

DETERMINATION OF OPTIMUM CONDITIONS EFFECT OF COAL
OXIDATIVE DESULFURIZATION TO PRODUCE PULVERIZED COAL*Yuriy Prysiachnyi¹*, Mariia Shved¹, Serhiy Pyshyev¹, Halyna Bilushchak²,
Anastasia Pyshieva³*<https://doi.org/10.23939/chcht12.03.355>

Abstract. The effect of oxidant composition on the oxidative desulfurization of low grade coal has been studied to obtain raw materials for the production of pulverized coal. The experimental-statistical model has been developed that allowed to establish optimum conditions of the investigated process.

Keywords: coal, sulfur, oxidative desulfurization, pulverized coal.

1. Introduction

According to the latest data published in the BP Statistical Review of World Energy [1-6], the world's proved reserves of coal do not decrease with time but demonstrate even a considerable increase (Fig. 1). At the same time the explored reserves of coal occupy a much larger share than other fossil fuels [6] (Fig. 2).

According to the statistics of British scientists [6], taking into account the current level of consumption, world oil reserves remain for about 61 years, natural gas – 53 years, and solid fuels – 114 years. Therefore, in the nearest future coal can become the main source of human needs for energy resources and, possibly, chemical raw materials.

However, the production and consumption of coal may be reduced (Figs. 3, 4) [1-6]. One of the reasons for such a deviation from the general trend is the poor quality of coal (first of all, because of high content of sulfur).

Currently, the main directions of coal application are [7]:

- electricity production – 59 % (thermal coal is used);
- coke industry – 36 % (metallurgical coal is used);
- other industries – 5 %.

Depending on application area of coal, it must meet certain quality requirements. This is especially true for the coke industry coal, because it must have specific properties, namely the ability to transform into a plastic state with the temperature rise and to caking with the formation of semi-coke.

Sometimes a deficit in the raw material occurs, for example, if the coke plants are geographically far from the deposits or if the prices for high-quality metallurgical coal rise. This, in turn, causes the problems in the operation of metallurgical enterprises, which in this situation are forced to look for alternative raw materials, the most common of which is pulverized coal (PVC) [8-10].

The technology of “pulverized coal injection” (PCI) involves the use of high-quality thermal coal, *i.e.* coal, the main application areas of which are the electricity production and blast-furnace production [11-13]. In this case, coke and natural gas are partially replaced by the above-mentioned thermal coal using the technology of its injection into the blast furnaces.

The implementation of pulverized coal injection technology in a blast-furnace production has several advantages:

- economic (reducing the cost of cast iron by decreasing the consumption of coke to 250 kg/t of cast iron and replacing the expensive natural gas [14-16]);
- strategic (this advantage relates to countries that do not have their own raw materials for gas and metallurgical coal, but have significant thermal coal reserves that will allow them to become less energy dependent).

Coal used in PCI technology must meet strict requirements. Thus, the ash content, as a rule, should not exceed 10 wt %, because the increase in its amount leads to the increase in PVC cost and the decrease in the furnace performance due to the increase in the amount of fuel (coke or PVC) and heat to convert ash into slag.

¹ Institute of Chemistry and Chemical Technology,
Lviv Polytechnic National University, 12, S.Bandery St., 79013 Lviv,
Ukraine

² Institute of Applied Mathematics and Fundamental Sciences,
Lviv Polytechnic National University, 12, S.Bandery St., 79013 Lviv,
Ukraine

³ Institute of Computer Science and Information Technologies
Lviv Polytechnic National University, 12, S.Bandery St., 79013 Lviv,
Ukraine

