Petroleum and Coal

Article **Open Access**

The pyrolytic interaction of coal tar pitches with various coals

Fedor F. Cheshko, Valeriia V. Karchakova, Valentin V. Koval

Ukrainian State Coal-Chemistry Institute, 61023, Kharkov, 7 Vesnina Str., Ukraine

Received July 20, 2019; Accepted November 3, 2020

Abstract

The effect of coal tar pitch on the sintering ability of individual coals, significantly differing in their properties, has been studied. When choosing coals, first of all, we focused on the yield of volatile substances and plastometric indicators. A technique developed by SE "UKHIN" was used to determine the caking ability of pitch with coal. An indicator of the sintering ability of coal by this method is an assessment of the strength of the sintered lump residue. The results can not be considered the absolute numerical characteristics of the studied coals and coal tar pitch, but they can be used to compare the nature of the interaction of coals of varying degrees of metamorphism with coal tar pitch during coking. It is shown that the influence of coal tar pitch on the process and properties of the product of coal coking is extremely selective and depends on such properties of coal as the yield of volatile substances and the ability to release plastic mass when heated.

Keywords: *Coal; Volatiles yield; Plastic layer thickness; Coking, Coal tar pitch; Mixture; Semi-coke; Shear strength; Sintering ability.*

1. Introduction

The possibility of introducing organic plasticizing and sintering additives over a number of years into the coal mixture for the production of metallurgical (primarily blast furnace) coke over the course of a number of years has caused the undiminishing interest of researchers. Coal peaks and other hydrocarbon materials of coal origin, plastics, and oil products are considered as such additives [1-2]. The main goal of this technological technique is to reduce the cost of coking charges by increasing the share of cheap low-caking coals in it due to more expensive coking grades. The introduction of such additives is all the more relevant for the coking of a partially briquetted coal charge – in this case, the mentioned materials are used as a binder for coal briquettes [3].

Among the listed additives, coal tar sands are distinguished not only by a number of unique technological properties that contribute to the best effect of coking in the coal mixture but also by increased carcinogenicity [4] – in particular, the ability to emit volatile carcinogenic substances during pyrolysis, which can have an extremely negative impact on environmental indicators of the coke production. The latter feature imposes severe restrictions on the quantitative participation of pitch in the composition of coking feedstock.

From the literature references, it follows, for example, that the maximum improvement in the strength properties of metallurgical coke is achieved with the participation in charge of 4% by weight of coal tar pitch [5-6]. Based on the carcinogenicity of this material, it seems advisable to further reduce its share in the coke charge. In this regard, an important role can be played by the method of introducing pitch into the coal mixture.

As is known, the initial charge for producing metallurgical coke may include 5-8 or more grades of coal, significantly differing in their properties [5-7]. The introduction of a hydrocarbon additive, in particular pitch, into the finished mixture or into one of its components before mixing them can have a significant impact on the nature of the formation of the properties of the resulting coke. Determining the optimal method of introducing the pitch into the charge, in turn, requires knowledge of the results of the interaction of coal tar pitch with coals of various grades during their pyrolysis. The study of this issue was the purpose of the work presented in this article.

2. Experimental

We have studied the effect of the coal tar pitch on the sintering capacity of individual coals, which differ significantly in their properties. Taking into account the possible mechanisms of the sintering of coal grains in the presence of the coal tar pitch, when choosing coals, we focused primarily on the yield of volatile substances and plastometric indicators. The properties of the coals used are presented in Table. 1.

Table 1. Characteristics of coal samples

Number of sample	Technical analysis, %			Plastometric indicators, mm	
	A^d	S^d_t	V^{daf}	*x*	*y*
1	9.7	2.58	38.6	42	11
2	8.7	1.07	31.7	12	21
3	8.0	0.71	18.3	10	12
4	1.8	0.50	5.4	does not form a plastic layer	

Plastometric properties of coals were determined according to DSTU 7722: 2015: Coal. Method for determination of plastometric indicators, according to which *x*, mm, is the value of plastometric shrinkage of coal, i.e., the final change in the height of the coal charge at the end of the test; *y*, mm, is the thickness of the plastic layer formed when the coal is heated, i.e., the maximum distance between the interfaces "coal-plastic mass-semi-coke". The properties of the pitches used for testing are presented in Table. 2.

