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COKE

Oxidation of Coke with Petroleum-Based Coking Additives

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Abstract—The properties of coking batch may be stabilized by means of DK coking additive based on the products of petroleum pyrolysis, characterized by low ash content ($A^d = 0.4\%$), high sulfur content ($S_t^d = 4.1\%$), and high yield of volatiles ($V^{daf} = 17.2\%$) relative to coal concentrates. Individual coking of DK coking additive yields a product (particle size >40 mm) with postreactive strength $CSR = 77–79\%$, reactivity $CRI = 18–22\%$, and density 1200–1400 kg/m^3. Differential scanning calorimetry of experimental coke samples reveals six stages in their heat treatment in air: preliminary heating, intense oxidation, gasification of carbon, surface combustion of the gaseous products, their flare combustion, and oxidation of the residue. The use of DK coking additive in the coking batch shifts the oxidation process to higher temperatures and ensures the largest interval of heat liberation at elevated heating rate, with up to 50% DK additive. With increase in the content of DK additive from 30 to 50%, the activation energy is increased by 4.56 kJ/mol for each additional 10%. In that case, the supply of atmospheric oxygen to the combustion zone must be improved

Keywords: coking additives, baseline batch, experimental batch, coking, oxidant, activation energy

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In shaft-type smelting furnaces, the fuel is generally metallurgical coke, which, in counterflow of the gases and solid materials, ensures relatively uniform initial distribution of the gaseous combustion products, high gas permeability, a vertical batch column, and the supply of the required heat to the lower region [1].

In that case, the solid-fuel pieces must have minimal mineral ballast (preferably no more than 12% slag-forming components, moisture, etc.); high strength when cold ($M_{25} > 85\%$, $M_{10} \leq 7.0\%$) and at high temperatures (postreactive strength $CSR \geq 60\%$); and optimal granulometric composition (at least 80% of the 25–40 mm class with a packing density of 430–480 kg/m^3) [2].

To ensure such coke properties, the initial components of the coking batch (the yield of volatiles, the clinkering and coking properties, the metamorphic stage, the vitrinite content, and the liquidity of the decomposition products) must be carefully chosen, as well as the preparation of the coal batch and the coking process [3]. The coking technology remains basically the same during batch clinkering [4]; its parameters are determined by the heating of the coke furnace. At the same time, the selection of the batch composition in industrial conditions will depend on the clinkering and coking properties of the individual coal components and their interaction in the batch on coking.

The properties of coking batch may be stabilized by means of coking additives based on the products of petroleum pyrolysis [5]. We consider DK coking additive (Technical Specifications TU 0258-229-0190437–2008) [6]. It is produced by slow coking, with holding of the solid petroleum residue at 500°C. The characteristics of the resulting product are as follows:

Analytical moisture content W^a, %	0.21
Ash content A^d, %	0.4
Yield of volatiles V^{daf}, %	17.2
Total sulfur content S_t^d, %	4.1
Fixed-carbon content FC^d, %	80.1
Clinkering index G	9
Gray–King coke type	G_4
Audibert–Arnu dilatometric characteristics:	
a	21
b	–29
Initial temperature of the plastic state t_{I}, °C	325
Maximum-compression temperature t_{II}, °C	470
Solidification temperature t_{so}, °C	495
Plastic temperature range Δt, °C	170
Gieseler maximum fluidity $F_{\max}$ in the plastic state, min^{-1}	39

Table 1. Characteristics of experimental coke samples

Rank of coal, batch	Composition, %, of batch					Coke quality, %	
	Batch	1	2	3	4	*CRI*	*CSR*
GZh	43	34.4	21.5	0	0	–	–
GZhO + Zh	0	0	0	20	0	–	–
Zh + KS	19	15.2	9.5	0	0	–	–
KS	19	15.2	9.5	0	0	–	–
KO	19	15.2	9.5	0	0	–	–
DK	0	20.0	50.0	80	100	–	–
Baseline batch	100	–	–	–	–	31.4	54.0
Batch 1	–	100	–	–	–	27.5	58.9
Batch 2	–	–	100	–	–	23.6	66.7
Batch 3	–	–	–	100	–	30.3	62.2
Batch 4	–	–	–	–	100	18.2	79.9

If DK coking additive is used as the main component of coking batch, the properties of the coke produced — its strength, reactivity, and ash content — may be regulated by changing the clinkering conditions. Individual coking of DK additive yields a product (particle size >40 mm) with postreactive strength *CSR* = 77–79%, reactivity *CRI* = 18–22%, and piece density 1200–1400 kg/m^3 [7].

