Study of cellulose additive effect on the caking properties of coal

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Abstract

Purpose. The work aims to study the effect of cellulose on the caking properties of various types of coking coal used in coking blends. The change in caking abilities has been analyzed to achieve the aim using standard techniques. At the same time, the effect of biomass additives on the plastic properties of coal has been analyzed comprehensively; the optimal amount of additive for practical purposes has been determined.

Methods. Multiple coal characteristics in the plastic stage have been studied using a dilatometric method, the enhanced swelling pressure method, the plastometric method, and the Roga index test. The first three methods make it possible to characterize the caking properties of coal; and the Roga index test characterizes its coking ability.

Findings. It has been identified that the optimal amount of biomass additive to study the effect on the properties of coal in the plastic state is more than 5 wt. %. In the paper, experimental dependences of the 5 wt. % cellulose addition influence on the caking properties of four coal grades have been obtained. The results showed a slight decrease in caking properties in terms of swelling, swelling pressure, thickness of the plastic layer, and caking ability. Simultaneously, the most sensitive methods for assessing the effect of cellulose addition on the coal plastic properties are the dilatometric method as well as the enhanced method for the swelling pressure determination.

Originality. A comprehensive study of the effect of pure cellulose as a component of lignocellulose biomass on the properties of different coal grades in the plastic state (i.e. caking prperteis) has been carried out. A slight change in the coal properties in the plastic state with adding 5 wt. % cellulose, decreasing caking properties, has been shown. An important, not previously reported, conclusion is that the cellulose additive does not have any noticeable effect on the physical properties of the coal charge owing to its loose structure.

Practical implications. A slight change in the caking properties of coal has been established with the addition of 5 wt. % which is of practical importance for the preparation of coal blends, and the coke production in the cases of using additives of lignocellulosic biomass without losing its quality. Additionally, renewable additive use while obtaining fuels and reducing agents is an approach to mitigate the negative environmental impact.

Keywords: coking coal, caking property, cellulose, coal plastic layer, swelling, swelling pressure

1. Introduction

In the last decade, solution to the issues of improvement and development of metallurgical processes has been actively taking into account the reduction of harmful emissions and greenhouse gases (GHGs); the decline in the formation of non-recyclable waste; and the increase in product quality as well as technical and economic indicators of production. Achieving Greenhouse Emission Neutrality by 2050 under the Paris Convention [1], [2] or early dates given by various countries and enterprises [3]-[9] requires a reduction in fossil fuel use with a gradual complete decline of it in metallurgical processes.

Coke production is an auxiliary metallurgical process that provides blast furnace (BF) and non-blast furnace (NBF) production with coke while consuming a large amount of fossil coal. In many countries, the active metallurgical infrastructure makes the coke production almost certainly a source of fuel and reducing agents in a smelting industry.

Such a renewable source as biomass can be used to reduce the impact of metallurgy on GHG emissions [10]-[15].

As many studies mention, use of biomass and its processing products can expand the potential of coke and chemical production while obtaining cokes of different grades for a wide range of manufacturing processes [16]-[22]. Additionally, the use of biomass waste will have a positive effect on the agricultural industry extension [23]-[25].

It should be mentioned that over the recent years, significant efforts have been made to use biomass and its products in the metallurgy [5], [14], [26]-[29]. The issues of injection of biomass, the torrefied biomass, and charcoal into a BF have been studied in detail [30]-[34] as well as charcoal BF charging [35], [36]; the use of charcoal and biocoke in the production of iron ore sinter [29], [37]-[44]; biomass for pellets [25], [45], [46]; charcoal for electric arc furnace (EAF) [21], [47]-[49]; and submerged arc furnace (SAF) [21], [50] to obtain

carbon composite agglomerates [45], [46], [51]. Studies show that biomass and the products of its processing can replace a significant amount of conventional sources of fuel and reducing agents (i.e. coal, coke, and natural gas); in the future, they will increase the replacement share for renewable sources with possible complete exclusion of fossil fuels in the context of certain metallurgical processes (i.e. production of pellets, direct reduction, and SAF).

