Specific Features of Solid Fuels Combustion in Oxygen Atmosphere with Recirculation of CO_2

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Article info

Abstract

Aspects of coal combustion have been experimentally studied under oxyfuel conditions, one of the promising technologies for carbon capture and storage (CCS). Here, the thermogravimetric analysis (TGA) method was chosen as an experimental technique. Coal pyrolysis tests performed under an O_2/CO_2 atmosphere were compared with a conventional O_2/N_2 environment in terms of reaction rate and total volatile yield. Combustion of the resulting chars in the corresponding atmospheres revealed somewhat different combustion rates with a less vigorous reaction in the O_2/CO_2 medium. The two manipulated factors – namely, the inherently different char reactivities due to the different atmospheres they were obtained in and the different atmospheres of the actual combustion process – were distinguished by performing another series of tests with chars pyrolysed under identical conditions using a standard routine. These chars also showed a weaker reaction in O_2/CO_2 atmosphere, which was attributed to the lower binary diffusion coefficient of the O_2/CO_2 pair. The activity of the char – CO_2 gasification reaction in an O_2/CO_2 environment was also investigated and revealed some contribution of this reaction to the conversion process. This was particularly noticeable at temperatures above 750 °C and under an internal diffusional controlled regime (zone II), implying displacement of oxygen out of the char particle pore volume, which allowed free reaction of CO_2 on the developed pore surface. Non-isothermal kinetic analysis of the intrinsic kinetics of the oxidation reaction in O_2/CO_2 revealed no particular difference compared to the O_2/N_2 medium, at least when the char-CO_2 reaction was inhibited. The obtained data were used to develop a coal combustion model under O_2/CO_2 conditions, which was then incorporated as a combustion module into circulating fluidized bed (CFB) computation software.

Nomenclature

$k(T)$ – chemical reaction rate constant,
k_0 – pre-exponential factor,
E – activation energy,
T – absolute temperature,
R – universal gas constant,
$F(X)$ – structural function (reflecting the change in the number of active sites on the reacting surface during conversion),
X – sample conversion degree (ratio of sample mass burned out so far, to the initial sample weight minus the weight of ash residue),
T_0 – initial temperature of the mixture,
T_a – adiabatic combustion temperature,
q_c – specific heat release,
$Y_{F,0}$ – initial mass fraction of fuel in the mixture,
A – constant.

Introduction

The term "oxygen enhanced combustion" implies a class of technologies that involve combustion of fossil fuels using oxygen as an active oxidant component, while the oxidant itself may differ quite significantly in both fractional composition and preparation method from conventional air combustion conditions. Within this class, two main directions are traditionally outlined [1].

The first direction involves burning fuel under a conventional air atmosphere, but providing oxidant enrichment by injecting extra oxygen into the system at a certain stage of the reaction or during component preparation.

The second direction assumes complete elimination of air out of the unit circuit and usage of pure

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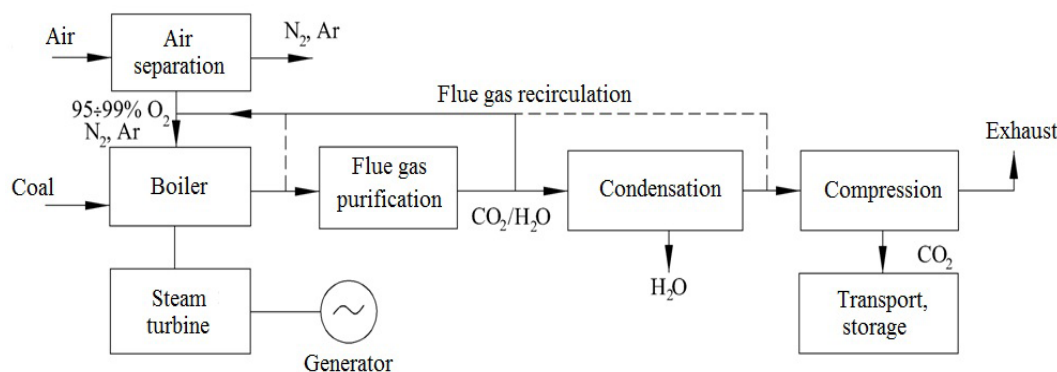* Corresponding author. E-mail: melnikovda-vti@yandex.ru

Fig. 1. Principle scheme of oxyfuel technology.

oxygen as an oxidizer with additional recirculation of flue gases back into the system. This scheme is referred to in the international literature as oxyfuel technology, and investigation of basic aspects of fuel combustion under these conditions is the subject of this paper.