* prysiazhnyi@ukr.net

© Prysiachnyi Y., Shved M., Pyshyev S., Bilushchak H., Pyshieva A.,
2018

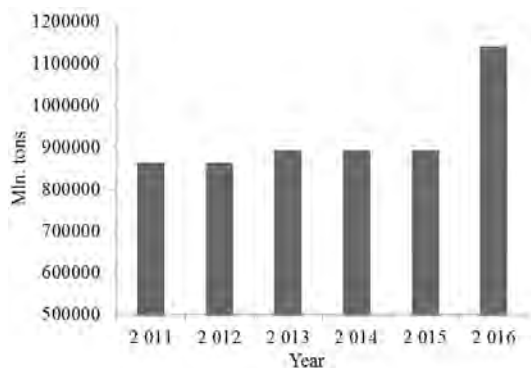


Fig. 1. The pattern of proved coal reserves

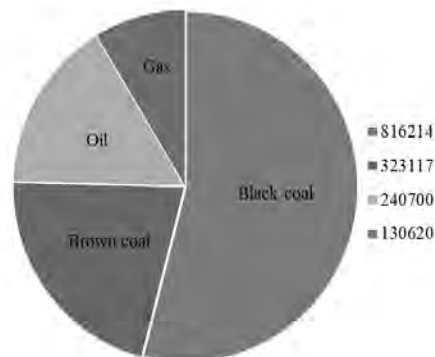


Fig. 2. The explored reserved of fossil fuels in the world, mln.tons

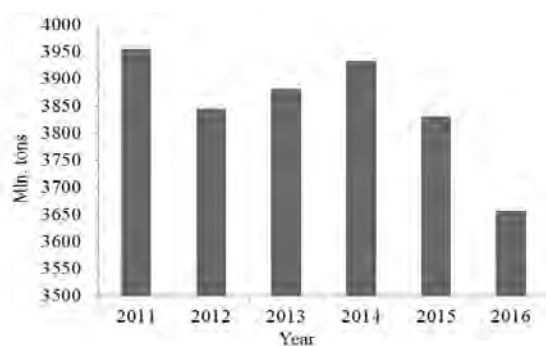


Fig. 3. The pattern of coal production in the world

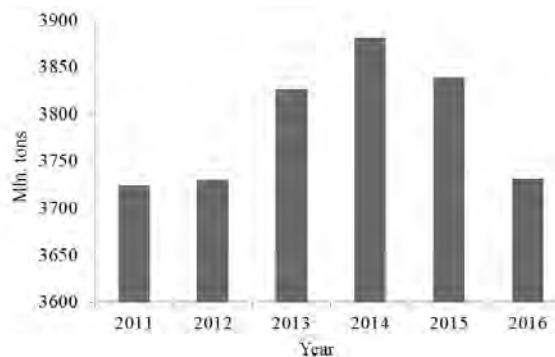


Fig. 4. The pattern of coal consumption

As regards the sulfur content, it should not exceed 1.0–1.5 wt %, because the high sulfur content of pulverized coal leads to the increase in fluxes amount to bind sulfur so that it does not fall into the cast iron. The reduction of sulfur content by 0.1 % reduces coke consumption by 0.8–3.5 % and increases blast furnace efficiency by 2–8 wt % [17].

Volatile substances in coal affect the process in two ways. It was found in [18] that the lower the content of volatile substances in PVC, the higher the carbon content in it, which leads to an increase in the amount of generated heat and the coefficient of coke replacement by coal. In addition, coal with a low content of volatile substances is easier to grind. Owing to this fact the productivity of mills increases by 40 % producing smaller particles which are better burned in the oxidation zone of blast furnaces. However, other studies [19] show that more quantitatively PVC burning is observed for pulverized coal with the increased amount of volatile substances. Since the latter escape from PVC and form pores, this leads to an easier oxidation of carbon. Therefore, for the production of PVC it is allowed to use coal with a relatively high yield of volatile substances.

Regarding the moisture content of coal, it should be less than 12 wt %, to ensure the materials friability [10].

On the basis of above-mentioned regularities and practical data, the requirements for raw materials for PVC production were formed [20]. Depending on the coal type and its size (0–100 mm), the total sulfur content must be ≤ 1.0 –1.5 wt %; ash content ≤ 8.0 –10.0 wt %; yield of volatile substances ≤ 38.0 –40.0 wt %; moisture content ≤ 10.0 –12.0 wt %.

Analyzing the above requirements, and also taking into account the quality of world coal reserves, we can assert that the amount of raw material for PVC production is small:

- coal with the lowest degree of metamorphism (lignite) cannot be used, because the volatile content exceed the permissible norm;
- deposits of coal with sulfur content of more than 1.2–1.5 % and ash content up to 10–12 wt % are insignificant.

One of the options for increasing the amount of raw material for PVC production is the preliminary improvement of the coal quality (its pretreatment). In particular, the required level of sulfur in coal can be achieved by its oxidative desulfurization (OD). The essence of this technology is that sulfur in coal, mainly pyrite one, contacts with an oxidant (air or steam-mixed mixture) and converts into gaseous sulfur-containing

components (SO_2 , H_2S). The concentration of these components (in contrast to the flue gases of thermal power plants) is high enough to extract them by known methods [21-23].

In previous studies, the process of oxidative desulfurization for various types of coal was investigated, in particular: brown coal [24-27], black coal of low [33, 34], medium [28-31] and high (including anthracite) [32] degrees of metamorphism. These works were carried out to obtain a desulfurized product (coal with a satisfactory sulfur content), which is proposed to be used as a raw material for thermal power plants. The demands for raw material for PVC production differ from those used in the energy sector. Thus, in [36-39], the influence of three factors on the OD process, namely, oxidant consumption, temperature, and process time, was determined. In addition, optimal hydrodynamic parameters of the process, which depend on the linear velocity of the oxidant movement and the size of the coal grains [35], have been established. To complete the research data and make final conclusions are still necessary:

- to study the influence of the oxidant composition on the OD of high sulfur coal of low degree of metamorphism;
- to establish optimal conditions of oxidation desulfurization of high sulfur low-metamorphized coal to obtain raw materials for the production of pulverized fuel.

2. Experimental

2.1. Initial Materials

The initial material was a low-metamorphized coal of the long-flame grade, which was selected at the Belorechensk mine of the Donetsk coal-and-coal basin [35-39]. Samples of coal were crushed and sieved to obtain fractions with different grain size. We used the fraction 0.1–0.25 mm. Its characteristics: total sulfur content (S_t^d) 3.16 wt %; pyrite sulfur content (S_p^d) 1.60 wt %; organic sulfur content (S_o^d) 1.20 wt %; sulfate sulfur content ($S_{SO_4}^d$) 0.36 wt %; ash content (A^d) 8.15 wt %; volatiles yield (V^{daf}) 38.08 wt %; moistness (W^d) 3.91 wt %. So, the content of sulfur does not meet the requirements for PVC, volatiles yield is somewhat higher compared with a required value, ash content and moistness are in acceptable limits.

2.2. Experimental Procedure

Oxidation desulfurization was carried out on a laboratory setup, the block diagram of which is depicted in [37]. The main apparatus is the ideal mixing reactor

(with a fluidized layer), operated in close to isothermal mode.

The influence of the oxidant composition on the OD process was studied changing the air:water ratio in the oxidant (vapor-air mixture) at fixed values of other factors (oxidant linear velocity, size of coal grain, oxidant flow rate, temperature and time). To characterize the oxidant flow rate we used the term “oxidant flow rate ratio” (OFR), which was calculated as the ratio of the volumetric flow rate of a steam-air mixture (m^3/h) to the mass of coal (kg).

The initial and desulfurized coals were analyzed according to standard methods.

The desulphurization gases produced during the process are analyzed by a chromatographic method. The qualitative and quantitative composition of desulphurization gases was determined using a LHM (N479) chromatograph with a thermal conductivity detector. Helium was a carrier gas.

