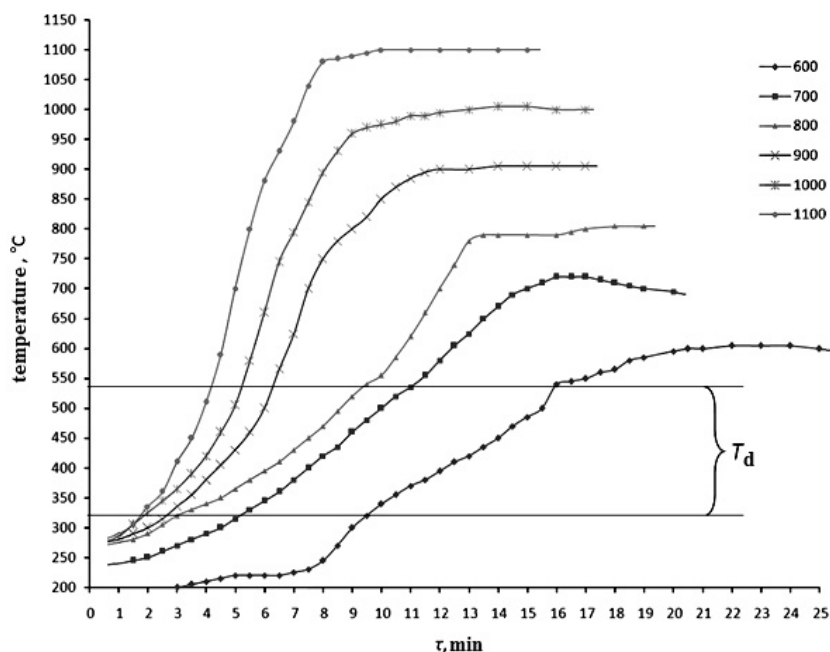


Figure 1. Dynamics of temperature changes in the coal layer at various initial temperatures in the furnace

The influence of temperature and coal heating rate on the structure and properties of the coking product was studied experimentally. The process of high-speed pyrolysis of coal was imitated by pre-heating the furnace to certain degree, which allowed heating the coal samples with varying temperature gradients [8]. The dynamics of the temperature change in the coal layer is shown in Figure 1 as a function of time and the initial temperature level in the furnace.

The data in Figure 1 show that in the temperature range of 320–540 °C corresponding to coal matter destruction processes the rate of coal heating depends on the preset temperature gradient and amounts to 29.4–90.9 degrees per min (Fig. 2), which is sufficient for the formation of a stable structure of the coke residue (semi-coke).

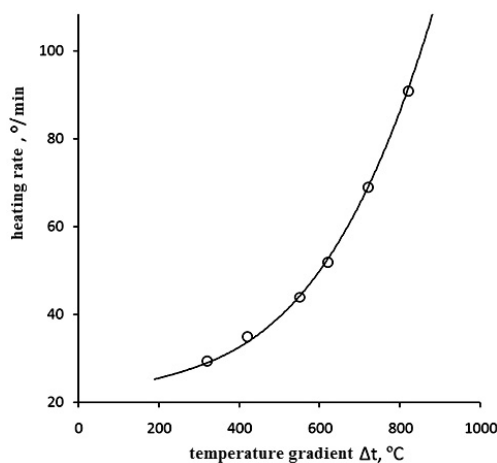


Figure 2. Effect of the temperature gradient on the coal heating rate

Table represents the data on the heating rate and the numerical values of coal mass loss and the results of the proximate analysis of semi-coke samples obtained in interval of 600–1100 °C and heating rates of 29.4–90.9 degrees per minute.