Table 2. Characteristics of coal pitch samples

Characteristics	Number of sample	
	pitch No 1	pitch No 2
Softening point (according to "Ring & Rod" method), °C	86	135
Viscosity at 185°C, cP	375	< 0,3
Volatiles yield at 850°C, %	53,4	38,3

For this purpose, we have chosen two samples of commercial coal tar pitch, differing in basic properties that are decisive for the sintering process with solid filler. These properties include: a softening temperature and viscosity, which are responsible for enveloping (wetting) filler grains with pitch, and the release of volatile substances, which determines both the amount of solid coke residue formed by a pitch and the degree of environmental hazard of the pitch in the process of its thermal transformations.

To determine the sintering capacity of pitches with coals, we used a technique developed at SE "UKHIN" [8-9]. An indicator of the sintering capacity of coals by this method is the assessment of the strength of the sintered lump residue. Since the process of sintering of coals and charges ends with the formation of semi-coke, it is the strength of the semi-coke that is an objective characteristic of sintering [8-9].

In the course of testing, the mixtures of individual coals and pitches ground to an analytical fineness (≤ 0.25 mm) were molded in a special matrix using a hydraulic press at the same pressure, then placed in a special electric furnace and heated at a rate of 10°C / min to a temperature of 680 °C, at which it was kept for 30 min. The content of coal and pitch in the samples was 97 and 3% by weight, respectively. All moldings before heating were cylinders 17 mm high and 11 mm in diameter. The solid residues obtained as a result of semi-coking were removed from the matrix, and their shear strength was determined. The results obtained (average of five determinations) were used as indicators of sinterability.

The results obtained cannot be considered absolute numerical characteristics of the studied coals and coal tar pitch, but they can be used to compare the nature of the interaction of coals of varying degrees of metamorphism with coal tar pitch during coking.

3. Result and discussion

The research results are presented in Table. 3.

Table 3. Results of determining the sintering capacity of coal with pitch

No	Coal	Pitch	Forming weight, g			Residue size after semi-coking, mm, height/diameter	Shear strength, MPa
			before semi-coking	after semi-coking	Weight loss, %		
1	1	1	2.43	1.49	38.7	21.0/12.0	26.58
2		2	2.37	1.48	37.6	21.8/11.5	30.79
3		-	2.38	1.50	37.0	22.0/12.0	21.67
4	2	1	2.38	1.58	33.6	30.0/12.5	3.82
5		2	2.42	1.64	32.2	36.0/12.3	2.75
6		-	2.42	1.60	33.9	32.0/12.0	11.77
7	3	1	2.34	1.77	24.4	24.0/12.0	23.92
8		2	2.37	1.79	24.5	23.0/11.5	28.05
9		-	2.32	1.77	23.7	20.0/12.0	38.05

Coal 4, which does not form a plastic mass upon heating and is characterized by an extremely low yield of volatile substances, showed no tendency to sintering either individually or in the presence of both studied pitches. Probably, for its sintering, an amount of sintering agent is required, significantly exceeding 3%. It should be recalled here that in electrode production for sintering fillers devoid of thermoplasticity, from 10-15 to 25-30% of pitch-binder can be introduced into them. In coal-coke production, due to the volume of raw materials processing and the specifics of the main equipment, the use of such quantities of pitch is unrealistic from the point of view of both available resources and production ecology.

Analyzing the data in Table 3, you can see the following.