A schematic diagram of a facility operating under oxyfuel technology is shown in Fig. 1.

The basic principle of this technology assumes the use of oxygen as an oxidizer instead of air. Keeping the unit regime parameters at appropriate level necessitates the presence of some type of ballast component, so a partial recycling of flue gases back into the system is assumed. The resulting mixture of oxygen with recycled flue gases acts as an oxidizing agent. This flow of flue gases, in this case, consists almost entirely of CO_2 (90% and more) with a small occurrence of other components.

The first proposals for implementation of this technology in the power industry appeared in the early 1980s. Back then, the possibility of using the flue gas flow from these units for enhanced oil recovery (EOR) was treated as one of the main argument in its favor [2]. At that time and somewhat later, other advantages of this technology over conventional air combustion were also established:

– increase in boiler efficiency by $1.5 \div 2.5\%$ [due to elimination of nitrogen that otherwise (within the traditional approach) is fed into the unit, heated, and after passing through the circuit, emitted into the atmosphere at higher temperatures, causing corresponding heat losses];

– decrease of draft fan power consumption due to a 4-5 – fold reduction in the amount of flue gases;

– decrease in the size of boiler passes as well as boiler aisles by 51%, and unit weight and price by 65% and 32%, respectively;

– under conventional combustion conditions, air nitrogen dilutes reactant concentrations in the furnace;

– under conventional combustion conditions, air nitrogen is the prime source of nitrogen oxides, which belong to 2 and 3 groups of pollutants and harm the environment.

Particular interest in this technology emerged in the 1990s and 2000s in the light of a general debate on the necessity to reduce greenhouse gas emissions (including CO_2). A stream of flue gases produced under oxyfuel mode (almost entirely consisting of CO_2) may simply be cleaned by capturing impurities, compressing, and transporting for further storage in saline aquifers or used for EOR, thereby accomplishing a so-called carbon capture and storage program (CCS). For this reason, many international companies are currently considering research and development in this area as a top priority.

In this regard, it is important to stipulate two aspects:

– seemingly the most relevant is deployment of oxyfuel technology conjointly with combustion of solid fossil fuels, which inherently produce the highest CO_2 emissions per unit of input heat.

– the most promising is application of this technology in conjunction with circulating fluidized bed (CFB) schemes [3].

The latter statement is based on the fact that the combustion process in CFBs inherently implies a long-term indwelling of a high amount of inert solid material within the circulation loop. This dispersed phase has a very high thermal capacity and circulates through the circuit at a solids flow rate, for large units, approaching one ton per second. These conditions determine the high stability of combustion process in CFB to variations, for example, in oxidant composition, and allow increased oxygen concentrations in O_2/CO_2 mixtures of up to 70%.

The aspects of oxyfuel technology of greatest scientific interest are certainly the processes of fuel combustion and pollutant emissions under O_2/CO_2 atmospheres and their comparison with convention-

al O_2/N_2 media. For this reason, many companies are currently putting much effort into the investigation of these aspects, and preliminary results are of some interest. Although the original assumption was that oxyfuel technology a priori provides favorable conditions for deployment of more efficient furnace regimes, later experimental and theoretical studies in a number of cases revealed the opposite [4-9], namely:

– the time required for homogeneous ignition of volatiles emerging from coal particles in the gaseous atmosphere, can, according to the theory of heat autoignition, be estimated as [10]:

$$\tau = \frac{c_v \cdot \left(T_0^2 / T_a\right)}{q_c \cdot Y_{F,0} \cdot A \cdot \exp(-T_a \cdot T_0)}$$

where c_v – isochoric (volume specific) heat capacity.

Since the isochoric heat capacity c_v of CO_2 at temperatures relevant to the ignition process is 1.7 times higher than the c_v of N_2, volatiles emitted into the nitrogen atmosphere will obviously ignite faster. Moreover, the isochoric heat capacity of H_2O is also higher then the c_v of N_2 (1.3 times), which, in the case of flue gas recirculation without preliminary water vapor condensation, will further delay ignition of volatiles.