Lately, biofuel production has increased significantly. Its further growth up to 25% is predicted in 2024 [52]. One of the ways of biomass use to generate fuel and reducing agents is coal and biomass co-pyrolysis. At the same time, different types of lignocellulosic biomass can be used as biomass, including the agricultural state inputs (i.e. straw, stalks, and leaves); forestry (i.e. sawdust); and various food processing waste (i.e. nutshell, rice husks, seeds etc.).

Along with heating conditions, the structural and technical properties of biomass, can have a key effect on coal caking and, consequently, on the manufactured coke grade. Features of thermal decomposition during the coal and biomass co-destruction are of particular interest; they were studied thoroughly [53]-[57]. At the same time, there is a discussion about active or inert biomass influence on the process of coal caking [58]-[60]. The study of biomass and well-coking coal co-pyrolysis has its own physical and chemical characteristics associated with the plastic layer properties (i.e. its quantity, composition, viscosity, and gas permeability). Therefore, studying the issue of biofuel obtaining through biomass and coal co-processing should involve theoretically based understanding of the thermal destruction processes along with practical confirmation.

The pyrolysis process of coal is continuous and non-isothermal with the destruction and formation of new chemical compounds. Destruction and synthesis processes during the pyrolysis are limited by the rate of thermochemical transformations of coal substances rather than by heat transfer within coal particles. Consequently, the coal pyrolysis effect will be influenced by additives that lead to changes in the processes of physical and chemical interaction of coal particles, primarily at the stage of a plastic state.

The plastic coal layer is a complex heterogeneous system consisting of steam-gas volatile matters, liquid (viscous) non-volatile as well as solid (highly condensed) products resulting from the thermal destruction of molecules of initial coal substances which vary continuously during heating without air access and interacting fragments differing in their molecular weight, composition, and structure. At the same time, co-occuring polycondensation processes play an essential role.

Caking is an important generalized coal characteristic in a plastic state which indicator is of primary importance for the analysis of coke formation conditions and control of the coal grade constancy. Reduction reactions soften caking of coal and its blends during pyrolysis; under static pressure and gas pressure, it is the ability of the residual material of coal grains to be coalesced as a result of diffusion and chemical interaction with a coke mass formation being of one or another strength.

Many scientists and researchers analyzed biomass influence on the caking properties of coking coal. Consequently, papers [61]-[69] studied impact by different types of biomass, and papers [62], [70]-[75] examined products of its processing to change the caking properties of coal. It has been understood that the increased biomass amount as well as charcoal additives results in the degraded coal caking

properties. At the same time, the charcoal influence is less noticeable compared to biomass additives. Simultaneously, paper [76] informs on the improved coal blend plasticity if the pre-heated biomass is added. It has been concluded that the release of hydrocarbons from high-temperature torrefied (pelletized sawdust of pine/spruce) and charcoal (mixture of pieces of pine, birch, alder, and aspen) occurs within the plasticity temperature range for the coal which contributes possibly to the better plasticity development of the blends.

Predominantly, the decrease in coal plasticity with the addition of the initial and processed biomass is explained by the negative effect of oxygen-functional groups [77], [78].

In studies, the amount of biomass or charcoal additive effecting coal caking properties is usually no more than 10 wt. %. At the same time, based on the analysis of papers, the optimal minimum additive amount is 5 wt. %. Commonly, in terms of the amount, a noticeable effect of the additive on the processes of thermal destruction of coal is observed.

Lignocellulosic biomass consists of carbohydrate polymers (cellulose, hemicellulose) and an aromatic polymer (lignin); it is the available renewable raw material for biofuel production. The percentage of lignocellulosic biomass contains approximately 30-50 wt. % cellulose; 15-30 wt. % hemicelluloses; and 15-30 wt. % lignin (Fig. 1) [79]. Cellulose is a part of the cell walls of plants. It makes up a large percentage share by the dry weight of the substance. Generally, cellulose is expressed using the empirical formula $(C_6H_{10}O_5)_x$ containing three free hydroxyls for every six carbon atoms. The cellulose molecule consists of 16-18 thousand or more carbon atoms. The technical features of lignocellulosic biomass are low ash and sulfur content, high volatile matter, and high moisture (hygroscopicity).
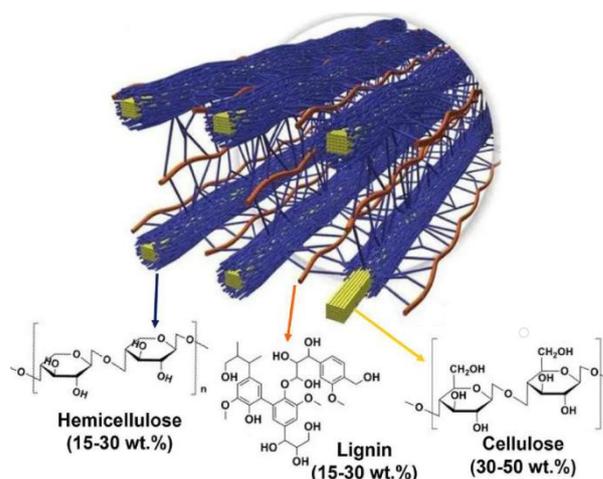
Figure 1. Structures of hemicellulose, cellulose, and lignin in lignocellulosic biomass [79]