The addition of both coal tar pitches led to an increase in weight loss during the semicoking of coals No. 1 and No. 3, which have a similar *y*-index (11 and 12 mm, respectively), as well as maximum (coal No. 1, V^{daf} = 38.6%) and minimum (coal No. 3, V^{daf} = 18.3%) among the investigated caking coals by the values of the yield of volatiles. Coal No. 2, characterized by the maximum value of the thickness of the plastic layer *y* (21 mm) and a sufficiently high yield of volatile substances (31.7%) in the presence of both pitches, demonstrated a slight decrease in weight loss during semi-coking, which indicates the intensification of thermochemical transformations leading to the transition of liquid and gaseous intermediate semi-coking products into the solid phase. This effect is especially noticeable in the presence of pitch with a lower yield of volatile substances and higher viscosity (pitch No. 2), which indicates the predominant participation of liquid rather than gaseous products in the intensification of thermal compaction processes. This is confirmed by the fact that the same coal-pitch pair (experiment No. 5) is characterized by the greatest increase in the linear dimensions of the char residue as compared to both the initial molding and the semi-coke residue of coal No. 2 without additive (experiment No. 6). This is a consequence of an increase in the viscosity of the plastic liquid phase of coal during its thermochemical interaction with the components of coal tar pitch, as a result of which the outflow of vapor-gas semi-coking products is impeded, and the swelling effect is observed. The latter is unambiguously negative from a technological point of view since the industry threatens with the destruction of coke oven masonry. Swelling of forming coal No. 2 without pitch additives is also the highest among the studied coals. It is characteristic that coal No. 3 with pitch additives swells much less pronounced, and the introduction of the pitch into coal No. 1 (having a higher yield of volatile substances, but almost half the *y*-index than coal No. 2) significantly reduces the swelling of the heat-treated molding.

Despite a slight increase in the semi-coke yield when the pitch is added to coal No. 2, the strength of the semi-coke residue, which is already extremely low for this coal, is further reduced by the addition of pitch. This can be explained both by the physicochemical properties of the products of the interaction of the components of the plastic mass of this coal with the components of the pitch and by the structure of the semi-coke residue. However, in Fig. 1, we see that the chips of semi-coke residues of all three coals, heat-treated both individually and with pitch additives, do not have distinct differences.

