

Influence of thermal and mass transfer, the properties of steam-oxygen oxidizer and structure of coke on the composition of the generating synthesis-gas at the gasification of fuel

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Abstract. A mathematical model of the solid fuel conversion process which is used to analyze the synthesis-gas that is the result of coke gasification is proposed. During the conversion of coke in an environment of high-temperature water vapor, synthesis-gas consisting of hydrogen, oxide and carbon dioxide is obtained. That is shown in the article. Hydrogen in the produced gas at any oxidizer temperatures is always over 50% of total volume. The ratio of oxide and carbon dioxide depends on the temperature of the oxidant. The lower the oxidant temperature, the greater the proportion of carbon monoxide. It is established that it is economically more advantageous to use water vapor with the addition of oxygen as an oxidizer in the gasification of fuel. With the use of such an oxidizer, synthesis-gas consisting of 100% of the combustion gas is obtained. The temperature of the steam-oxygen oxidant after the fuel has ignited can be significantly reduced practically before the beginning of the process of vapor condensation. The synthesis-gas produced in this gasification process will contain in volume proportions about 25% hydrogen and 75% carbon monoxide.

1 Introduction

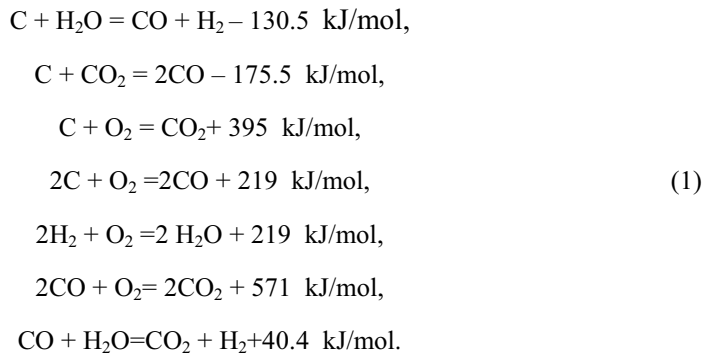
Solid fuel in the total amount of fuel consumed in the energy sector takes a significant share. In particular, in Europe and the US, coal accounts for about 60% of the energy sector. In the energy sector of Russia, the use of coal is approximately 18%. According to the development strategy of the Russian coal industry, it is planned to significantly increase the export of coal for the coke-chemical industry. Such an increase in coal production and planned exports will lead to an even greater increase in accumulated waste, which, as a rule, consists of slimes and fines. Burning of these wastes is ineffective, since their ash content is high, up to 50% and higher.

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The universal method of processing such wastes is their gasification. In modern gas generators, as a rule, steam-air or steam-oxygen blowing is used. This technology has both advantages and disadvantages. In particular, the disadvantages include the content of ballast admixtures in the synthesis gas, the part of the carbon burns in the gas generator. In connection with this the creation of a mathematical model of a gasifier for the conversion of solid fuels in an environment of various oxidants is an urgent task. Such a mathematical model can serve as a tool for estimating the composition of gasification products and for finding the optimal regimes for the gasification process.

2 Mathematical formulation of the problem

We consider a cylindrical capsule filled with coke, through which a heated steam heated up to a high temperature or a steam-oxygen oxidizer is pumped. In accordance with the work [1] and proceeding from experimental studies conducted at the department of the Kuzbass State Technical University [2], the following chemical reactions were considered:



Research objective: The determination of the synthesis-gas in the conversion of coke, the analysis of the composition of the gas formed, depending on the conditions of heat and mass transfer, the structure of the coke sample under study and the properties of the oxidant.