Many scientific sources analyze biomass pyrolysis as a mechanism using individual pyrolysis behaviour of cellulose, hemicellulose, and lignin [80]-[82]. It has been reported that the temperatures of the beginning of thermal degradation of the lignocellulosic biomass components are as follows: 200-220°C for hemicelluloses; 275°C for cellulose; and almost 280°C for lignin [83], [84]. At the same time, in terms of coking coals, the minimum temperature to start the destruction of the main macromolecular structure is more than 300°C; the temperature should be about 360°C to transit to the plastic state.

Regarding the influence of individual components of lignocellulosic biomass, as [85] has been identified, lignin has negligible detrimental effect on the coal fluidity to compare with cellulose or raw biomass. Therefore, an important conclusion has been drawn concerning the predominant impact of cellulose (rather than lignin) on a coke grade. Thus, the study of the individual effect of cellulose on the caking ability of coal in the process of coke production is an important practical task.

Based upon the abovementioned, the aim is to study experimentally the effect of cellulose, being the main component of biomass, on the caking properties of coal, varying in grade, as a part of coking blends. Among the parameters characterizing the caking ability of coal, swelling, swelling pressure, the amount of plastic layer, and its caking ability according to the Roga index were under focus.

2. Materials and methods

The subject of the study was coking coal grades from Ukraine (A and C coal ranks) and the USA (B and D coal ranks). Table 1 represents the coal characteristics relying upon proximate analysis and the mean vitrinite reflectance (R_{om}). Coal proximate analysis was based upon ASTM D3172-13 [86]; and indicator R_{om} analysis was based upon ISO 7404-2:2009, ISO 7404-3:2009, ISO 7404-5:2009 [87]-[89].

Table 1. Characteristics of coking coal

Coking coal	Proximate analysis, wt. %				Vitrinite reflectance, %
	M	A^d	V^d	S_t^d	R_{om}
A	8.5	9.6	35.9	1.67	0.68
B	6.8	7.5	32.8	0.99	1.02
C	8.4	8.1	26.0	0.71	1.20
D	7.7	8.6	17.5	0.75	1.55

M – moisture; A^d – ash (dry basis); V^d – volatile matter (dry basis); S_t^d – total sulfur (dry basis)

Figure 2 shows vitrinite reflectance-volatile matter ratio being a standard for coking coal [17], [90].
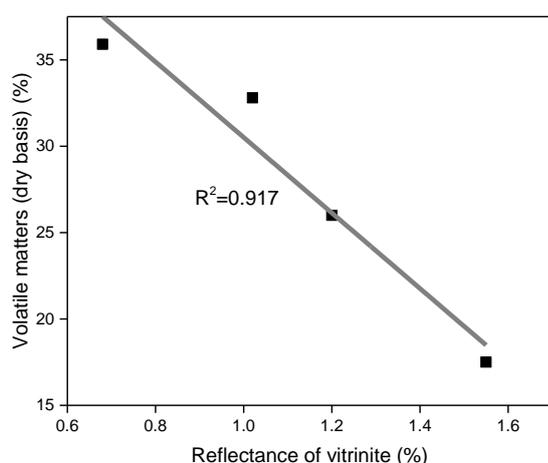
Figure 2. Vitrinite reflectance-volatile matter ratio in the context of studied coal grades

According to Ukrainian classification [91], [92], the coal grades are gaseous (A); fat (B); coking (C); and lean-caking (D) minerals; or low, medium, and high volatile bituminous coal in terms of ASTM D-388-19a [93].