To study the oxidation kinetics of coke produced in a laboratory furnace, in the presence of DK coking additive, by the procedure in State Standard GOST 9521–74, six experimental batches are prepared. The mass of the charge is 2 kg; the piece size is ≤3 mm; the width of the retort is 110 mm; the charge is heated to 1000°C in 3 h. Table 1 presents the composition of the baseline and experimental batch and the quality of the coke produced, assessed in terms of *CRI* and *CSR*, in accordance with State Standard GOST R 54250–2010 (ISO 18897:2006 standard).

Analysis of the characteristics of the experimental coke shows that increasing the DK content in the initial batch reduces *CRI* as follows

$$CRI = 0.0002\mathrm{DK}^2 - 0.0602\mathrm{DK} + 30.017,\ \%.$$

The increase in *CSR* may be described as follows

$$CSR = 0.0004\mathrm{DK}^2 - 0.166\mathrm{DK} + 55.136,\ \%.$$

Such variation in the coke properties is evident from the indirect characteristics of coke oxidation on heat treatment in shaft-type smelting furnaces.

To analyze the reaction between the combustible coke components and atmospheric oxygen, we conduct differential scanning calorimetry of representative samples in the initial state and after roasting at 2.5, 5.0, 10.0, and 20.0°C/min in air. In Fig. 1, we show the complete curve for the differential scanning calorimetry of a coke sample without DK additive on heating at 5°C/min in air.

In accordance with the data obtained for sample heating at constant rate, we may identify six stages in their heat treatment in air [8]. The initial heating of the coke samples (stage 1) is accompanied by increase in their heat content, with gradual activation of the oxidation of carbon and the liberation of excess heat at temperatures above 482°C. At ~533°C, equilibrium between heat absorption and heat liberation is reached in the experimental samples. This is the ignition temperature of the coke. Further heating of the sample (stage 2) is accompanied by significant increase in the heat liberation. However, marked change in their mass is only noted above 582°C. In further heating, the sample mass declines until the carbon has been completely oxidized.

Heat generation in the oxidation of coke pieces corresponds to the laws of solid-fuel combustion, which basically correspond to the development of the reactions [8]

$$\mathrm{C} + \mathrm{O_2} = \mathrm{CO_2} + 34000\ \mathrm{kJ/kg}, \qquad (1)$$

$$\mathrm{C} + 0.5\mathrm{O_2} = \mathrm{CO_2} + 10\,300\ \mathrm{kJ/kg}, \qquad (2)$$

$$\mathrm{CO_2} + \mathrm{C} = 2\mathrm{CO} - 13\,500\ \mathrm{kJ/kg}. \qquad (3)$$

Heat is liberated in Eqs. (1) and (2); the reactions develop predominantly in the surface layers of the samples, where there is excess oxygen concentration (stage 2). This stage continues until conditions develop for the predominance of the endothermal processes in Eq. (3). For Eq. (3), elevated temperatures are required, and the combustion products must contain CO$_2$. Therefore, at ~640°C, the maximum heat liberation due to oxidation of the carbon in the fuel is observed.

With further increase in sample temperature, endothermal gasification of the carbon in the coke is observed (stage 3). The temperature of the coke pieces declines. The thermal effect of these processes dominates up to ~890°C. Further increase in sample tem-