The simulation of the non-stationary mode of heat and mass transfer during coke conversion was carried out on the basis of the mathematical model [3]. It was assumed that there was no free moisture in the pores during the conversion, then the volume fraction of moisture (φ_2) is zero, and since the coke was considered, the volume fraction of solid fuel (φ_1) is also zero. Therefore, according to [3] and the reactions (1) we have the following system of equations:

- conservation of coke mass

$$\rho_3 \cdot \frac{\partial \varphi_3}{\partial \tau} = -R_C, \quad R_C = R_{C1} + R_{C2} + R_{C3} + R_{C4}; \tag{2}$$

- continuity of the gas phase

$$\frac{\partial \rho_s \varphi_s}{\partial \tau} + v \cdot \frac{\partial \rho_s \varphi_s}{\partial z} = R_C; \tag{3}$$

- continuity α – of the gas phase component

$$\frac{\partial(\rho_s \varphi_s c_\alpha)}{\partial \tau} + v \frac{\partial(\rho_s \varphi_s c_\alpha)}{\partial z} = \frac{\partial}{\partial z}(\rho_s \varphi_s D_\alpha \frac{\partial c_\alpha}{\partial z}) + R_{s\alpha} + R_{s\alpha}, \quad \alpha = \overline{1,4}, \tag{4}$$

here parameter with an index $\alpha = 1$ corresponds to the oxygen (O_2), $\alpha = 2 - CO$, $\alpha = 3 - CO_2$, $\alpha = 4 - H_2$, $\alpha = 5 - H_2O$;

- conservation of energy of the gas phase

$$\rho_s \varphi_s c_{ps} \left(\frac{\partial T}{\partial \tau} + v \cdot \frac{\partial T}{\partial z} \right) = \frac{\partial}{\partial z} \left((\lambda_s + \lambda_r) \varphi_s \frac{\partial T}{\partial z} \right) - A_s (T - T_s) + q_{CO}^1 R_{CO}^1 + q_{CO}^2 R_{CO}^2 + q_{H_2} R_{H_2} - \frac{2}{r_0} \alpha_1 \varphi_s (T - T_s); \tag{5}$$

- conservation of energy of the condensed phase (coke)

$$\sum_{i=3}^4 \rho_i \varphi_i c_{pi} \frac{\partial T_s}{\partial \tau} = \frac{\partial}{\partial z} \left(\lambda_s \frac{\partial T_s}{\partial z} \right) + q_{C1} R_{C1} + q_{C2} R_{C2} - q_{C3} R_{C3} - q_{C4} R_{C4} + A_s (T - T_s) + \frac{2 \cdot r_1}{r_0^2} \alpha_2 (T_s - T_E) + q_R; \tag{6}$$

- the gas motion in the pores (in the form of a quadratic filtration law) and the equation of state

$$v = \frac{k}{\mu + k \cdot \beta \cdot \rho_s \cdot |V|} \cdot \frac{\partial p}{\partial z}, \quad p = \frac{\rho_s \cdot R \cdot T}{M_s}. \tag{7}$$

The system of equations (2) - (7) was solved under the boundary conditions:

$$\tau = 0: \quad \varphi_i = \varphi_{iH}, \quad i = \overline{3,4}; \quad c_\alpha = c_{\alpha H}, \quad \alpha = \overline{1,4}, \quad T = T_s = T_H, \quad p = p_H; \tag{8}$$

$$z = 0: \quad T = T_G, \quad (p v)_w = const, \quad \lambda_s \cdot \frac{\partial T_s}{\partial z} = \alpha_1 \cdot (T_s - T_G), \quad c_\alpha = c_{\alpha G}, \tag{9}$$

$$z = h: \quad \frac{\partial c_\alpha}{\partial z} = \frac{\partial T}{\partial z} = 0, \quad p = p_H, \quad \lambda_s \frac{\partial T_s}{\partial z} = 0.$$