– similarly, the higher isobaric heat capacity (volume specific) of CO_2 and H_2O in comparison with N_2 will lower the temperature level and therefore retard all the stages of fuel particle ignition and combustion under oxyfuel conditions (Fig. 2).

– further reductions in combustion temperature (yet with possible rise in conversion degree) may result from more intense endothermic gasification and pyrolysis reactions on the char particle surfaces at elevated concentrations of CO_2 or H_2O, according to:
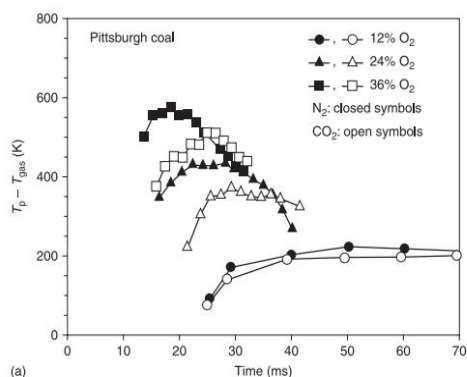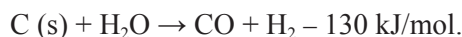
$$C\,(s) + CO_2 \rightarrow 2CO - 173 \text{ kJ/mol}$$

$$C\,(s) + H_2O \rightarrow CO + H_2 - 130 \text{ kJ/mol}.$$

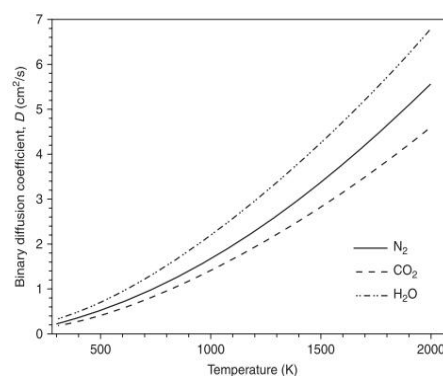Fig. 2. Temperature profiles of burning particles in various environments.

Fig. 3. Binary diffusion coefficients of oxygen in CO_2, N_2, and H_2O.

– another key factor is a lower value of the binary diffusion coefficient of oxygen in CO_2 medium (by 20%, in comparison with nitrogen atmosphere). This will reduce char and volatile combustion rates, at least in the intermediate and diffusionally controlled modes of the process. Note that in an H_2O environment, the diffusion coefficient of oxygen is higher by 20% when compared to the O_2/N_2 pair (Fig. 3).

– the elevated CO_2 concentration in the reaction atmosphere promotes directly or acts as a catalyst for recombination of hydrogen radicals that actively participate in the gas phase combustion process during traditional air firing, according to:

$$CO_2 + H \rightarrow CO + OH; \; H + O_2 + M \rightarrow + HO_2 + M.$$

Note, however, that various studies containing experimental data, (e.g., release rate and total amount of volatile yield, swelling ratio of formed char particles, morphology and kinetics of subsequent char burnout, etc.) have reached quite contradictory conclusions. Thus, this key aspect certainly requires further investigation.

2. Experimental

The current paper provides a comparative kinetics analysis of solid fuel burnout in O_2/N_2 and O_2/CO_2 environments, performed on a standard Derivatograph Q-1500 D by thermogravimetric methods (TGA). This is a fundamental method for studying macro kinetic parameters of a wide range of chemical reactions and, along with experiments using tube flow reactors, is a very common instrument for studying coal combustion.

The apparatus consists of an electrically heated chamber, into which crucibles with fuel samples are placed. The mass and temperature of each sample is continuously recorded. The chamber is purged with gas mixture of certain composition and flow rate.

The fuel investigated here was bituminous coal whose ultimate analysis, ash composition, fuel particles size distribution and other experimental conditions depicted in Tables 1-3.