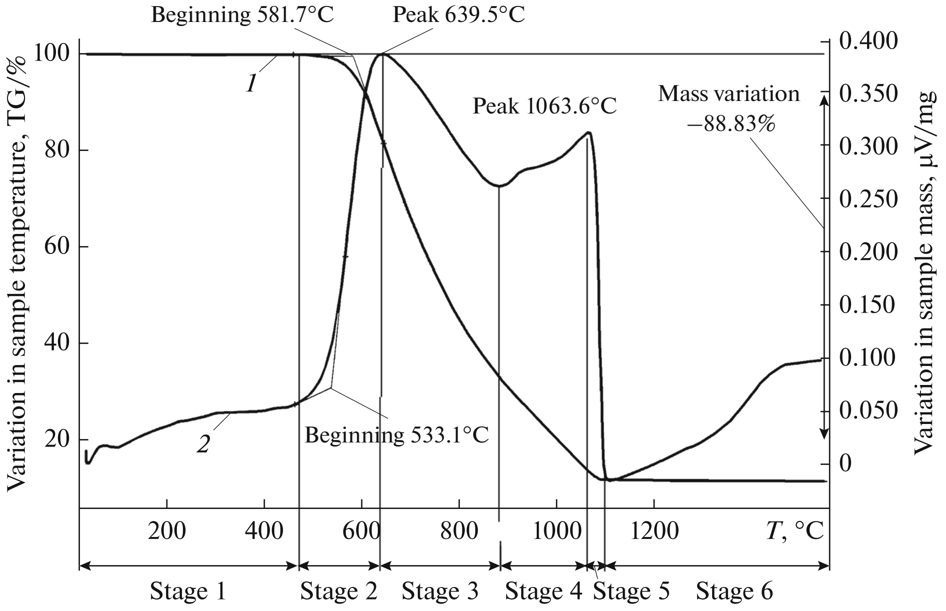

Fig. 1. Differential scanning calorimetry of the initial coke sample without DK coking additive: (*1*) mass loss (TG); (*2*) thermal effects (DTA).

perature in the presence of atmospheric oxygen (stage 4) ensures complete combustion of the gaseous products close to the sample surface. In that case, the thermal state of the coke pieces is characterized by increase in their mean temperature.

This is accompanied by gradual shift of the zone of CO combustion from the sample surface into the gas phase (flare combustion of the gaseous products). That sharply reduces the sample temperature on heating to 1100°C (stage 5). Further increase in temperature of the coke samples (stage 6) is accompanied by diffusion of oxygen molecules into the pore structure of the coke and the oxidation of internal layers of the carbon residue. This stage continues until the carbon has been completely oxidized.

In terms of heat generation, the kinetic assessment of the oxidation of the carbon in coke relies on data for stages 1 and 2, since the subsequent stages are mainly determined by the reaction of the gas phase with the solid coke surface.

Table 2 presents the oxidation conditions of the coke carbon in the presence of different quantities of DK coking additive.

In Fig. 2a, we show experimental results for the temperature at which the thermal effect of coke oxidation begins as a function of the quantity of DK additive and the rate of sample heating. With increase in heating rate, their oxidation is shifted to higher temperatures, on account of change in the heating of the coke pieces.

With increase in the content of DK coking additive, we note a minimum of 516°C in the ignition temperature of the coke at a low heating rate (2.5°C/min), with ~50% DK additive. Increasing the heating rate shifts the minimum to lower DK concentrations. Thus, at 5°C/min, the minimum is 522°C with 40% DK additive; at 10°C/min, the minimum is 539°C with 35% DK additive; at 20°C/min, the minimum corresponds to the absence of DK additive.

In Fig. 2b, we see that, along with the oxidation of carbon, mass loss from the heated coke is also associated with gasification and the removal of volatiles. The temperature at which such mass transfer begins increases with increase in the heating rate.

The influence of the DK content is seen only in increased heating rates (above 5°C/min). The temperature at which mass losses begin is lowest with 50% DK additive.

Increasing the heating rate of the coke pieces also increases the sample temperature corresponding to the maximum thermal effect (Fig. 2c). The greatest effect is seen at heating rates above 8–10°C/min.

At the same time, the temperature corresponding to the maximum thermal effect is greatest with ~50% DK additive. Note also that the corresponding dependence is most pronounced at heating rates above 8–10°C/min.

The temperature T at which coke oxidation begins, its heating rate v, and the Kissinger activation energy Q may be described by the relation

$$\ln\left(\frac{v}{T^2}\right) = -\frac{Q}{RT} + \ln(n),$$

where R is the universal gas constant ($R = 8.314$ J/mol K); n is the preexponential factor.