2.3. Techniques for Processing the Experimental Results

2.3.1. Calculation of process efficiency

The processing (evaluation) of the research results was carried out by calculating the efficiency of the OD process. The main demand is to minimize the conversion of coal organic mass in order to obtain raw materials for pulverized coal injection technology. At the same time, it is desirable that the volatile content should be less than in the initial coal, and the change of ash content should be minimal.

Therefore, on the basis of obtained values (the weight of the initial coal, the yield of the decomposition resin of coal organic matter (COM), content of sulfur in the initial and desulfurized coal, the volume and composition of the desulfurization gases) we calculated efficiency factors of the process. The formulas are given in [37].

Efficiency factors:

- the degree of total or pyrite sulfur conversion (DTSC or DPSC), %;
- the degree of pyrite sulfur removal (DPSR), %;
- the degree of coal organic matter conversion (DCOM), %;
- efficiency factor of COM conversion (K_{ef});
- the degree of ash increase (DAI), %;
- change of volatiles yield (CVY), %

The first factor (DTSC or DPSC) characterizes the amount of sulfur converted into gaseous sulfur-containing products which will not enter the environment while further use of desulfurized coal (the level of environmental pollution reduction), *i.e.* it characterizes the ecological efficiency of the OD process.

The second factor (DPSR) depends on the sulfur final content in the produced coal; it is determined by the rate ratio of the desired (pyrite sulfur conversion) and undesirable (conversion of COM) reactions.

To characterize the COM conversion depth, the third factor (DCOM) was calculated, which characterizes the relative amount of coal spent on the formation of resin and desulfurization gases.

The factor K_{ef} defines the directions of COM conversion, *i.e.* the ratio of COM amount, from which the combustible products were formed, to its burned out amount (which was spent for the formation of CO_2).

Fifth and sixth factors characterize the influence of OD process performance on the ash content and volatiles yield of the desulfurized coal.

2.3.2. Development of experimental-statistical model

The experimental-statistical model (ESM) was developed with the aim of establishing optimal conditions of the OD process. Under the “optimal conditions” we understand the conditions under which we obtain the product which meets the requirements for raw materials for the PVC production.

For the description (development) of ESM we used the following symbols (response functions and the process parameters): Y_1 – the degree of pyrite sulfur conversion, %; Y_2 – the degree of volatiles yield change, %; Y_3 – the degree of ash content increase; X_1 – temperature, °C; X_2 – process time, min; X_3 – water vapor content in the oxidant, vol %; X_4 – oxidant flow rate ratio (OFR), $m^3/(h \cdot kg)$.

To evaluate the adequacy of the developed model, the values of X_1 – X_4 were substituted in the dependences $Y_i = f(X_1$ – $X_4)$ and for each experiment the expected values of the response functions (Y_{ij}^{reg}) were found.

The model adequacy was evaluated by 4 parameters: average relative error of approximation (ε_i), determination coefficient (R_i^2), F -test (F_i) and F -statistic (F_{ri}).

Average relative error of approximation:

$$e_i = \frac{1}{n} \sum_{j=1}^n \left| \frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}} \right|, \quad (1)$$

where n – number of experiments; Y_{ij} – obtained experimental values; Y_{ij}^{reg} – response functions, calculated by the regression equations; i – the number of the response functions (criterion, parameter); j – the number of the experiment.

The F -test, which was calculated according to formula (2), was used to check the adequacy of the multifactor regression model:

$$F = \frac{S_{reg_i}^2}{S_{res_i}^2}, \quad (2)$$

where S_{reg}^2 – variance of the experimental response functions relative their mean values; $S_{res_i}^2$ – residual variance of the response functions.

$$S_{reg_i}^2 = \frac{1}{n-1} \sum_{j=1}^n (Y_{ij} - \bar{Y}_i)^2, \quad (3)$$

where \bar{Y}_i – mean experimental value of the response function.

$$S_{res_i}^2 = \frac{1}{n-m_i} \sum_{j=1}^n (Y_{ij}^{reg} - Y_{ij})^2, \quad (4)$$

where m_i – the number of coefficients in the regression equation.

The F -test should be greater than the table value at the significance level α and the degrees of freedom ($n-1$) and ($n-m_i$). It shows how many times the scattering of data points changes relative to the line of the obtained regression equation in comparison with the scattering relative to the mean value [40, 41].

The determination coefficient (R), which characterizes the significance of the dependence of the response functions on the process parameters has values from 0 to 1 and is determined by the methods described in [42].

The measure of statistical significance (R_i^2) is the F -statistic, which was calculated according to [43]:

$$F_{ri} = \frac{n - k_i - 1}{k_i} \cdot \frac{R_i^2}{1 - R_i^2}, \quad (5)$$

where k_i is the number of coefficients of the regression equation without a free member.

The value F_{ri} was compared with the critical value F_{rcr_i} determined by the tables at the level of significance α and the degrees of freedom k_i and ($n-k_i-1$). If $F_{ri} > F_{rcr_i}$, we can state the statistical significance of the regression equation.

3. Results and Discussion

3.1. Effect of Oxidant Composition on the OD Process of the High Sulfur Low-Metamorphized Coal

In [35] it was proposed the process of oxidative desulphurization of low-metamorphized coal in order to obtain raw materials for PVC to be carried out with a grain size of 0.1–0.25 mm and at a linear velocity of the oxidant equal to 0.044 m/s. Fixed values of other parameters were taken on the basis of previous results [36–39]. All of them are shown in Table 1.

The experimental results are represented in Tables 2–4 and Figs. 5–9.