As a cellulose additive, the widely available softwood pulp results from a pulping process. The additive amount is 5 wt. %. It has been selected based on the analysis of scientific sources, namely on the idea that the initial biomass affects significantly the coking coal caking with a minimum 5 wt. % amount. The cellulose size was less than 0.2 mm.

2.1. Determination of dilatometric indicators

A plastic layer viscosity and a volatile matter release dynamics determine coal swelling. Usually, the most significant values of swelling volume are coal characteristics; the plastic layer viscosity in the plastic state is minimal, and the amount of the released volatiles is maximal. The plastic layer of coal offers less resistance to a gas movement (i.e. it is more gas permeable), and more coal viscosity in the state of the greatest degree of fluidity.

Dilatometric parameters of different coal grades have been determined according to [94]. 2 ± 0.01 g of the compressed coal heats up in a metal tube at 218 MPa pressure; the heating period until the beginning of swelling (P_{bs}, s); the swelling period (P_s, s); and the swelling amount (swelling index I_s, mm) are identified under the conditions of the coal free swelling in the tube. The research was carried out using a modified apparatus, which made it possible to determine dilatometric parameters for all coal grades at the same heating 500ºC temperature. Each trial was repeated at least twice.

2.2. Determination of swelling pressure

Coal swelling pressure is the ability of coal to exert pressure within the limiting surface when heated in the fixed volume. The swelling pressure nature is explained by the fact that the coal plastic layer, being in the fixed volume and having a certain thickness and viscosity, resists passing volatile and gaseous products of the thermal coal destruction. Depending on its type, preparation method, and heating conditions, each coal grade develops a certain swelling pressure.

The method is to heat rapidly 2 ± 0.01 g coal sample compressed at 218 MPa and constant 500ºC temperature, and determine the swelling pressure dynamics in the context of 2 MPa initial external load [94]. In the course of the study, following indicators of coal swelling pressure dynamics have been determined: a being a period of thermal stability of coal before the softening started, s; b being a coal softening period, s; P_1 being softening exertion or primary shrinkage of coal, Pa; c being an equilibrium period of external pressure and coal loading pressure, s; d being the duration of swelling pressure action, s; P_2 being the maximum swelling pressure, Pa; e being an equilibrium period of the external pressure and the pressure of the coal plastic layer, s; f being a penetration period of the thermocouple cover into the plastic layer or the period of its pu-shing, s; and P_3 being the plastic layer pushing force, Pa. In addition, it is possible to use several complex indicators for better coal differentiation by properties, among which $P_2 \cdot d / 100$ is indicator with the most significant differential ability. Each trial was repeated at least twice.

2.3. Determination of plastometric indicators of coal

The method is to heat slowly the coal at a 3ºC/min rate in the 250 to 730ºC interval, and determine following plastometric parameters: plastic layer thickness (y, mm); and plastometric shrinkage (x, mm) in the special metal cup. At the same time, the measurement takes place in two cups placed above the silite heaters. The test sample weight is 100 g with less than 1.6 mm size at an external 9.1 MPa loading pressure [17].

2.4. Determination of caking ability of coal by Roga index

Caking is the ability of the separated coal grains, when heated without air access, to cake various inert (non-caking) materials with the formation of a solid residue of one or another strength. The Roga index determines coal caking ability with the help of mechanical strength of the residue obtained in a crucible during carbonization of the thoroughly mixed blend of 1 g of coal and 5 g of reference anthracite at the temperature of $850 \pm 10°C$ during 30 min. The resulting residue is examined in a drum using strictly established approach; the Roga index is calculated based on [95]. Each trial was repeated at least twice.

3. Results and discussion

Table 2 shows determination results of swelling dynamics of the initial coal with 5 wt.% cellulose additives (5 wt. % CLS).