Table 2. Oxidation of coke samples with different DK content

DK content, %	Heating rate, °C/min	Mass loss, %	Temperature, °C			Rate of mass loss,* %/min	Rate of heat liberation,* (mJ/mg)/min
			onset of mass losses	onset of thermal effect	peak thermal effect		
0 (baseline)	2.5	91.59	567.4	526.7	633.6	0.88	0.0075
	5	90.7	581.9	534.4	637.5	0.97	0.016
	10	88.58	686.2	562.1	686.7	1.42	0.054
	20	78.65	690.7	564.2	717.2	1.7	0.078
20	2.5	94.05	546.5	513.2	606.2	0.26	0.008
	5	92.92	600.8	532.1	670.7	0.93	0.013
	10	92.19	618.2	540.9	691.6	1.29	0.044
	20	80.8	710.2	562.2	739.6	1.87	0.05
50	2.5	99.98	590.6	523.2	620.6	0.645	0.0012
	5	99.12	590.9	535.7	620.6	1.18	0.015
	10	62.57	609.7	537.8	692.3	1.29	0.043
	20	60.6	620.8	548.5	726.3	1.96	0.062
50	2.5	44.15	573.3	511.6	–	0.011	–
	5	30.4	602.4	526.5	–	0.014	–
	10	17.14	648.4	550.1	–	0.029	–
	20	4.43	728.2	688.3	–	0.042	–
80	2.5	99.04	551.9	509.6	614.8	0.617	0.0094
	5	98.94	577.1	526.7	650.8	0.807	0.027
	10	98.17	597.7	554.8	662.6	1.18	0.058
	20	72.95	617.6	567.6	701.9	1.53	0.099
100	2.5	26.7	579.4	534.2	–	0.009	–
	5	13.9	611.3	589.6	–	0.021	–
	10	3.61	666.9	597.4	–	0.037	–
	20	1.53	738.1	698.5	–	0.044	–

* In steady conditions.

Given that the temperature at which thermal effect begins corresponds to Fig. 2a, we may define the activation energy of oxidation as the slope of the straight line $\log(v/T^2) = f(1000/T)$. Table 3 presents experimental results for the activation energy.

The experimental data show that, with increase in the DK content to ~30%, the activation energy of the coke declines from 45.88 to 32.2 kJ/mol—that is, by 4.56 kJ/mol for each additional 10% of DK additive.

Further increase in DK content requires significant increase in the energy consumption—by 20.84 kJ for each additional 10% of DK additive, on average. The preexponential factor declines continuously with increase in the DK content. This behavior is most pronounced up to 60% DK.

Given that the activation energy is mainly determined by the ignition temperature of the coke, which increases from 15°C at a heating rate of 2.5°C/min to 100°C at 20°C/min, according to Fig. 2a, we conclude that the kinetics of coke consumption does not depend greatly on the ignition temperature and require limitations on the DK content in the initial batch.

Since the preexponential factor is determined by the conditions of gas flow around the batch pieces in the organization of coke combustion, reduction in the preexponential factor entails improved access of

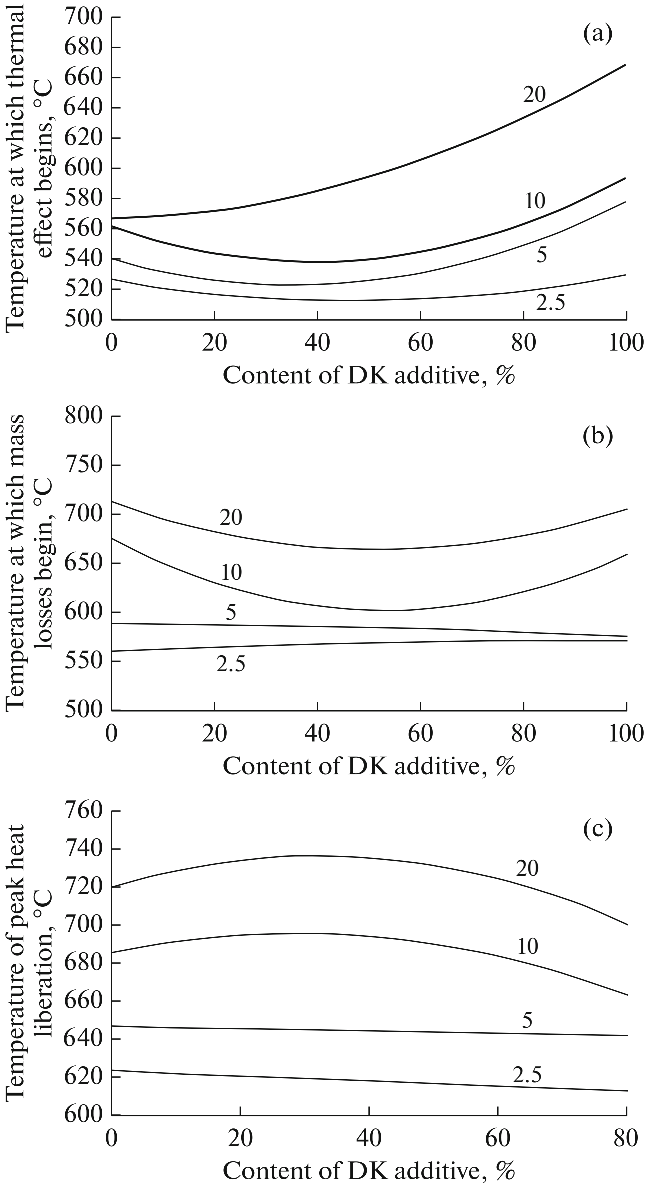

Fig. 2. Temperature at which thermal effect begins (a), temperature at which mass losses begin (b), and temperature of peak heat liberation (c) as a function of the DK content and the heating rate (°C/min, given on the curves).