Table 1

Experimental conditions to study the effect of oxidant composition on the OD process

Parameter	Value
Coal grain size, mm	0.1–0.25
linear velocity of the oxidant, m/s	0.044
Temperature, K	698
Time, min	15
OFR, m ³ /(h·kg)	4.80

Table 2

Dependence of desulfurization gases composition on the oxidant composition

Content in the oxidant, vol %		Content, vol %								
water vapor	O ₂	CH ₄	C ₂ -C ₃	SO ₂	H ₂ S	CO ₂	CO	N ₂	O ₂	Ar
0	21.0	0.55	0.34	0.29	0.02	11.49	0.86	79.00	6.54	0.91
4.5	20.1	0.61	0.52	0.36	0.02	11.20	0.95	78.99	6.44	0.91
15	17.8	0.64	0.60	0.55	0.11	10.51	1.07	79.37	6.24	0.91
30	14.7	0.71	0.71	1.46	0.09	10.01	1.28	78.90	5.93	0.91
50	10.5	1.17	0.76	1.37	0.06	9.11	1.90	79.65	5.06	0.92
70	6.3	1.33	0.88	1.44	0.02	8.80	2.24	79.50	4.87	0.92

Table 3

Dependence of desulfurized coal characteristics on the oxidant composition

Water vapor content in the oxidant, vol %	Moisture content, (W ^d), wt %	Ash content (A ^d), wt %	Degree of ash increase (DAI), %	Volatiles yield (V ^{def}), wt %	Change of volatiles yield (CVY), %
0	0.98	12.24	50.18	31.28	17.86
4.5	1.08	11.88	45.75	32.10	15.71
15	1.13	10.98	34.77	33.23	12.72
30	1.17	10.13	24.28	37.66	1.10
50	1.25	8.99	10.34	38.59	-1.34
70	1.32	8.67	6.44	39.46	-3.62

Table 4

Dependence of sulfur content in the desulfurization gases on the oxidant composition

Content in the oxidant, vol %		Sulfur content, wt %			
water vapor	O ₂	total, S _t ^d	pyrite, S _p ^d	sulfate, S _{SO₄} ^d	organic, S _o ^d
0	21.0	2.74	1.24	0.30	1.19
4.5	20.1	2.43	1.01	0.28	1.13
15	17.8	1.92	0.86	0.26	0.80
30	14.7	1.36	0.28	0.22	0.85
50	10.5	1.52	0.39	0.23	0.89
70	6.3	2.25	0.94	0.27	1.03

One can see from Fig. 5, the yield of desulfurized coal increases due to the increase of water vapor content in the vapor-air mixture. The amount of the decomposition resins decreases slightly, as well as the DCOM value (Fig. 6). The total amount of solid desulfurized products is increasing (Fig. 5) due to the fact that the water vapor retards the burning-out of COM.

Data in Fig. 7 show the increase in the K_{ef} value by about seven points due to the increase in content of water vapor in the vapor-air mixture. Such increase also indicates a significant retardation of COM burning-out. This fact is confirmed by the decrease of CO₂ content in

desulfurization gases (Table 2). At the same time the number of COM conversion products in the desulfurization gases increases; water vapor can participate in their formation (CO and hydrocarbon gases).

The maximum amount of SO₂ in the desulfurization gases is observed at the water vapor content of 30 vol % (Table 2). The reason is the increase in the amount of removed pyrite sulfur (Fig. 8) with the increase in water vapor content from 0 to 30 vol %. A further relatively high content of sulfur dioxide is caused by the decrease in the total volume of the desulfurization gases.

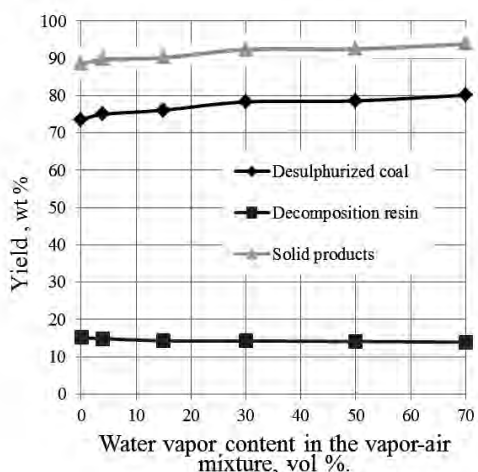


Fig. 5. Dependence of desulfurized products yield on the oxidant composition

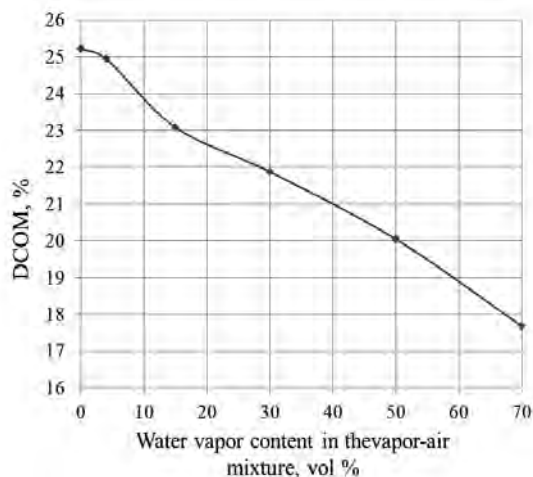


Fig. 6. Dependence of the degree of coal organic matter conversion on the oxidant composition

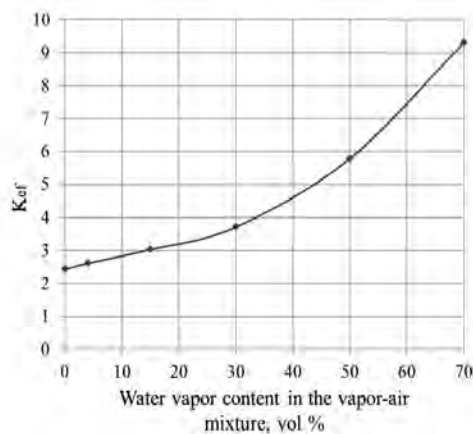


Fig. 7. Dependence of efficiency factor of COM conversion on the oxidant composition