Table 2. Results of swelling dynamics

Coal	P_{bs}, s		P_s, s		I_s, mm		$I_s \cdot P_s$, mm·s	
	Initial	5 wt. % CLS	Initial	5 wt. % CLS	Initial	5 wt. % CLS	Initial	5 wt. % CLS
A	398	373	54	56	4	5	216	280
B	415	385	398	395	89	83	35422	32785
C	490	466	322	298	50	45	16100	13410
D	531	520	488	465	23	19	11224	8835

Coal B and then coal C are characterized by the highest caking ability. They have the highest swelling indices; the additive effect is the most noticeable one for the coal grades (Fig. 3). As it is seen, cellulose participation in the process of coal caking leads to a decrease in I_s as well as in P_s. Therefore, cellulose addition has a thinning effect on the coals caking; and its behavior is similar to inert addition. In the context of A and D coal grades, according to the complex indicator $I_s \cdot P_s$, the total negative effect is reduced owing to the lower value of the swelling index as well as owing to high stability of the plastic layer for D grade coal (Fig. 4). It is important to note that the heating period before coal transition to its plastic state (P_{bs}) shortens noticeably if cellulose is added because of its poorer thermal stability to compare with coal.

Figure 3. Swelling index (I_s, mm) of the initial coal; swelling index with the added cellulose
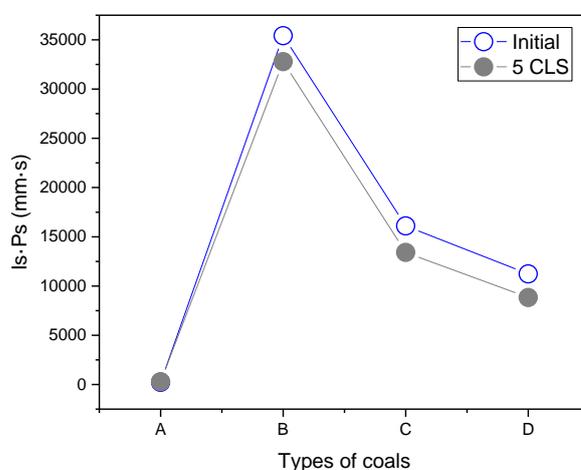
Figure 4. Complex swelling index ($I_s \cdot P_s$) of the initial coal; complex swelling index with the added cellulose

Table 3 demonstrates the results of cellulose additive effect on the swelling pressure of coal.

Cellulose addition saves time of coal transition to a pre-plastic state (*a, c*) as in case with P_{bs}.

Table 3. Indicators of pressure dynamics of the initial coal swelling without cellulose addition and with it

Coal	P_1, kPa	P_2, kPa	P_3, kPa	*a*, s	*b*, s	*c*, s	*d*, s	*e*, s	*f*, s	$P_2 \cdot d / 100$, kPa·s
A	740	3421	2954	230	175	11	60	4	82	2052.6
95A/5CLS	761	3398	3007	218	170	12	55	5	88	1868.9
B	1175	1562	1327	202	87	10	63	13	92	984.1
95B/5CLS	1203	1534	1371	198	85	10	56	12	100	859.0
C	1567	3670	2761	302	103	9	119	15	260	4367.3
95C/5CLS	1574	3642	2786	286	99	10	109	13	274	3969.8
D	2033	4094	1488	365	113	13	165	17	276	6755.1
95D/5CLS	2040	4073	1508	349	106	12	156	17	287	6353.9

At the same time, the softening (P_1) increases indicating greater susceptibility of the load to soften under external pressure. Cellulose role during the period (*a + b*) remains clearly neutral since it cannot affect external pressure unlike coal particles. Softening time (*b, c*) remains almost unchangeable; however, it has a natural tendency to decrease.

The indicators of the maximum coal swelling pressure with cellulose addition decrease slightly (Fig. 5) as well as a swelling pressure action period. Consequently, the cellulose influence is inert despite the significant amount of volatile matter formed during the heating process. However, the cellulose structure does not have any noticeable effect on the transformation of the coal load in the plastic state and, as a result, on the development of swelling pressure. Practically, the swelling pressure becomes less due to the smaller amount of the loaded coal. Reducing the amount of carbon in the charge also results in easier penetration of the thermocouple cover into the plastic layer (P_3) even as the penetration time is slightly increased (*f*, s). The total swelling potential of coal $P_2 \cdot d / 100$ (Pa·s) is reduced if a cellulose additive is used (Figs. 5 and 6); that shows additionally the inert role of the biomass component on the course of the thermal destruction processes of coking coal.
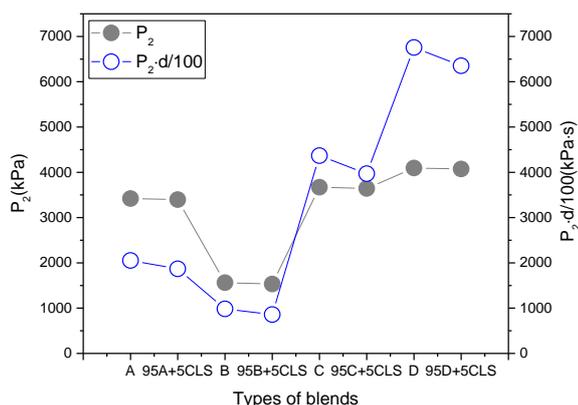
Figure 5. Swelling pressure (P_2) and swelling potential ($P_2 \cdot d / 100$) of the initial coals without cellulose addition and with it