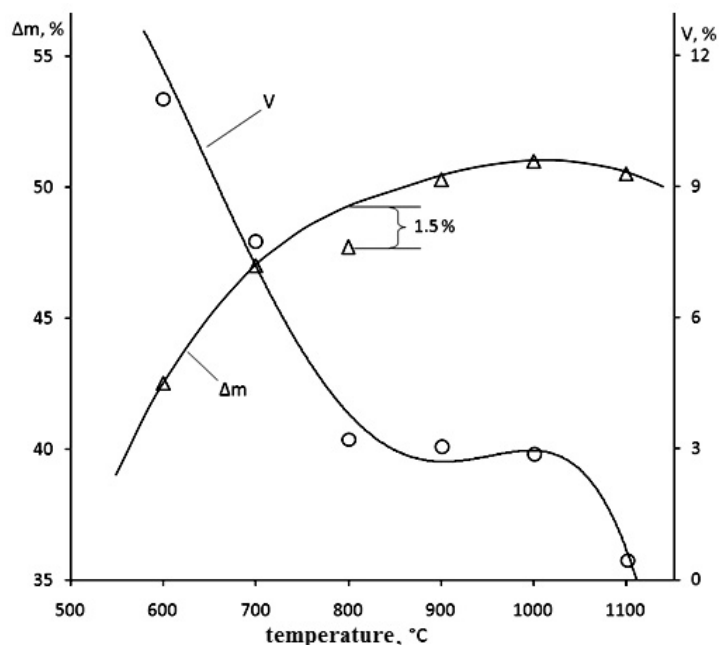
Table

Parameters of high-speed coking process and proximate composition of semi-coke

Temperature, °C	Heating rate, °/min	Mass loss, %	Proximate composition of the product, %		
			A ^c	V ^d	W ^r
600	29.41	42.5	3.01	11.02	2.76
700	35.7	47.0	3.23	7.74	3.54
800	45.45	47.8	3.48	3.22	4.17
900	53.57	50.3	3.61	3.04	4.31
1000	65.22	51.0	3.80	2.86	3.16
1100	90.90	49.8	3.95	0.45	3.37

As we can see, the residual amount of volatiles in the semi-coke (see Table) is in full compliance with coal mass loss (Fig. 3). It can be seen that the most intensive loss of coal mass is observed at low temperatures of 600–800 °C where the greatest decrease of volatiles level takes place. The level of volatile substances stabilizes after 800 °C and varies insignificantly from 3.22 to 2.86 % up to 1000 °C. It is only above 1100 °C, that the volatiles level sharply decreases, reaching 0.45 %. At a temperature of 950–1000 °C the structure of the semi-coke begins to decompose with the release of heavy resins containing hydrogen.

Evaluation of structural strength and reactivity of semi-coke samples obtained at different heating rate and temperature was carried out in accordance with State Standards, namely, «State Standard 9521–74» and «State Standard 10089–89». Evaluation results are shown in the Figure 4. The structural strength of the semi-coke is minimal (no more than 50 %) in the low temperature range of 600–700 °C and at a heating rate below 40 degrees per min. The most noticeable increase in the structural strength occurs in the interval of 700–800 °C and the heating rate range of 40–60 degrees per minute, where structural strength reaches 72 %.

Figure 3. Dependence of mass loss (Δm) and residual volatiles level (V) from the coking temperature

The monotonous growth of the structural strength up to 80 % is observed at a heating rate of 90° degrees per minute and a temperature of 1100 °C. The rate of heating and the final temperature of coking are, therefore, the most important control factors ensuring the production of lump coke with sufficient strength, as follows from the experimental data.