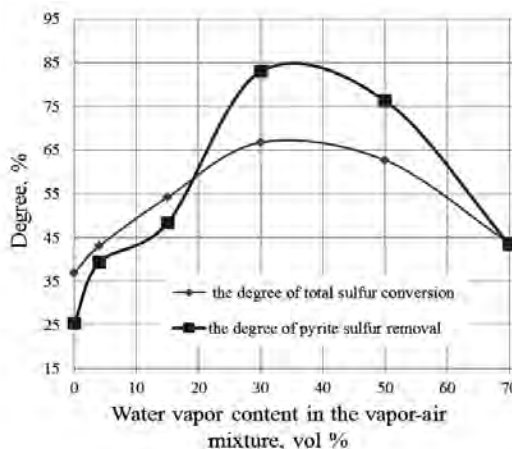


Fig. 8. Dependence of the degree of sulfur removal/conversion on the oxidant composition

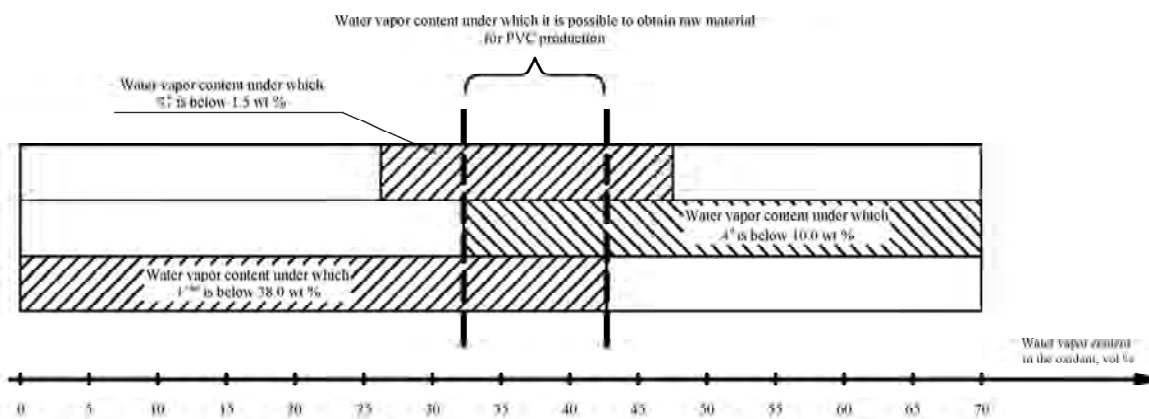


Fig. 9. Content of water vapor in the oxidant under which the production of raw material for PVC technology is possible

One can see from Table 3, when the water vapor content in the vapor-air mixture increases, the ash content of the desulfurized coal decreases. DAI decreases by 44 % as a result of the weakening of the COM burning-out reactions. Another tendency is observed with the volatiles yield: the increase of water vapor content in the oxidant increases the amount of volatiles and decreases CVY. This is explained by the fact that the water vapor intensifies the formation of low molecular and/or thermally unstable compounds that remain in coal and evaporate/decompose during the determination of volatiles yield.

With the increase of water vapor content in the oxidant, the amount of pyrite and total sulfur in coal passes through the minimum (Table 4), which corresponds to the maximum in the dependences of DTSC and DPSR curves (see Fig. 8). The reason is that the addition of the first portions of water vapor not only inhibits the COM burning-out, but also intensifies the process of pyrite oxidation. The decrease of DPSR value after reaching the maximum is explained by the lack of oxygen in the reagent (decrease of its concentration in the reaction volume).

Fig. 9 represents a rather wide region of water vapor content in the vapor-air mixture (32.3–42.7 vol %), under which it is possible to achieve the required characteristics of desulfurized coal, which meet the requirements for raw materials for PVC production. It should be noted a relatively large yield of solid desulfurization products (92.5 wt %, Fig. 5) and high concentration of sulfur dioxide in the desulfurization gases (Table 2), which is quite important aspect of SO₂ further extraction.

So, it is advisable to carry out OD process with water vapor content within the range of 33–42 vol %.

3.2. Development of Experimental-Statistical Model (ESM)

Taking into account previous [36–39] and above-mentioned results the following conditions for ESM development were chosen: temperature of 698–773 K; time 10–60 min; water vapor content in the oxidant 15–70 vol %; OFR 2.99–12.83 m³/(h·kg). The results are presented in Table 5.

The purpose of ESM development was finding the optimal conditions for the investigated OD process, namely those conditions under which it would have been possible to achieve the highest values of the degree of pyrite conversion sulfur (response function) under following limitations of other response functions: CVY ≥ 0.25 % and DAI ≤ 22.69 %.

Different types of dependencies on the process parameters were developed for the response functions. We chose those of them, which showed the best conformity with the experimental data (Eqs. (6)–(8)).

$$Y_1 = -2.61128 - 0.042721 \cdot X_2^2 - 0.013453 \cdot X_3^2 - 1.04597 \cdot X_4^2 + 0.171645 \cdot X_2 \cdot X_3 + 0.559559 \cdot X_2 \cdot X_4 + 0.711020 \cdot X_3 \cdot X_4 + 0.369708 \cdot X_1 - 4.23107 \cdot X_2 - 4.79155 \cdot X_3 - 11.1441 \cdot X_4 \quad (6)$$

$$Y_2 = 0.114128 - 0.001298 \cdot X_1^2 - 0.007936 \cdot X_2^2 + 0.004725 \cdot X_3^2 - 0.203869 \cdot X_4^2 - 0.020244 \cdot X_1 \cdot X_2 - 0.013733 \cdot X_1 \cdot X_3 - 0.002929 \cdot X_1 \cdot X_4 + 0.296141 \cdot X_2 \cdot X_3 + 0.132179 \cdot X_2 \cdot X_4 + 0.156875 \cdot X_3 \cdot X_4 - 0.202102 \cdot X_1 + 0.090766 \cdot X_2 - 0.106417 \cdot X_4 \quad (7)$$