atmospheric oxygen to the combustion zone. Note that, with >80% DK additive in the initial batch, stable coke ignition is impossible without changing the air supply. The best coke oxidation corresponds to no more than 50% DK additive in the batch. According to the experimental data, satisfactory heat generation in the bed requires 2–3% increase in the gas flow rate for each additional 10% of DK additive.

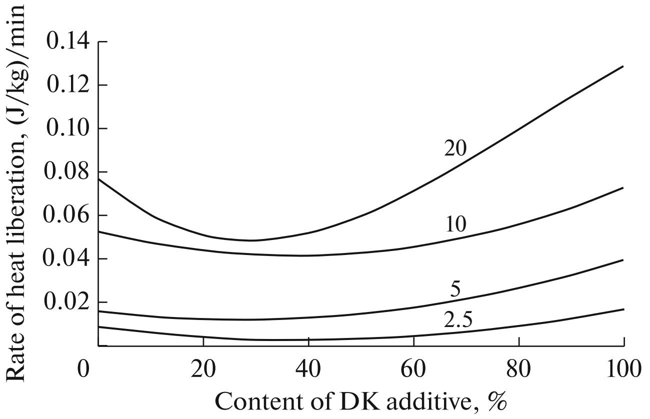

Fig. 3. Rate of heat liberation in the oxidation of carbon from coke as a function of the DK content in the batch and the heating rate (°C/min, given on the curves).

In Fig. 3, we show the rate of heat liberation in the heating of coke samples in an oxidative atmosphere, with different quantities of DK additive. Analysis shows that, regardless of the heating rate, the rate of heat liberation is least with around 30–50% DK additive in the initial batch. Increasing the heating rate boosts the rate of heat liberation in the oxidation of the coke.

CONCLUSIONS

(1) Analysis of the characteristics of the experimental coke samples shows that increasing the content of DK coking additive in the initial batch reduces the reactivity *CRI* and increases the postreactive strength *CSR* of the coke.

(2) On heating coke samples at constant rate in air, six stages are observed: preliminary heating up to 482°C; intense oxidation up to 640°C; gasification of carbon up to 890°C; surface combustion and then flare combustion of the gaseous products up to 1100°C; and oxidation of the residue.

(3) With increase in the heating rate of the initial components, their oxidation is shifted to higher temperatures on account of change in the heating conditions of the coke pieces.

(4) When the content of DK additive in the batch is up to ~30%, the ignition temperature of the coke rises. More profound oxidation of the carbon requires improved access of atmospheric oxygen to the working bed.

(5) Increasing the DK content in the batch to 30% lowers the activation energy of the coke from 45.88 to 32.2 kJ/mol and reduces the preexponential factor. That entails limitation of the DK content in the batch and improvement in the oxygen supply to the combustion zone.

(6) Regardless of the heating rate of the coke, the rate of heat liberation is least with around 30–50% DK additive in the initial batch. Increasing the heating rate boosts the rate of heat liberation in the oxidation of the

Table 3. Activation energy of batch oxidation

DK content, %	n,* s^{-1}	Activation energy, kJ/mol		Correlation coefficient	Order of reaction
		experimental value	standard deviation		
0 (baseline)	$2.51 \pm 1.79 \times 10^{-2}$	45.8803	0.29	0.993	1.52
20	$2.26 \pm 1.73 \times 10^{-2}$	40.3632	0.31	0.996	1.41
50	$3.64 \pm 3.43 \times 10^{-2}$	41.7267	0.23	0.983	1.15
50	$2.20 \pm 1.77 \times 10^{-2}$	50.6551	0.31	0.994	1.51
80	$3.71 \pm 2.06 \times 10^{-2}$	73.5370	0.50	0.988	1.19
100	$2.68 \pm 1.74 \times 10^{-2}$	178.0768	0.48	0.893	1.29

* Preexponential factor in the Arrhenius equation.

coke, predominantly on account of gasification of the fuel and the liberation of volatiles.

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