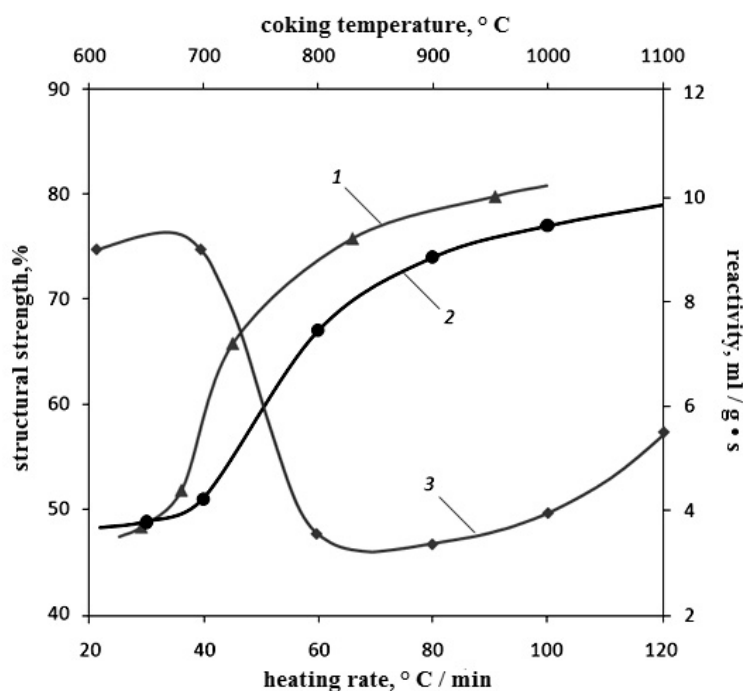


Figure 4. Influence of heating rate (1) and temperature (2) on structural strength and temperature (3) on the reactivity of semi-coke

It follows from the data in Figure 4 that the level of reactivity of semi-coke varies within 3.5–9.7 ml/g·s in the investigated temperature range, and, while the coking temperature grows monotonically, the reactivity variation follows more complicated pattern. Semi-coke has greatest reactivity, which reaches 9.7 ml/g·s, at 600–700 °C. Growth of coking temperature from 600 to 700 °C has very slight influence on overall reactivity. However, the latter sharply decreases to 3.5 ml/g·s in the interval of 700–800 °C and remains practically unchanged up to 900 °C, after which point it begins to increase faster to reach 5.6 ml/g·s at 1100 °C.

Conclusion

Thus, the results of this work allow us to conclude that the most rational temperature range for smokeless fuel production by means of high-speed pyrolysis of young high-volatile coal is found within 600–700 °C (the temperature interval of semi-coking). The production of the most reactive material, with a sufficiently high strength and a residual volatile content of about 8–11 %, is ensured under these conditions. This semi-coke considering its basic physical-chemical and technological properties can be proposed as a high-quality intermediate material for further production of smokeless fuel.

The work was performed within the program-purpose financing O. 0787 Project for 2018–2020. «Development of smokeless fuel production technology and creation of an experimental coal coking plant».

References

- 1 Ким В.А. Промышленные испытания технологии термоокислительного коксования угля Шубаркольского разреза / В.А. Ким, М.Ж. Ахмеров, А.К. Надырбеков // *Промышленность Казахстана*. — 2001. — № 2. — С. 101–103.
- 2 Ким В.А. Получение спеккокса из шубаркольских углей / В.А. Ким, А.М. Ли, А.К. Надырбеков // *Комплексная переработка минерального сырья: материалы совещ.* — Алматы, 2002. — С. 411–415.
- 3 Глезин И.Л. Полукоксование длиннопламенных углей Шубаркольского месторождения в газогенераторах / И.Л. Глезин, В.М. Шампаров, В.М. Страхов, И.В. Суворцева // *Кокс и химия*. — 2009. — № 8. — С. 25–29.
- 4 Matuszek K. Carbonaceous smokeless fuel and modern small-scale boilers limiting the residential emission. Part 2. Experimental tests of a new carbonaceous smokeless fuel / K. Matuszek, P. Hrycko, S. Stelmach, A. Sobolewski // *Przemysl Chemiczny*. — 2016. — Vol. 95, No. 2. — P. 228–230.
- 5 Bai Y. Gasification of coal char in H₂O/CO₂ atmospheres: Evolution of surface morphology and pore structure / Y. Bai, P. Lv, X. Yang // *Fuel*. — 2018. — Vol. 218. — P. 236–246.
- 6 Wang H.P. Thermal decomposition mechanisms of coal and coal chars under CO₂ atmosphere using a distributed activation energy model / H.P. Wang, Z.C. Chen, X.Y. Zhang // *Thermochimica Acta*. — 2018. — Vol. 662. — P. 41–46.