$$Y_3 = 0.111027 + 0.002395 \cdot X_1^2 - 0.014426 \cdot X_2^2 + 0.006024 \cdot X_3^2 - 0.307674 \cdot X_4^2 - 0.029509 \cdot X_1 \cdot X_2 - 0.021324 \cdot X_1 \cdot X_3 - 0.006784 \cdot X_1 \cdot X_4 + 0.462636 \cdot X_2 \cdot X_3 + 0.163834 \cdot X_2 \cdot X_4 + 0.216878 \cdot X_3 \cdot X_4 - 0.432638 \cdot X_1 + 0.090191 \cdot X_2 + 0.113302 \cdot X_4 \quad (8)$$

When checking the validity of Eqs (6)–(8), the following results were obtained.

Calculated mean relative errors of approximation are: $\varepsilon_1 = 0.1192$ (11.92 %); $\varepsilon_2 = 0.3208$ (32.08 %); $\varepsilon_3 = 0.2567$ (25.67 %).

According to [44], at $\varepsilon = 0$ –10 % the prediction accuracy is high, at $\varepsilon = 10$ –20 % – good, and at $\varepsilon = 20$ –50 % – satisfactory. So, the developed model is valid.

The values of F -test are: $F_1 = 2.88$; $F_2 = 20.81$; $F_3 = 32.11$.

According to [41] at equal significance $\alpha = 0.05$ the table values of F -tests are: $F_{1cr} = F(0.05; 23.13) = 2.43$; $F_{2cr} = F(0.05; 23.10) = 2.74$; $F_{3cr} = F(0.05; 23.10) = 2.74$, i.e., they are less than the calculated ones. This also confirms the model adequacy.

The values of determination coefficients are: $R_1^2 = 0.8039$; $R_2^2 = 0.9791$; $R_3^2 = 0.986532$. It means that 80.39; 97.91 and 98.65 % change of response functions (Y_1 , Y_2 and Y_3 , respectively) are determined by selected factors of a process control (X_1 – X_4). The values $R_1 = 0.8966$; $R_2 = 0.9895$ and $R_3 = 0.9932$ are close to 1, indicating the presence of a “strong” connection between Y_1 , Y_2 and Y_3 and selected factors (X_1 – X_4).

The values F -statistic are: $F_{r1} = 15.27$; $F_{r2} = 9.54$; $F_{r3} = 17.26$.

According to [41] at equal significance $\alpha = 0.05$ the table values of F -statistic are: $F_{r1} = F(0.05; 10; 13) = 2.67$; $F_{r2} = F(0.05; 13; 10) = 2.89$; $F_{r3} = F(0.05; 13; 10) = 2.89$. This indicates the statistical significance of the determination coefficients R_i^2 ($F_{r_i} < F_{\alpha}$).

Table 5

Experimental data, calculated response functions and relative errors

X_{1s} °C*	X_{2s} min	X_{3s} vol %	X_{4s} m ³ /(h·kg)	Y_{1s} %	Y_{1s}^{res} %	Y_{2s} vol %	Y_{2s}^{res} vol %	Y_{3s} %	Y_{3s}^{res} %	Relative errors			
										ε_1	ε_2	ε_3	
350	15	30	4.80	40.99150	40.17864	-1.95323	-2.02809	0.95283	0.09707	0.01983	0.038329	0.898125	
375	15	30	4.80	51.33000	49.42133	-1.31303	-1.80073	1.34969	4.82443	0.037184	0.371438	2.574473	
400	15	30	4.80	64.44875	58.66402	-0.33495	0.0489	19.9766	12.54602	0.089757	1.145981	0.371964	
425	15	30	4.80	86.29225	67.90672	1.10179	3.52079	24.27612	23.26184	0.213061	2.195506	0.041781	
450	15	30	4.80	92.74100	77.14941	11.98731	8.61495	36.60813	36.97188	0.16812	0.281327	0.009936	
475	15	30	4.80	91.73381	86.39210	14.30366	15.33138	59.22916	53.67614	0.058231	0.07185	0.093755	
500	15	30	4.80	90.89000	95.63479	23.30315	23.67007	70.81	73.37464	0.052204	0.007102	0.036219	
425	15	30	12.83	74.16241	69.03856	19.06151	19.22872	30.23334	29.4438	0.069089	0.008772	0.026115	
425	15	30	8.98	72.27089	85.32250	15.19489	14.97863	29.02666	31.42997	0.180593	0.014233	0.082797	
425	15	30	6.74	68.96538	80.51257	10.72555	9.71046	27.93595	28.37958	0.167435	0.094643	0.01588	
425	15	30	3.85	51.93316	58.83602	-0.62601	-0.08251	18.66118	19.90053	0.132918	0.868203	0.066413	
425	15	30	2.99	32.90671	49.06623	-2.50579	-3.63651	14.52938	16.40366	0.491071	0.451242	0.129	
425	5	30	4.80	28.75975	40.40929	-6.05943	-4.95143	3.27251	4.00412	0.405064	0.182856	0.223562	
425	10	30	4.80	59.22550	55.22603	-0.87462	-0.51692	15.80841	13.99363	0.06753	0.408983	0.114798	
425	25	30	4.80	87.86000	86.85994	7.42105	10.40578	36.56442	39.63437	0.011382	0.402197	0.08396	
425	30	30	4.80	89.45200	93.13247	12.37468	13.25306	46.95204	46.73869	0.041145	0.070982	0.004544	
425	45	30	4.80	90.02000	99.13376	21.06092	19.41405	66.01227	63.72387	0.101242	0.078196	0.034666	
425	60	30	4.80	90.84663	85.91060	21.57594	22.00376	73.34194	74.21738	0.054334	0.019829	0.011937	
425	15	0	4.80	43.43538	44.13380	17.86415	18.51612	50.18345	50.30294	0.01608	0.036496	0.002381	
425	15	4	4.80	53.11250	48.70262	15.70851	16.02533	45.74583	46.07095	0.083029	0.020168	0.007107	
425	15	15	4.80	59.56656	59.04715	12.72358	9.9553	34.77449	35.42695	0.00872	0.217571	0.018763	
425	15	50	4.80	80.83881	70.30249	-1.33685	-1.75098	10.33626	11.25859	0.130337	0.309777	0.089232	
425	15	60	4.80	75.18000	67.46453	-2.28466	-2.96933	3.80368	7.06422	0.102627	0.299678	0.857204	
425	15	70	4.80	53.41863	61.93601	-3.62001	-3.24265	6.43563	4.07467	0.159446	0.104242	0.366858	
Mean relative errors of approximation, ε													
											0.119184	0.320816	0.2567279