Table 1
Coal ultimate analysis

Parameter	Analytical sample
moisture content, %	4.4
ash content, %	20.5
sulphur content , %	2.5
carbon content, %	57.3
hydrogen content, %	4.4
nitrogen content, %	1.2
oxygen content, %	9.7
high calorific value, Mj/kg	7700
low calorific value, Mj/kg	7392

Table 2
Ash chemical composition

Component	wt., %
SiO_2, %	60.3
TiO_2 %	0.4
Al_2O_3, %	19.6
Fe_2O_3, %	12.7
CaO, %	2.3
MgO, %	2.4
K_2O, %	1.0
Na_2O, %	0.1
SO_3, %	1.2
Sum, %	100.0
microelement content, mg/kg	
vanadium – V	56
cobalt – Co	14
manganese – Mn	232
copper – Cu	118
arsenic – As	27
nickel – Ni	66
plumbum – Pb	171
strontium – Sr	370
chrome – Cr	31
zinc – Zn	132
Sum	1217 (0.12%)

Table 3
Coal particle size distribution of 100÷160 micron sample

Fraction, μm	Result wt. %
>160	28.1
150÷160	6.6
140÷150	7.7
130÷140	8.4
120÷130	9.2
110÷120	8.9
100÷110	8.0
<100	23.1
Sum, %	100.0
D_5, μm	34.4
D_{10}, μm	72.8
D_{50}, μm	130.9
D_{90}, μm	206.8
D_{95}, μm	237.4

3. Results and Discussion

3.1. Pyrolysis tests

The first experimental series involved coal pyrolysis in a nitrogen and carbon dioxide environment, with subsequent analysis of volatile yield under these conditions. A 500 mg coal sample was placed in a standard platinum crucible and placed in the chamber. The system was then purged with the desired gas component (N_2 or CO_2) for 45 min at ambient temperature, and then heated at a rate of 20 K/min to a final temperature of 950 °C.

Figure 4 shows the resulting set of thermograms: sample mass loss with time (upper pair of curves), mass loss rate (DTG curves), and curve of linear rising temperature inside the chamber.
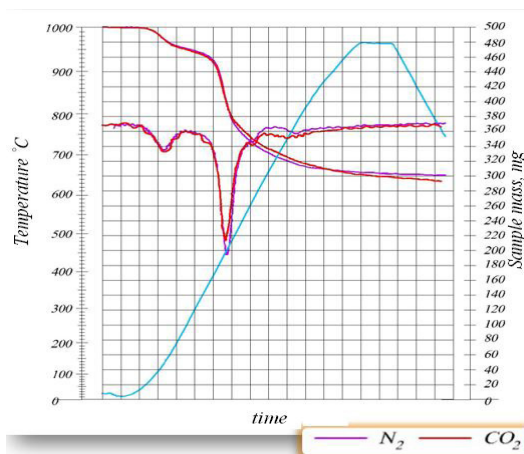

Fig. 4. Derivatograms of pyrolysis tests in N_2 and CO_2·

Results analysis reveals that the total volatile yields in N_2 and CO_2 atmospheres differ insignificantly. The somewhat higher values in CO_2 should apparently be attributed to intensification of the gasification reaction at the high temperature region of the process. This means that besides the thermal decomposition of unstable molecular fragments of

coal during devolatilization, a very slow process of char conversion in CO_2 atmosphere is initiated in the final phase of the experiment. The confirmation of this assumption, among others, is presence of a mass loss curve gradient at the final point of the process, which is not observed in a nitrogen atmosphere. Another notable aspect is the less rapid volatile release in CO_2, as indicated by the peak rate of sample decomposition on the DTG curve.

This observation is most probably due to the difference in the thermal properties of the specific gaseous atmospheres (Table 4).

As seen from the table, despite the close values for thermal conductivity and isobaric mass heat capacity of the gases, substantial differences in gas densities lead to significantly lower values of thermal diffusivity of CO_2. This gas property is known as a key parameter in the transient heat conduction problem that describes the process of sample heating in TGA apparatus. Smaller values of thermal diffusivity for CO_2 will result in less heat flow to the sample and consequently, less rapid volatile release.

3.2. Char combustion tests

Chars obtained after the procedure described above were then subjected to non-isothermal combustion in O_2/N_2 and O_2/CO_2 atmospheres with an oxygen concentration of about 20% vol in both cases (Fig. 5). The char burnout in O_2/CO_2 is less vigorous, which can be explained by the lower diffusion coefficient of oxygen in CO_2 atmosphere, and hence an earlier process transition to the internal diffusion mode, which inhibits the combustion process and results in lower reaction rate.
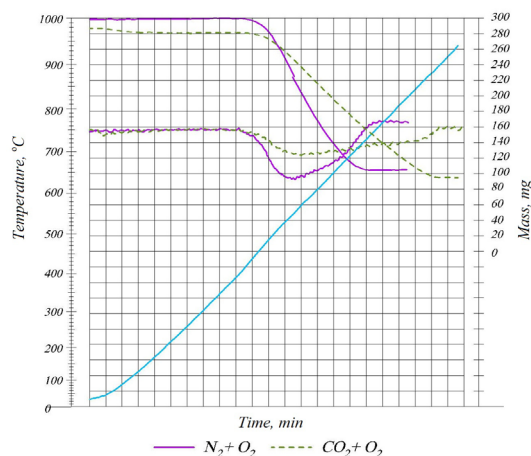