7 Сысков К.И. Термоокислительное коксование углей: монография / К.И. Сысков, О.Н. Машенков. — М.: Металлургия, 1973. — 176 с.

8 Мирошниченко Д.В. Влияние технологических факторов подготовки и коксования углей на реакционную способность кокса / Д.В. Мирошниченко // Кокс и химия. — 2009. — № 2. — С. 37–42.

С.В. Ким, V.A. Kim, О.Р. Сариев, С.Х. Кударинов,
О.А. Богоявленская, А.С. Орлов, В.В. Орлова, А.В. Жданов

Көмірді термиялық өңдеу режимдерінің түтінсіз отынның физика-химиялық қасиеттеріне әсерін зерттеу

Отандық энергетикалық көмірлерден түтінсіз отынды өндіру технологиясын жасау шарасында жоғары жылдамдықты термототықтырғыш пиролиз тәсілімен ұзын жалынды көмірлерді кокстау бойынша зерттеу жұмыстары жүргізілді. Кокстау процесінің негізгі технологиялық параметрлерінің (қыздыру жылдамдығы, кокстау температурасы) жартылай кокстың — брекettelген түтінсіз отынды алуға арналған бастапқы материалдың соңғы физика-химиялық қасиеттеріне әсері орнатылды. Зерттеу өндірістік шахталы пештердегі көмірді кокстау процестерін келтіретін, 600–1100 °С температурада Таммана кедергілі пешінде жүргізілді. Зерттеу мәліметтерінің талдауы кокстаудың қыздыру жылдамдығы және соңғы жылдамдығы кесекті және берік жартылай коксты алуына ықпал ететін анықтағыш негізгі фактор болып есептеледі. Зерттелген температура аралығында жартылай кокстың реакциялық қабілеті күрделі заңдылық бойынша өзгереді және 3,5–9,7 мл/г·с шамасы аралығында ауытқиды. Қыздыру жылдамдығын және температурасын жоғарылату барысында қыздыру температурасы 90 град/мин және температурасы 1100 °С кезінде 80 % жететін жартылай кокстың монотонды құрылымдылық өсуі байқалады. Зерттеу шешімі бойынша бастапқы ұшқыш заттардың жоғары мөлшеріне не жас көмірлерден жоғары жылдамдықты пиролиз тәсілімен алынатын түтінсіз отынды термиялық өңдеу температурасы 600–700 °С (жартылай кокстау және жартылай коксты алу температурасы интервалы) неғұрлым ұтымды болып келеді. Жартылай кокстың жеткілікті құрылымдық беріктігін қамтамасыз ету үшін көмірді қыздыру жылдамдығы 30 °С/мин кем болмауы керек. Бұнын өзінде жоғары белсенді материал, реакциялық қабілеті 9 мл/г·с кем емес, жеткілікті беріктікке не және қалдық ұшқыш заттар мөлшері 8–11 % болатын алу қамтамасыз етіледі.

Кілт сөздер: түтінсіз отын, термототықтырғыш пиролиз, энергетикалық көмір, жартылай кокс, кокстау температурасы, құрылымдық беріктік, реакцияға қабілеттілік, ұшқыш заттар шығыны.

С.В. Ким, V.A. Kim, О.Р. Сариев, С.Х. Кударинов,
О.А. Богоявленская, А.С. Орлов, В.В. Орлова, А.В. Жданов

Влияние режимов термообработки угля на физико-химические свойства бездымного топлива