Note: here temperature is given in Celsius degree, as necessary for ESM

Table 6

Optimum conditions of OD process and results obtained under them

Parameters				Coal yield, wt %	Pyrite sulfur content (S_p^d), wt %	Response functions					
T , K	Time, min	OFR, $m^3/(h \cdot kg)$	Water vapor content in the oxidant, vol %			Degree of pyrite sulfur conversion, %		Degree of volatiles yield decrease, %		Degree of ash increase, %	
						$Y_1\zeta$	$Y_1^{predict}$	$Y_2\zeta$	$Y_2^{predict}$	$Y_3\zeta$	$Y_3^{predict}$
Calculated values											
703	15	5.10	47.0	–	–	–	78.57	–	0.42	–	15.40
Experimental results											
703	15	5.10	47.0	77.54	–	85.14	–	0.52	–	13.37	–

Table 7

Technical analysis of desulfurized coal

Moisture content, (W^d), wt %	Ash content (A^d), wt %	Volatiles yield (V^{daf}), wt %	Total sulfur content (S_t^d), wt %
1.16	9.24	37.88	1.38

The obtained data testify to the ESM adequacy for the low-metamorphized coal desulfurization, the statistical significance of the results and the existence of a connection between the response functions and the selected factors of the process control.

Optimal conditions of the process were found on the basis of regression equations by the method of uniform search of their maximum values under the following limits: $400 \leq X_1 \leq 450$ (with step ± 5); $10 \leq X_2 \leq 50$ (with step ± 1); $30 \leq X_3 \leq 50$ (with step ± 1); $3.0 \leq X_4 \leq 5.0$ (with step ± 0.1); $Y_1 \leq 95$; $Y_2 \leq 0.25$; $Y_3 \leq 22.6$.

The optimum conditions and the predicted results are presented in Table 6, the technical analysis of coal under optimal conditions – in Table 7.

Thus, it is possible to obtain the desulfurized product, which fully meets the raw material requirements for the production of PVC.

4. Conclusions

In order to obtain raw material for PVC production, the oxidative desulfurization of high-sulfur low-metamorphized coal must be carried out with the water vapor content in the oxidant of 33–42 vol % at other fixed parameters (the size of coal grain 0.1–0.25 mm, the oxidant linear velocity 0.044 m/s, the temperature 698 K, process time 15 min, oxidant flow rate ratio 4.80 $m^3/(h \cdot kg)$). On the basis of developed experimental-statistical model the optimal conditions of the investigated process were determined, namely: the process temperature 703 K; time 15 min; oxidant flow rate ratio 5.10 $m^3/(h \cdot kg)$; water vapor content in the oxidant 47.0 vol %. The resulting product obtained under optimum conditions meets the raw materials requirements

for the production of pulverized fuel and has the following characteristics: moisture content 1.16 wt %; ash content 9.24 wt %; volatiles yield 37.88 wt %; total sulfur content 1.38 wt %.

Acknowledgments

The work was carried out under financial support of the grant DB/Bitum No. 0117 U 004451 of the Ministry of Education and Science of Ukraine.

References

- [1] BP statistical review of world energy 2012. <https://www.laohamutuk.org/DVD/docs/BPWER2012report.pdf>
- [2] BP statistical review of world energy 2013. <http://large.stanford.edu/courses/2013/ph240/lim1/docs/bpview.pdf>
- [3] BP statistical review of world energy 2014. https://www.bp.com/content/dam/bp-country/de_de/PDFs/brochures/BP-statistical-review-of-world-energy-2014-full-report.pdf
- [4] BP statistical review of world energy 2015. <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf>
- [5] BP statistical review of world energy 2016. <https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf>
- [6] BP statistical review of world energy 2017. <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf>
- [7] International Energy Outlook 2016. [https://www.eia.gov/forecasts/ieo/pdf/0484\(2016\).pdf](https://www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf)
- [8] Langner K.: Stahl und Eisen, 2005, **11**, 91.
- [9] Längen H.: Fachtagung Kokereitechnik im Rellinghaus der RAG, 11-12 May 2006.
- [10] Drozdnik I., Starovoi A., Gusak V. et al.: Ugli dlia Koksovania i Pyleugolnogo Topliva. Kontrast, Kharkov 2011.