Fig. 5. Derivatograms of char combustion tests in O_2/N_2 and O_2/CO_2.

At this point, however, note that the described approach, implying combustion of chars that had been previously obtained during pyrolysis in different atmospheres, a priori does not provide an opportunity for unique identification of the cause of the differences in the recorded conversion curves. These may either be a result of combustion atmosphere changes or a result of inherently different char reactivities, since they also had been obtained earlier in different environments. In this regard, some authors have resorted to variant experimental procedures by combinatorially changing the conditions of pyrolysis and subsequent char combustion tests. For instance, chars generated in different atmospheres are the burned out in identical conditions, or vice versa, which allows elimination of unnecessary factors influencing the process.

Table 4
Thermal properties of basic components of considered gaseous atmospheres

| P = 760 mm Hg	N$_2$	CO$_2$	H$_2$O
t = 0 °C			
Gas density, kg/m³	1.250	1.964	0.804
Thermal conductivity, W/(m·K)	0.024	0.014	0.017
Isobaric heat capacity, kJ/(kg·K)	1.039	0.818	1.8597
Kinematic coefficient of viscosity, mm²/s	13.28	6.960	11.52
Thermal diffusivity, mm²/s	18.48	9.093	11.57
t = 900 °C			
Gas density, kg/m³	0.291	0.457	0.187
Thermal conductivity, W/(m·K)	0.075	0.079	0.122
Isobaric heat capacity, kJ/(kg·K)	1.200	1.277	2.413
Kinematic coefficient of viscosity, mm²/s	150.6	96.12	235.5
Thermal diffusivity, mm²/s	213.6	135.8	269.7

Fig. 6. Derivatograms of standard char combustion tests in O_2/N_2 and O_2/CO_2.
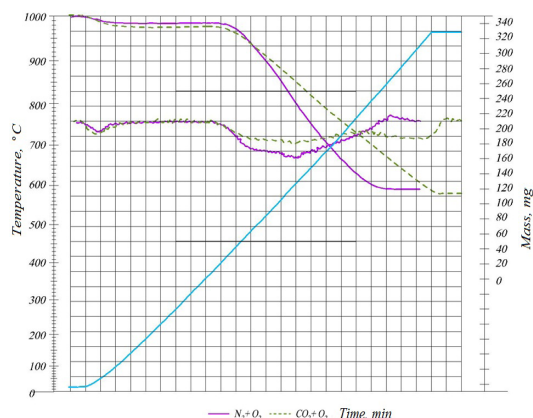
Fig. 7. Derivatograms of standard char combustion and gasification tests in O_2/N_2 and O_2/CO_2.

Following this approach, a third series of experiments was performed by combusting chars devolatilized beforehand under identical conditions (exposed for 7 min in a muffle furnace). Combustion atmospheres were as before with respect to O_2/N_2 and O_2/CO_2 (Fig. 6).

These curves illustrate that although the chars are somewhat less reactive compared to the ones discussed above, the qualitatively established principles are still valid: combustion of char in O_2/CO_2 is less vigorous. Moreover, note that the general pattern of the conversion curve in O_2/CO_2 has a somewhat atypical nature comprising not one but two local minima. The second one, although less pronounced, is reached at the end of the conversion process. Apparently, this is due to the fact that under these conditions, typical reactions between char and oxygen, with a fast process transition to the internal diffusion mode, occur in the first stage of the process. As the temperature progressively increases, the oxidative reaction on the developed porous surface of char particles becomes increasingly more severe. For this reason, oxygen frequently fails to diffuse deeper into the carbon array, and is now primarily consumed within the outer surface layers of the burning particles. Oxygen is thus essentially displaced from the pore volume: its concentration along the particle radius decreases sharply, but as CO_2 still remains there, it starts to freely react on the surface of the carbon pores according to the gasification mechanism, and this is what leads to intensification of the conversion in the final phase of the process. This assumption is confirmed by a pronounced endothermal effect of the DTA curve that is also recorded during the experiment.