In the equations (2) - (7) the following notation is introduced: $c_{p5} = \sum_{\alpha=1}^5 c_{p\alpha} c_\alpha$,

$$\lambda_s = \sum_{i=3}^4 \lambda_i \varphi_i, \quad \lambda_r = \frac{16 \sigma T^3}{s}, \quad M_s = 1 / \sum_{\alpha=1}^7 \frac{c_\alpha}{M_{4\alpha}}, \quad R_{C1} = s \rho_s \varphi_s c_7 k_{s1} \varphi_3 \exp\left(\frac{-E_{C1}}{R \cdot T_s}\right),$$

$$R_{CO}^2 = k_{CO}^2 (c_1 M / M_{s1})^{0.25} (c_2 M / M_{s2}) \cdot T^{-2.25} \exp\left(\frac{-E_{CO}^2}{R \cdot T}\right), \quad R_{C2} = s \rho_s \varphi_s c_3 k_{s2} \varphi_3 \exp\left(\frac{-E_{C2}}{R \cdot T_s}\right),$$

$$R_{C3} = s \rho_s \varphi_s c_1 k_{s3} \varphi_3 \exp\left(\frac{-E_{C3}}{R \cdot T_s}\right), \quad R_{CO}^1 = k_{CO}^1 c_2 c_7 \exp\left(\frac{-E_{CO}^1}{R \cdot T}\right), \quad R_{H_2} = k_{H_2} c_1 c_4 \cdot \exp\left(\frac{-E_{H_2}}{R \cdot T}\right),$$

$$R_{s2} = \gamma_5 R_{C1} + \gamma_6 R_{C2} + \gamma_7 R_{C4}, \quad R_{s4} = \gamma_{13} R_{C1} + \gamma_{14} R_{CO}^1 - \gamma_{15} R_{H_2}, \quad R_{s7} = \gamma_{16} R_{H_2} - \gamma_{17} R_{C1} - \gamma_{18} R_{CO}^1,$$

$$R_{s1} = -(\gamma_1 R_{C2} + \gamma_2 R_{C3} + \gamma_3 R_{H_2} + \gamma_4 R_{CO}^2), \quad R_{s3} = \gamma_8 R_{C3} - \gamma_{10} R_{C2} + \gamma_{11} R_{CO}^1 + \gamma_{12} R_{CO}^2,$$

$$R_{C4} = s \rho_s \varphi_s c_1 k_{s4} \varphi_3 \exp\left(\frac{-E_{C4}}{R \cdot T_s}\right). \text{ All other notations coincide with the notation introduced}$$

in [3, 4 and 6].

3 Analysis of numerical results

The comparison of experimental and numerical studies [5] showed that good agreement on the percentage content of gasification products after sample heating is achieved. The temperature in the sample layer, found numerically, also agrees with the results of laboratory studies. Thus, this mathematical model adequately simulates the process under investigation and can be used for analysis of the gas composition when studying the processes of conversion of organic fuel. The values of thermophysical and kinetic properties at which numerical calculations were performed are given in [3, 4].

With the help of the mathematical model proposed above, studies of the yield of synthesis gas depending on the temperature of the supplied vapor (T_G), on the initial porosity and the specific surface of pores of the gasified solid fuel (coke) were conducted. The results of all numerical calculations for different values of porosity, specific surface of pores and three values of the temperature of the blown oxidant (water vapor) are given in tables 1, 2, 3.

In Tables φ_{SH} – initial porosity of coke, S_* – specific surface of pores. The set of these two parameters determine the structure of coke. Analyzing the results presented in Tables, we come to the conclusion that as the porosity decreases at any specific surface area of the pores S_* the fraction of CO in the synthesis gas decreases, and the fraction of CO₂ and H₂ increases.

Table 1. Composition of synthesis gas at a water vapor temperature $T_G = 873$ K.

φ_{SH}	Volumetric composition of gas synthesis, %	$S_* = 5 \cdot 10^2$, 1/m	$S_* = 5 \cdot 10^3$, 1/m	$S_* = 5 \cdot 10^4$, 1/m
0.9	CO	41.5	46.9	51.2
	CO ₂	6.0	1.7	0.3
	H ₂	52.5	51.4	48.5
0.5	CO	39.3	45.2	47.1
	CO ₂	6.4	2.4	1.0
	H ₂	54.3	52.4	51.9
0.1	CO	35.4	42.1	44.6
	CO ₂	10.0	3.8	1.6
	H ₂	54.6	54.1	53.7

Analyzing the results given in the tables, it can be concluded that when the fuel is converted, the yield of the gas composition depends significantly less on the porosity than on the specific surface of the pores.

