ATLANTIS PRESS
Advances in Engineering Research, volume 176
The 9th Russian-Chinese Symposium. Coal in the 21st Century: Mining, Intelligent Equipment and Environmental Protection

Steam Gasification of Bituminous Coals with CaO Additives

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***Abstract*—The results of experimental studies on steam oxygen-free gasification of carbonized coal in a dense layer with addition of calcium oxide. The effect of the amount of added calcium oxide on the process rate and composition of produced gas was determined. The possibility of adjusting the hydrogen/carbon monoxide ratio in the resulting synthesis gas is shown.**

Keywords—steam gasification, superheated steam, conversion rate, oxides of alkali-earth metals.

I. INTRODUCTION

Recently, a significant reduction in coal consumption occurred in the world due to the tightening of environmental standards in Europe and Asia. One of the promising directions of coal processing is its gasification with synthesis gas production, which is used for further processing into the products with high added value. The parameters of gasification process depend largely on the composition and properties of raw materials. With increasing degree of coal metamorphism, the gasification rate decreases [1]. This may be caused, depending on the amount of carbon in coal, by reactivity of carbon in carbonizate, its texture properties, and catalytic effect of the mineral components contained in coal [2-5]. Steam gasification with addition of 3 mass % of sodium, potassium and calcium cations as a catalyst was studied in [6]. The catalyst was applied by wet impregnation. The obtained results confirmed the positive effect of catalysts on the gasification process.

The research is aimed at determination of the effect of addition of model alkaline and alkaline-earth oxides on conversion kinetics and qualitative composition of generator gas. In this work, calcium oxide, added by physical mixing, was used.

The study was performed on the experimental setup, where superheated steam under the atmospheric pressure was supplied to the working section with carbonizate (the coke residue of coal after devolatilization). The temperature of steam fed to gasification of the carbon-containing material was maintained within 700 – 1200°C. After conversion of steam with carbon, the resulting generator gas (syngasgas was sent to the condenser to separate condensed liquid and non-condensible gaseous substances; then, the cooled synthesis gas was sent to the gas analyzer. The amount of produced generator gas was determined by the drum gas counter. The rate of conversion was determined by a decrease in the mass of carbonizate sample at the known duration of the process. The experiment duration at a given temperature in all the cases was of 25 minutes. The description of experimental setup and investigation and measurement procedures are given in [7].

II. EXPERIMENTAL PART

In the current research, we used the samples of coal of the CCr grade from Mezhdurechensky open-cast with the following characteristics (A^d = 14.4%; V^{daf} = 16.6%; I_0 = 0.25; CRI = 15.7) (Table I).

TABLE I. ELEMENTAL COMPOSITION OF COAL OF MEZHDURECHENSKIY OPEN-CAST (MASS %)

C	*Al*	*Si*	*S*	*Ca*
76.95	1.13	1.29	0.20	0.16

The fractional composition of particles was 3…4 mm; mass of carbonizate loaded into the working section was 3…3.3 g. Experimental studied were carried out with and without addition of calcium oxide (3 mass%, 5 mass% and 10 mass%) in the same temperature range.

III. RESULTS AND DISCUSSION

The qualitative and quantitative composition of synthesis gas during the process of steam gasification without addition of calcium oxide is shown in Figure 1.

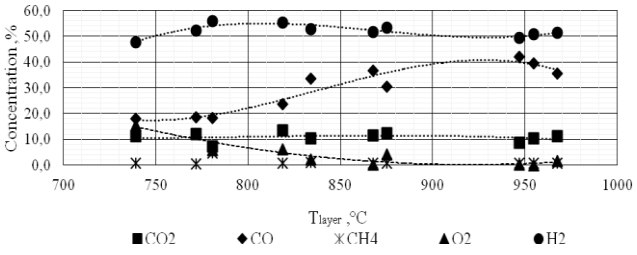

Fig. 1. Composition of synthesis gas components at steam gasification (without CaO addition).

Data presented in Figure 1 show that in the temperature range of 720-780°C, the changes in concentrations of synthesis gas components were not observed, except a small increase in CO; the main change in composition occurs in the temperature range of 800-950°C: concentration of CO almost doubles; in the range of 950-980°C, composition of synthesis gas also changed insignificantly as in the range of 720-780°C.

Figure 2 shows the results of investigation with addition of CaO (3%, 5% and 10% of the working sample mass).