В рамках создания технологии производства бездымного топлива из отечественных энергетических углей проведена серия экспериментов по коксованию длиннопламенных углей методом высокоскоростного термоокислительного пиролиза. Установлено влияние основных технологических параметров процесса коксования (скорости нагрева, температуры коксования) на конечные физико-химические свойства полукокса — исходного материала для получения брикетированного бездымного топлива. Опыты проводили в печи сопротивления Таммана при температуре 600–1100 °С в условиях, имитирующих процесс коксования угля в промышленной шахтной печи. Анализ экспериментальных данных указывает на то, что скорость нагрева и конечная температура коксования являются определяющими, наиболее важными факторами, влияющими на получение кускового и прочного полукокса. В исследованном диапазоне температур величина реакционной способности полукокса изменяется по сложной закономерности и колеблется в пределах 3,5–9,7 мл/г·с. При повышении температуры и скорости нагрева наблюдается монотонный рост структурной прочности полукокса, достигающей 80 % при скорости нагрева 90 град/мин и температуре 1100 °С. По результатам исследований определено, что для бездымного топлива, получаемого методом высокоскоростного пиролиза из молодых углей с высоким исходным содержанием летучих веществ, температура термообработки 600–700 °С (температурный интервал полукокса и получения полукокса) является наиболее рациональной. Для обеспечения достаточной структурной прочности полукокса скорость нагрева угля должна быть не менее 30 °С/мин. При этом обеспечивается получение высокоактивного материала с реакционной способностью не менее 9 мл/г·с, с достаточно высокой прочностью и содержанием остаточных летучих веществ около 8–11 %.

Ключевые слова: бездымное топливо, термоокислительный пиролиз, энергетические угли, полукокс, температура коксования, структурная прочность, реакционная способность, выход летучих веществ.

References

- 1 Kim, V.A., Akhmerov, M.Zh., & Nadyrbekov, A.K. (2001). Promyshlennye ispytaniia tekhnologii termookislitelnoho koksovaniia uhliia Shubarkolskoho razreza [Industrial tests of technology of thermo-oxidative coking of coal of Shubarkolsky mine]. *Promyshlennost Kazakhstana — Industry of Kazakhstan*, 2, 101–103 [in Russian].
- 2 Kim, V.A., Li, A.M., & Nadyrbekov, A.K. (2002). Poluchenie spetskokska iz shubarkolskikh uhlei [Obtaining a special coke from Shubarkol coals]. *Kompleksnaia pererabotka mineralnogo syria [Complex processing of mineral raw materials]*. Almaty [in Russian].
- 3 Glezin, I.L., Shamparov, V.M., Strakhov, V.M., & Surovtseva, I.V. (2009). Polukoksovanie dlinnoplamennykh uhlei Shubarkolskoho mestorozhdeniia v hazoheneratorakh [Semicoking of long-flame coals of the Shubarkol field in gas generators]. *Koks i khimiia. — Coke and chemistry*, 8, 25–29 [in Russian].
- 4 Matuszek, K., Hrycko, P., Stelmach, S., & Sobolewski, A. (2016). Carbonaceous smokeless fuel and modern small-scale boilers limiting the residential emission. Part 2. Experimental tests of a new carbonaceous smokeless fuel. *Przemysl Chemiczny*, 95, 2, 228–230.
- 5 Bai, Y., Lv, P., & Yang, X. (2018). Gasification of coal char in H₂O/CO₂ atmospheres: Evolution of surface morphology and pore structure. *Fuel*, 218, 236–246.
- 6 Wang, H.P., Chen, Z.C., & Zhang, X.Y. (2018). Thermal decomposition mechanisms of coal and coal chars under CO₂ atmosphere using a distributed activation energy model. *Thermochimica Acta*, 662, 41–46.
- 7 Syskov, K.I., & Mashenkov, O.N. (1973). *Termookislitelnoe koksovanie uhlei [Thermo-oxidative coking of coals]*. Moscow: Metallurhiia [in Russian].
- 8 Miroshnichenko, D.V. (2009). Vliianie tekhnolohicheskikh faktorov podhotovki i koksovaniia uhlei na reaktsionnuu sposobnost kokska [The influence of technological factors in the preparation and coking of coals on the reactivity of coke]. *Koks i khimiia — Coke and chemistry*, 2, 37–42 [in Russian].