Table 4 shows the results of coal plastomeric parameter determination with 5 wt. % cellulose additives.

Table 4. Plastometric indicators of coal determination with 5 wt. % cellulose addition

Coal	Plastometric parameters of the initial coal		With cellulose addition	
	y, mm	x, mm	y, mm	x, mm
A	8	60	8	63
B	21	31	21	34
C	15	22	14	23
D	12	11	11	10

According to plastometric parameters, the bioadditives cannot change significantly coking coal properties. The plastic layer thickness remains within the standard deviation as plastometric shrinkage does. Plastometric indicators turned out to be insensitive to the effect of 5 wt. % cellulose addition on the coal caking ability (Fig. 6).
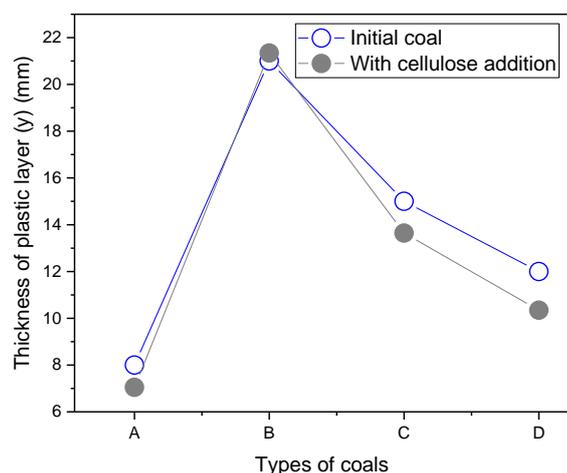
Figure 6. Plastic layer thickness (y) of the initial coal without cellulose addition and with it

Table 5 demonstrates the research results on the influence of 5 wt. % cellulose adding to the certain coal according to the Roga index. It should be mentioned that during standard tests (1 g of coal and 5 g of anthracite), coal A did not reveal caking properties, so the reasearch was conducted in the 2:4 ratio.

The caking ability of coal varies within the standard deviation for all the studied coal samples; a tendency to decrease caking ability is observed (Fig. 7).

Generally, the study of cellulose addition effect shows a decline in coal caking ability.

Table 5. The results of tests by the Roga index

Coal	Roga index of initial coal	Roga index of coal with cellulose addition
A	15	14
B	27	25
C	21	20
D	16	15
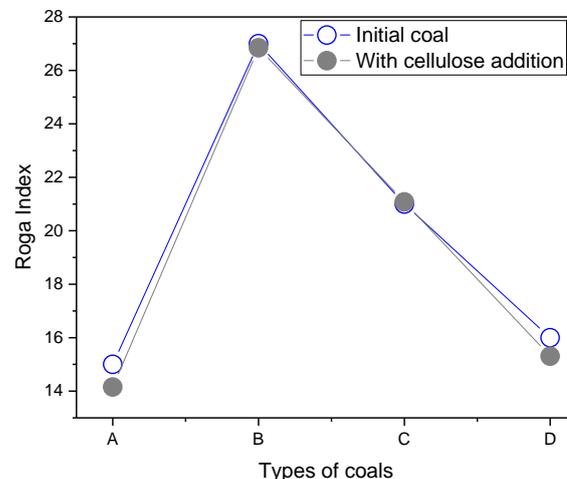
Figure 7. Roga index of the initial coal without cellulose addition and with it

The abovementioned can be explained as an increase in the proportional release of oxygen-containing groups during heating as it has been also noted by [71], [77], and features of the cellulose structure which does not lead to an additional effect on caking and shrinkage processes in the coal charge at the stages of the pre-plastic and plastic state.