A more reliable determination of the activity of gasification reaction was obtained by performing an additional experimental test under the same conditions but in a pure CO_2 atmosphere (Fig. 7).
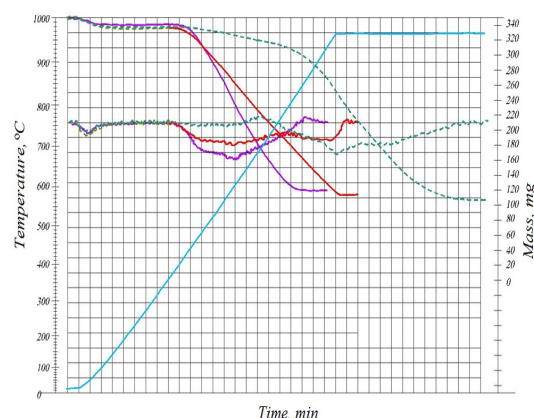
The depicted thermograms reveal that under these conditions, a chemical reaction of CO_2 reduction begins on the char surface at temperatures of about 750 °C. Note that the maximum reaction rate during gasification test is comparable (in case of O_2/N_2), or even higher (O_2/CO_2), than in the tests in oxidative atmospheres. This is obviously due to the specific feature of the non-isothermal TGA method; namely, a linear increase in temperature in the chamber. As a result, the more intensive oxidation reaction starts and terminates in the low temperature zone (reaching the highest rate at 600 °C), while it is not yet observed in a pure CO_2 atmosphere. The conversion rate in pure CO_2 reaches a maximum at 950 °C (corresponding to the maximum operating temperature of the apparatus), whereas the reaction in oxidative medium is already completed or has become sluggish, since the sample conversion is almost finished by that time and the number of active sites on the surface of reacting particles is minimal. Thus, deployment of an oxidation reaction primarily in the low-temperature zone leads to comparable sample conversion rates in these tests, despite the undoubtedly lower intensity of gasification reactions under otherwise identical conditions.

3.3. Non-isothermal kinetic analysis of char combustion

The selection of conditions for thermogravimetric studies of fossil fuel combustion, interpretation of the obtained results and extrapolation of those results to industrial scale equipment must consider the following methodological aspects. The conditions of the complex processes associated with coal particle combustion during thermogravimetric analysis are significantly different from the conditions prevailing in commercial scale units in many different physical and chemical aspects. For instance, the maximum

rate of sample heating in TGA rarely exceeds a few tens of degrees per minute (in this work it was 20 K/min). In fluidized bed combustors (FBCs), by contrast, coal particles 5–50 mm in diameter fed into the bed will be heated up at a rate of 100 K/s [11], and the fuel particle heating rate in the pulverized coal (PC) boiler flame is higher still, by two orders of magnitude. The maximum temperature during a TGA test is usually about 1000 °C (sometimes higher), which covers the temperature range of FB and CFB boilers, but is much lower than the maximum temperature inside a PC boiler flame. The bulk concentration of sample particles in the crucible is likely to correspond to the poured random packing particle bulk volume fraction i.e. ~ 0.6 m^3/m^3. In FB and CFB boilers, local concentrations of particles in some zones can be this high, but inside the PC boiler flame, the coal dust concentration is lower by 3–4 orders of magnitude. Furthermore, the conditions of mass transfer to the sample in TGA apparatus are obviously different from the conditions typical for both FB and PC boilers.

These discrepancies will inevitably lead to a sharp difference in many factors, including the intensity of particle heating, rate of release, composition and total yield of volatiles, swelling ratio, probability of particle fragmentation, development of porous inner surface of forming char particle, ignition and combustion of volatiles, and char burnout mode. Therefore, since the TGA tests do not reproduce the process conditions that are typical for commercial sized units, the extrapolation of quantitative laws observed during experimental study (e.g., reaction rate as a function of conversion degree) to these conditions is incorrect. Moreover, extrapolation of qualitative results (for example, the observed decrease in conversion rate in O_2/CO_2), is also inadmissible.