Table 2. Composition of synthesis gas at a water vapor temperature $T_G = 1173$ K.

φ_{SH}	Volumetric composition of gas synthesis, %	$S_* = 5 \cdot 10^2$, 1/m	$S_* = 5 \cdot 10^3$, 1/m	$S_* = 5 \cdot 10^4$, 1/m
0.9	CO	7.4	37.0	47.8
	CO ₂	27.2	6.9	0.6
	H ₂	65.4	56.1	51.6
0.5	CO	3.2	28.5	44.9
	CO ₂	29.3	11.8	2.3
	H ₂	67.5	59.7	52.8
0.1	CO	1.4	184	37.6
	CO ₂	29.2	16.3	6.2
	H ₂	69.4	65.3	56.2

It also should be noted that for the same porosity, the composition of the gas is strongly dependent on the specific surface area of the pores (pore size). If the pores are very small ($S_*=5 \cdot 10^4$, 1/m), the synthesis gas by more than 90% will consist of carbon monoxide and hydrogen. For samples with big pores ($S_*=5 \cdot 10^2$, 1/m) the resulting synthesis gas will have about 30% of carbon dioxide and about 70% of hydrogen and a negligible amount of CO (Tables 2 and 3).

It should be noted that during gasification of coke in a water vapor environment, the proportion of combustion gas in the gasification products is the higher, the higher the oxidant temperature. In particular, at an oxidizer temperature of 873 K the carbon dioxide fraction is the lowest (less than 10%) for any porosity and specific surface area of the pores. Numerical calculations have shown that the method of gasification using high-temperature water vapor is not economically profitable. Because even at the temperature of the supplied steam of 1473 K, the volume fraction of the combustion gas at the outlet from the gasifier is only about 3% and 97% is water vapor.

Table 3. Composition of synthesis gas at a water vapor temperature $T_G = 1473$ K.

φ_{SH}	Volumetric composition of gas synthesis, %	$S_*=5 \cdot 10^2$, 1/m	$S_*=5 \cdot 10^3$, 1/m	$S_*=5 \cdot 10^4$, 1/m
0.9	CO	1.3	21.5	43.4
	CO ₂	30.5	15.6	1.8
	H ₂	68.2	62.9	54.8
0.5	CO	0.5	14.9	41.8
	CO ₂	30.7	18.7	3.8
	H ₂	68.8	66.4	54.4
0.1	CO	0.3	12.2	33.7
	CO ₂	30.3	19.6	8.9
	H ₂	69.4	68.2	57.4

At an oxidizer temperature of 873 K, water vapor is 99%, and combustion gases are only 1%. Therefore, the resulting combustion gases are not enough even for heating to the desired temperature of the oxidant. In connection with this, further studies on gasification were carried out in an oxidizer environment consisting of water vapor and oxygen.

Table 4 presents the results of calculating the coke gasification in a steam-oxygen oxidant environment with the same initial porosity as for pure water vapor, the mass concentration of oxygen was 0.4 and the mass concentration of water vapor was 0.6.

Table 4. The composition of the synthesis gas produced at the initial oxidant temperature $T_G = 873$ K.

φ_{SH}	Volumetric composition of gas synthesis, %	$S_*=5 \cdot 10^2$, 1/m	$S_*=5 \cdot 10^3$, 1/m	$S_*=5 \cdot 10^4$, 1/m
0.9	CO	72	75.3	76
	H ₂	25	24.5	24
	CO ₂ / O ₂	0.4 / 2.6	0.05 / 0.15	0 / 0
0.5	CO	73.1	75.8	76.2
	H ₂	26.8	24.2	23.8
	CO ₂ / O ₂	0.1 / 0	0 / 0	0 / 0
0.1	CO	73.5	75.1	76.6
	H ₂	26.5	24.9	23.4
	CO ₂ / O ₂	0 / 0	0 / 0	0 / 0

Analyzing the results given in Table 4, we come to the conclusion that irrespective of the porosity and specific surface of the pores in the steam-oxygen gasification, we obtain a

combustion gas consisting in volume approximately by (23-27) % of hydrogen and by (77-73) % of carbon monoxide. A small amount of oxygen and carbon dioxide remains unreacted for samples with large porosity and (or) a small specific surface of the pores. It should be noted that under these gasification conditions, water vapor reacts completely, and there is no need to separate the vapor from the gasification products. From the reactor comes carbon monoxide diluted in volume by about a quarter by hydrogen. In some cases (with a large porosity of gasified fuel), a small amount of carbon dioxide and not consumed oxygen appears.