4. Conclusions

Using biomass additives in a coke production can contribute to the solution of the existing problems of metallurgy, agriculture, and other related industries processing biomass. First of all, it is the use of renewable raw materials instead of fossils, in particular deficient coking coal; utilization of biomass; obtaining a new product biocoke, which properties meet modern consumer requirements (without quality degradation); and reduction of greenhouse gas emissions as well as mitigation of the environmental impact in the region and globally.

For coking coal, a plastic layer formation during heating without air access is important. For coking, a blend of coals has individual properties affecting the caking process differently. Consequently, there are quantitative and qualitative results of obtaining coke and gaseous products. The interaction between coal and organic additives during pyrolysis can influence directly both yield and quality of coking products.

The studies carried out in the paper concerning the effect of 5 wt. % cellulose adding to different coking coal grades showed a decrease in caking properties in terms of swelling; swelling pressure, thickness of the plastic layer, and caking ability. Hence, cellulose addition promotes inhibition of a plastic layer formation. Although it reduces the time of transition to a plastic state, cellulose use as an additive affects negatively a plastic layer formation, above all quantitatively. Adding cellulose and replacing coal proportion in the load increase the release of oxygen-containing groups in the pyrolysis process. Moreover, cellulose is not of a dense structure; hence, there is no noticeable effect on physical properties of coal charge.

It has been identified that the plastometric parameters were the most insensitive while studying the effect of 5 wt. % cellulose adding. Furthermore, the minor impact of cellulose addition on the change in the Roga index is observed. The accelerated method of swelling pressure determination as well as dilatometric method turned out to be the most sensitive methods characterizing the changes in coal properties under a co-pyrolysis process with cellulose addition.

Acknowledgements

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Дослідження впливу целюлози на спікливі властивості вугілля

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Мета. Вивчення впливу целюлози на спікливу здатність різних видів коксівного вугілля, що використовується в коксівній суміші. Для досягнення цієї мети було змінено спікливість та спікливу здатність за допомогою стандартних методів. Одночасно проведено комплексний аналіз впливу добавок біомаси на пластичні властивості вугілля та визначення оптимальної кількості добавки для практичних цілей.

Методика. За допомогою дилатометричного методу, прискореного методу визначення тиску розпирання, пластометричного методу та методу Рога досліджено численні характеристики вугілля в пластичній стадії. Перші три методи дають змогу охарактеризувати здатність вугілля до спікання, а метод Рога характеризує спікливу здатність.

Результати. Встановлено, що оптимальна кількість добавки біомаси для вивчення впливу на властивості вугілля в пластичному стані становить більше 5 мас. %. У роботі наведено експериментальні залежності впливу додавання 5 мас. % целюлози для спікання та спікливої здатності чотирьох видів вугілля. Результати показали незначне зниження спікливої здатності щодо розпирання, тиску розпирання та товщини пластичного шару, а також щодо спікливої здатності. Водночас найбільш чутливими методами оцінки впливу додавання целюлози на пластичні властивості вугілля були дилатометричний та прискорений метод визначення тиску розпирання.

Наукова новизна. Проведено комплексне дослідження впливу чистої целюлози, як компонента лігноцелюлозної біомаси, на властивості вугілля різних видів у пластичному стані, а саме на спікливість та спікливу здатність. Показано незначну зміну властивостей вугілля в пластичному стані з додаванням 5 мас. % целюлози, а саме зниження спікливих властивостей. Важливий висновок, про який раніше не повідомлялося, полягає в тому, що добавка целюлози не має помітного впливу на фізичні властивості вугільної шихти через її пухку структуру.

Практична значимість. Встановлено незначну зміну спікливих властивостей вугілля при додаванні 5 мас. %, що має практичне значення для підготовки вугільних сумішей і виробництва коксу у випадках використання добавок лігноцелюлозної біомаси без втрати її якості. Крім того, використання поновлюваних добавок при отриманні палив і відновників є підходом до зменшення негативного впливу на навколишнє середовище.

Ключові слова: коксівне вугілля, спіклива здатність, целюлоза, вугільна пластична маса, спучування, тиск розпирання