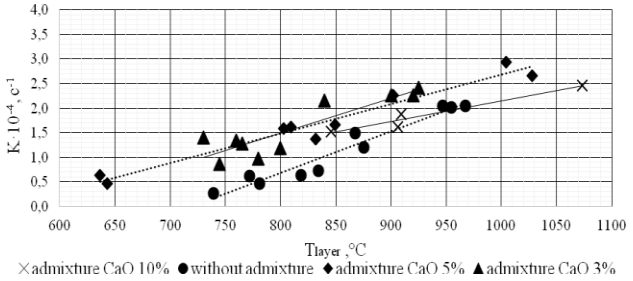

Fig. 2. Effect of CaO addition on the conversion rate of coal carbonizatefrom Mezhdurechenskiy open-case in the temperature range 640…1070 ºC.

The obtained experimental data indicate that when calcium oxide is added in the volume of 3-5% of the working mass, the conversion rate increases on average by one and a half times; when 10 mass % of calcium oxide is added, an increase in the conversion rate is also observed, but it is less significant than at 5%. In addition, when the temperature in the working section (sample) rises, a further increase in the conversion rate is not observed, and therefore, the addition of a model oxide of more than 5% does not make sense.

Figure 3 shows the composition of synthesis gas, produced during the process with addition of 3% of calcium oxide.

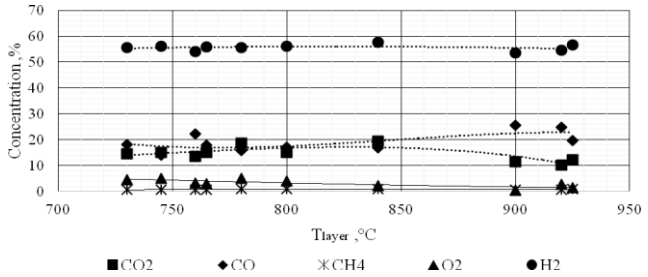

Fig. 3. Concentration of synthesis gas components at steam gasification with of 3% of CaO in the temperature of 730…925 ºC.

Figure 4 shows the composition of synthesis gas, produced during the process with addition of 5% of calcium oxide.

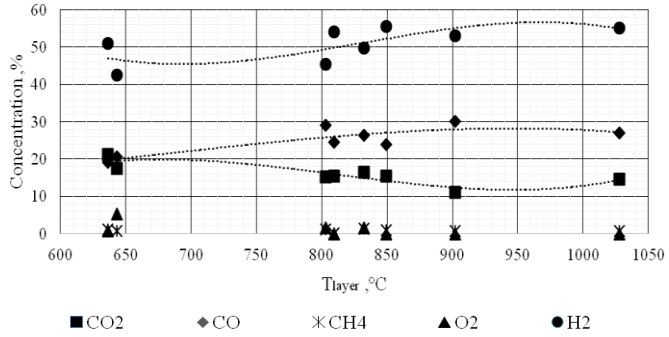

Fig. 4. Concentration of synthesis gas components at steam gasification with addition of 5% of CaO in the temperature range of 640…1030 ºC.

The qualitative and quantitative compositions of synthesis gas, produced during the process with addition of 10% of calcium oxide to the mass of sample are shown in Figure 5.

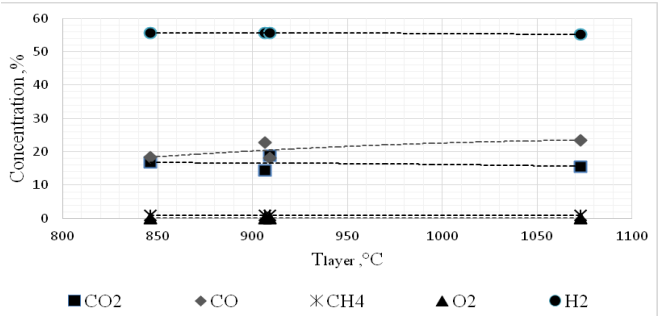

Fig. 5. Concentration of synthesis gas components at steam gasification with addition of 10% of CaO in the temperature range of 800…1070°C.

When analyzing the diagram (Figure 5), it can be seen that concentration of synthesis gas components with the addition of 10% of CaO with the increasing layer temperature did not change.

The results of the gasification process with the addition of CaO at various temperatures are summarized in Table II.