The results on the effect of the proportion of oxygen in the oxidant on the composition of synthesis gas are presented in Table 5. Analyzing the data in the table, we come to the conclusion that when the mass concentration of oxygen C_1 varies from 0.1 to 0.3 and the mass concentration of water vapor C_5 varies from 0.9 to 0.7, the volumetric composition of synthesis gas varies rather weakly, the maximum temperature of the gasification process increases quite strongly, especially the temperature of the coke. Therefore, by changing the oxidizer composition, it is possible to control the gasification temperature and consequently the conversion rate of the coke. The composition of the resulting synthesis gas will vary slightly in this case.

Table 5. The gas composition and temperature of the gasification products at different ratios of oxygen and water vapor in the oxidizer ($\varphi_{\text{SH}} = 0.1$, $S_* = 5 \cdot 10^4$, 1/m).

The composition of the oxidizer C_1 / C_5		0.1 / 0.9	0.15 / 0.85	0.2 / 0.8	0.25 / 0.75	0.3 / 0.7
Volumetric composition of gas synthesis, %	CO	61.7	62.5	65.9	67.8	70.5
	H ₂	38.3	37.5	34.1	32.2	29.5
Maximum temperature, K	gas	1216	1356	1586	1723	1907
	coke	1250	1527	2038	2368	2753

In addition to the results presented above, studies of the influence of the initial temperature of the oxidizer on the gasification process were carried out. Figure 1 shows the distribution of temperature in the coke along the depth of the fuel for three values of the initial temperature of the oxidizer. Distribution 1 was obtained at an initial oxidant temperature of 873 K.

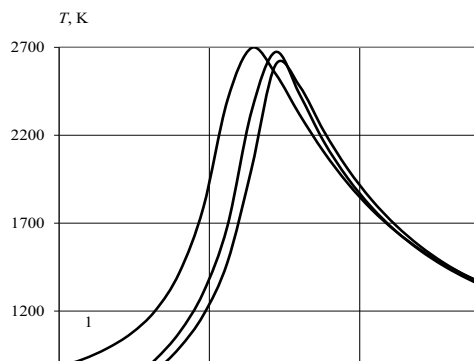


Fig. 1. Temperature profiles in coke at different initial oxidizer temperatures.

If the initial temperature of the oxidizer is further reduced, the temperature profile will move to the right (Fig. 1, curve 2). The maximum temperature will decrease slightly, and the profile will shift deep into the gasified fuel. If the oxidizer temperature drops to 373 K, the maximum temperature will slightly decrease and shift to the right (Fig. 1, curve 3). In all three cases, the composition of the synthesis gas produced is practically the same.

Consequently, after the coke has ignited and the gasification process has begun, the oxidizer temperature can be reduced to a minimum.

4 Conclusions

Based on the numerical calculations performed, the following conclusions can be drawn: the formulated mathematical model describes the process of conversion of solid fuel with sufficient accuracy for practice and it can be used to predict the composition of synthesis-gas in the gasification of solid fuels. During steam gasification the change in the temperature of the oxidizer, the speed of its supply and the porosity of the fuel affect the composition of the combustion gas formed. The temperature of the oxidizer exerts the greatest influence on the yield of synthesis gas during steam gasification.

In the case of steam-oxygen gasification, the influence of the fuel structure (porosity and specific surface of the pores) is small. The determining parameter of the process is the proportion of oxygen in the oxidant. By changing it, different regimes can be obtained, both in speed and in gasification temperature.

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