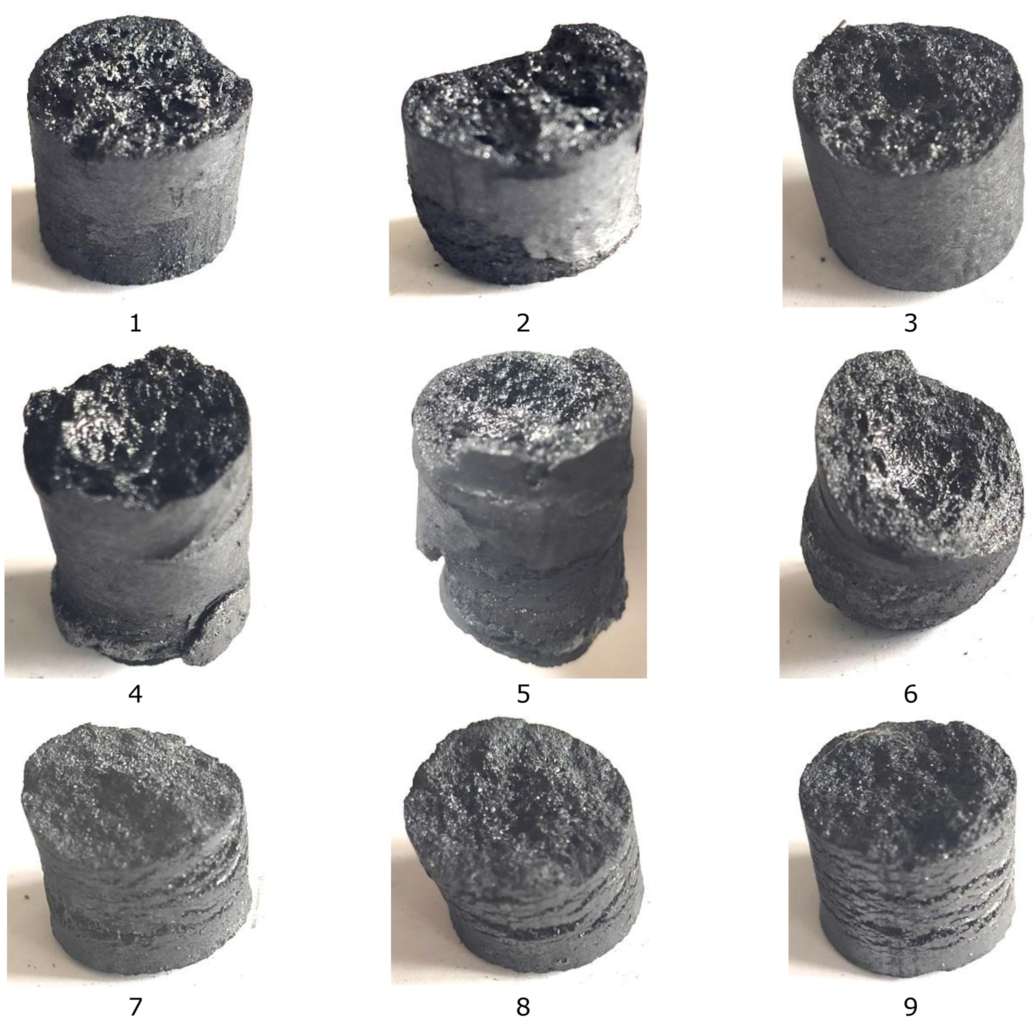

Fig. 1. Type of chips of semi-coke moldings obtained as a result of experiments 1-9 (see Table 3)

On the chips of semi-cokes based on coal No. 2 (Fig. 1, 4-6), the pores of an average size of an oval cross-section are visible, and the cleavage of this coal obtained with the addition of pitch No. 1 (Fig. 1, 4) appears to be loose; the chips of semicoke coal No. 3 (Fig. 1, 7-9) have a fine-grained structure; however, the presence of pores and graininess is also typical for the chips of samples obtained on the basis of coal No. 1 (Fig. 1, 1-3). Proceeding from the absence of visually pronounced differences in the structure of the obtained semi-cokes, it is permissible to assume that the differences in their strength (and, consequently, the caking ability of the initial components) are determined mainly by the physicochemical properties of the starting materials and the semi-coke.

On the whole, from those results given in Table 3, the following main differences are seen between semicokes based on coal No. 1: of the investigated, this is the only coal, the introduction of coal tar pitch into which led to a decrease in swelling (an increase in the linear dimensions of the molding as a result of semicoking) and contributed to an increase in the strength of the semicoke (sintering).

Thus, in the course of these studies, the positive effect of the addition of coal tar pitch was demonstrated by coal with an insignificant indicator of the thickness of the plastic layer and the maximum yield of volatile substances. At the same time, the positive effect for pitch No.

2 is more noticeable than for pitch No. 1. The worst effect was noted for the pitch with the maximum plastic layer thickness and swelling (plastic layer thickness + volatile matter yield at the level of coal No. 1).

4. Conclusion

The influence of coal tar pitch on the process and properties of the coking product of individual coals is not the same and depends on such properties of coal as the yield of volatile substances and the ability to release plastic mass when heated.

The addition of coal tar pitch to coal, characterized by a high (about 38%) yield of volatile substances and a low (11-12 mm) thickness of the plastic layer, can reduce the swelling of coal during coking and improve the mechanical strength of the resulting coke. According to the classification adopted in Ukraine and the CIS countries, such coals belong to the so-called gas group. In this case, the positive effects are more noticeable for the pitch with a higher softening point. Additions of coal tar pitch to coals, which, when heated without access to the air, release significant amounts of plastic mass (y-value at 20 mm), can not only negatively affect the properties of the resulting coke but also intensify the factors of serious technological risk.

Additives of coal tar pitch to non-caking coals can give a positive effect only when the amount of pitch significantly exceeds 3% of the coal mass. The problem raised requires a deeper study, including in a production environment.

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To whom correspondence should be addressed: Dr. Fedor F. Cheshko, Ukrainian State Coal-Chemistry Institute (UKHIN), 61023, 7 Vesnina str., Kharkov, Ukraine, E-mail: chishkof@ukr.ne t