TABLE II. COMPOSITION OF SYNTHESIS GAS WITH ADDITION OF CAO

Mezhdurechenskiy coal	Temperature, °C	Concentration, %				
		CO_2	CO	H_2	CH_4	O_2
Without CaO	800	14.8	28.2	55	0.7	0.1
	850	13	27.2	55.1	0.8	2.7
	900	11.1	33.2	54	0.8	0.1
3% CaO	800	15	17.1	56.2	1	4
	850	19.4	17	57.6	1	2.2
	900	11.6	25.5	53.7	0.7	0.4
5% CaO	800	15.5	24.5	54.1	0.1	0
	850	15.4	23.8	55.5	1	0
	900	11	30	53	0.8	0
10% CaO	850	16.8	18.3	55.7	0.9	0
	900	18.8	18.2	55.7	0.9	0

Conducting gasification processes in the temperature range studied led to a change in the concentration of the main components of the generated gas as a function of the time of the process, with the component concentrations increasing to a certain value, followed by achieving a quasi-stationary regime for H_2 and CO yields and decreasing CO_2 yields (Figs. 6-8).

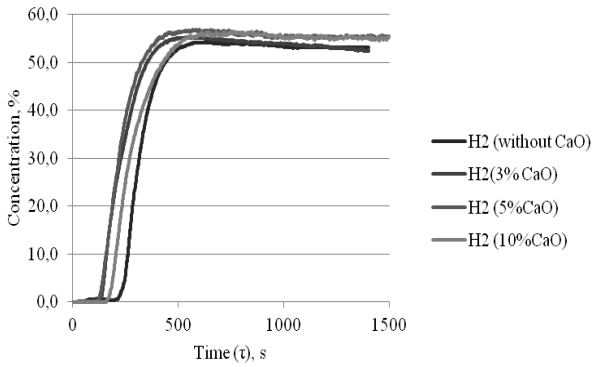

Fig. 6. Concentration of synthesis gas H_2 at steam gasification with addition (and without) of CaO in the temperature range of 900°C.

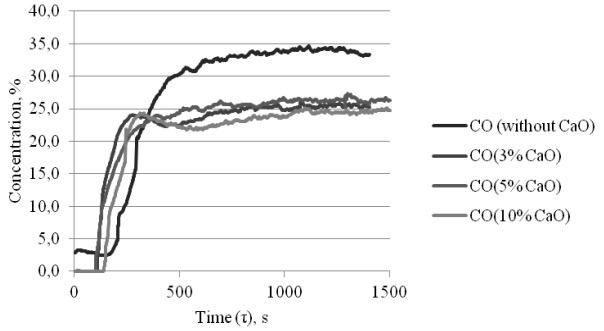

Fig. 7. Concentration of synthesis gas CO at steam gasification with addition (and without) of CaO in the temperature range of 900°C.

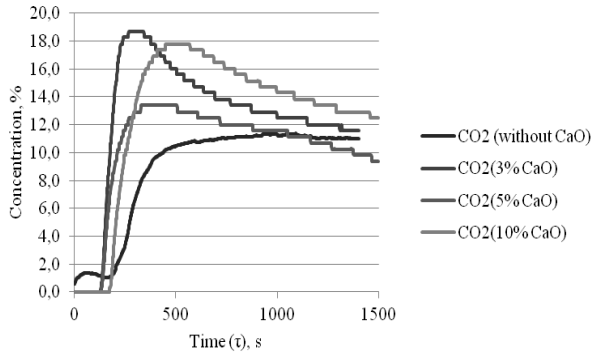

Fig. 8. Concentration of synthesis gas CO_2 at steam gasification with addition (and without) of CaO in the temperature range of 900°C.

The addition of CaO to carbonizate has an effect on the quantitative and qualitative composition of the synthesis gas at steam gasification. Based on Figures 1, 3, 4 and 5 and table 2 the following changes occurred:

- with the addition of 3% CaO, the amount of CO decreased by an average of 10%, at 5% - on 5%, at 10% - on 15%;
- a small increase in CO_2 is observed with an increase in CaO addition;
- the concentration range of H_2 in all cases is almost the same; concentration of CH_4 is also constant and tends to zero in all experiments.

IV. Conclusions

At relatively low and moderate temperatures (< 800-900°C), the process rate increases with increasing CaO concentration; such a fact, in opinion of the authors of this work, is related to a rise in the concentration of active sites.

At higher process temperatures (> 900°C), a reverse situation is observed: the activity of the 10% sample is lower than that of the 5% one. Such behavior can be explained by the progress of sintering processes of calcium oxide particles at these temperatures of steam gasification.

When CaO is added to carbonizate composition, an increase in the conversion rate and change in quantitative composition of produced synthesis gas are observed.

Addition of model calcium oxide of more than 3% does not lead to a significant increase in the rate of coke residue conversion.

By changing the amount of added CaO, the H_2/CO ratio changes, and this can be used for further processing (Fischer-Tropsch synthesis) and production of chemical products.

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