- [11] Osorio E., Gomes M., Vilela A. *et al.*: Int. J. Coal Geolog., 2006, **68**, 14. <https://doi.org/10.1016/j.coal.2005.11.007>
- [12] Ishii K.: Advanced Pulverized Coal Injection Technology and Blast Furnace Operation. Elsevier Science Ltd 2000.
- [13] Zhao Z., Tang H., Quan Q. *et al.*: Procedia Eng., 2015, **102**, 1667. <https://doi.org/10.1016/j.proeng.2015.01.303>
- [14] Vodennikov S., Anosov V., Laptiev D.: Metalurgia: Naukovi Praci ZDIA, 2013, **30**, 16.
- [15] Logutova T., Poltoratska O.: Innovats. Ekonomika, 2015, **1**, 18.
- [16] Iaroshevskiy S.: Vplavka Chuguna s Primeneniem Pyleugolnogo Topliva. Metallurgija, Moskva 1988.
- [17] Bratychak M., Pyshyev S., Rudkevych M.: Khimia ta Technologia Pererobky Vugillia. Beskyd Bit, Lviv 2006.
- [18] Brouwer R., Toxopeus H.: ATS. Conference on Steel Production, Paris 1990, 28.
- [19] Anosov V., Fomenko A., Krutas N., Tsaplina T.: Metalurgia: Naukovi Praci ZDIA, 2009, **20**, 37.
- [20] <http://mozdocs.kiev.ua/vysnovki.php?docnum=&object=%22-%22&manufacturer=&page=5648>.
- [21] Rozenkop Z.: Izvlechenie Dvuoiksi Sery iz Gazov. GHI, Moskva 1952.
- [22] Yavorsky V.: Technologia Sirky i Sulfatnoi Kysloty. Vyd-vo Lvivska Polytechnika, Lviv 2010.
- [23] Wienczkowska J., Bratychak M., Topilnytsky P.: Katalitychno-Adsorbtsiynе Znesirchennia Gaziv. Vyd-vo Wroclaw Politechnic, Wroclaw 2000.
- [24] Pysh'yev S., Gunka V., Bratychak M., Grytsenko Y.: Chem. Chem. Technol., 2011, **5**, 107.
- [25] Gunka V., Pyshyev S.: Int. J. Coal Sci. Technol., 2014, **1**, 62. <https://doi.org/10.1007/s40789-014-0009-2>
- [26] Gunka V., Pyshyev S.: Int. J. Coal Sci. Technol., 2015, **2**, 196. <https://doi.org/10.1007/s40789-015-0056-3>
- [27] Pyshyev S., Gunka V.: Petroleum and Coal. –2015 – V. 6 – P. 696-704.
- [28] Pysh'yev S., Shevchuk K., Chmielarz L. *et al.*: Energ. Fuel., 2007, **21**, 216. <https://doi.org/10.1021/ef060251e>
- [29] Pyshyev S., Prysiazhnyi Iy., Miroshnichenko D. *et al.*: Chem. Chem. Technol., 2014, **8**, 225.
- [30] Pyshyev S., Prysiazhnyi Iy., Kochubey V., Miroshnichenko D.: Chem. Chem. Technol., 2014, **8**, 467.
- [31] Pyshyev S., Gunka V., Shevchuk Kh. *et al.*: Uglekhim. Zh., 2009, **5-6**, 11.
- [32] Shevchuk Kh., Bratychak M., Pysh'yev S. *et al.*: Ecol. Chem. Eng., 2007, **14**, 747.
- [33] Bratychak M., Gajvanovych V., Brzozowski Z. Ecol. Chem. Eng., 2004, **11**, 59.
- [34] Pysh'yev S., Gayvanovych V., Pattek-Janczyk A., Stanek J.: Fuel, 2004, **9**, 1117. <https://doi.org/10.1016/j.fuel.2003.12.008>
- [35] Pyshyev S., Prysiazhnyi Yu., Shved M.: Technolog. Audit i Rezervy Vyrobnystva, 2016, **3**, 48.
- [36] Shved M., Pyshyev S., Prysiazhnyi Yu.: Uglekhim. Zh., 2017, **2**, 16.
- [37] Shved M., Pyshyev S., Prysiazhnyi Y.: Chem. Chem. Technol., 2017, **11**, 236. <https://doi.org/10.23939/chcht11.02.236>
- [38] Pyshyev S., Prysiazhnyi Yu., Shved M.: Uglekhim. Zh., 2015, **6**, 10.
- [39] Shved M.: PhD thesis, Lviv Polytechnic National University, Lviv 2018.
- [40] Sautin S., Punin E.: Teoreticheskie Osnovy Planirovaniya Eksperimentalnykh Issledovaniy v Khimii i Khimicheskoi Technologii. Leningrad 1979.
- [41] Pinchuk S.: Organizatsia Experimentu pry Modeliuvanni te Optyimizatsii Technichnykh System. Dnipro-VAL, Dnipropetrovsk 2009.
- [42] Dreiper M., Smith G.: Prikladnoi Regressionnyi Analiz. Finansy i statistika, Moskva 1986.
- [43] Yerina A.: Statystichne Modeluvannia ta Prognozuvannia. Kyiv 2001.
- [44] Tsehelyk G.: Osnovy Ekonometrii. Lviv. Univ. im. Franka, Lviv 2011.

Received: December 12, 2017 / Revised: January 20, 2018 / Accepted: February 15, 2018

ВСТАНОВЛЕННЯ ОПТИМАЛЬНИХ УМОВ ПРОЦЕСУ ОКСИДАЦІЙНОГО ЗНЕСІРЧЕННЯ ВУГІЛЛЯ З МЕТОЮ ОДЕРЖАННЯ СИРОВИНИ ДЛЯ ВИРОБНИЦТВА ПИЛОВУГІЛЬНОГО ПАЛИВА

***Анотація.** Вивчено вплив складу оксиданту на процес оксидативного знесірчення кам'яного вугілля низького ступеня метаморфізму, що здійснювався з метою одержання сировини для виробництва пиловугільного палива. На основі сукупності всіх результатів експериментальних досліджень по вивченні вищезгаданого процесу розроблено експериментально-статистичну модель, яка дала можливість встановити оптимальні умови досліджуваного процесу.*

***Ключові слова:** вугілля, сірка, оксидативне знесірчення, пиловугільне паливо.*