The latter statement is explained by the multiple-factor nature of the combustion process. Specifically, heterogeneous char combustion is defined by chemical (chemical reaction kinetics) as well as by physical factors (heat and mass transfer, diffusion processes). Changing the reaction atmosphere by substituting air nitrogen with carbon dioxide may alter these factors not only by differences in degree, but in different directions. As already stated, the diffusion component of the reaction will clearly drop, whereas chemical kinetics could change inversely, or not change at all. But then, if combustion in the TGA study occurs in a diffusional mode, the absence of thorough analysis of the process mechanisms will result in a conclusion declaring a reduction in the reaction rate. Further spread of these findings to PC boiler regimes, for example, where fine particles of some fuels can locally burn under kinetically controlled mode, will lead to erroneous predictions.

The only way to obtain practically meaningful results in TGA studies is apparently to carry out an experiment with strict control of process conditions, distinguishing between individual regimes (kinetically or diffusionally controlled), and establishing and analyzing process parameters under these regimes. This is followed by development of a mathematical model based on empirical data on individual stages, and then extrapolation of these results to the working conditions of industrial scale plants by means of the formulated model.

This type of approach is particularly common and suitable for investigation of char combustion. The preliminary pyrolysis process, being very complex for such an analysis, is usually carried out in a tube flow reactor under conditions close to the PC boiler flame to ensure equivalence of this stage of the process to the regime typical for industrial scale units. Since most aspects of diffusional processes can be predicted quite reliably (both under experimental and industrial scale conditions), the TGA experiments in these cases are carried out so that the conversion process is shifted as far as possible to the kinetically controlled mode (zone I). Analysis of data obtained under this methodological scheme provides an answer to the key question about the alteration of the actual oxidation reaction kinetics parameters when shifting from a conventional reaction atmosphere of O_2/N_2 to an O_2/CO_2 medium.

For this purpose, the next set of experiments assumed combustion of earlier obtained chars in O_2/N_2 and O_2/CO_2 atmospheres with lower oxygen concentration (5–10% vol.) and a sample heating rate of 5 K/min. The sample mass was 100 mg. Results analysis, with an estimation of the oxidation reaction activation energy, was performed by linear regression analysis of the following classical conversion equation [12]:

$$\frac{dX}{dT} = k(T) \cdot F(X)$$

The results of the analysis of conversion curves describing char burnout in both atmospheres are shown in Fig. 8 in semi-logarithmic coordinates of $ln(dX/dT \cdot 1/F(X))$ and inverse temperature 1000/T. The data reveal that:

1. Within the first low-temperature stage of the process in both environments (1.3<1000/T<1.42 in O_2/N_2 and 1.33<1000/T<1.45 in O_2/CO_2), the linear behavior of the plot is detected, which indicates combustion occurring in the internal kinetics regime (zone I).

2. The slopes of the curves within the first stage are identical for both environments, and correspond

to the activation energy of 166 kJ/mol.

3. Transition to a high-temperature region in both environments ($1.1 < 1000/T < 1.27$ in O_2/N_2 and $1.17 < 1000/T < 1.32$ in O_2/CO_2) leads to a sharp change in the curve slope, with distinctive linear behavior of both curves within this temperature interval.

4. The slope of both curves in the high temperature region is identical and corresponds to 79 kJ/mol.

5. Items 3 and 4 indicate the process transition to an internal diffusion regime (zone II) that, strictly speaking, cannot be described by activation energy (because of so-called "diffusional falsification", [13]), but its "observed" value is known to be half the value of the true activation energy, which agrees well with items 2 and 4.

6. Transition of the combustion process to an internal diffusion mode (zone II) occurs earlier (at $1000/T = 1.34$ or 473 °C) in O_2/CO_2 than in O_2/N_2 (at $1000/T = 1.3$ or 496 °C), which is a result of lower oxygen diffusion activity in a CO_2 medium.

This analysis leads to the following main conclusion: the chemical reaction of char carbon oxidation in O_2/N_2 and O_2/CO_2 atmospheres proceeds identically and can be described by the same set of kinetic parameters (activation energy E, and bearing in mind its relation to the pre-exponential factor – the so-called compensation effect, the same k_0 as well as the structural profile). This conclusion served as a basis for development of a program module describing the chemical reaction kinetics of carbon particles in an O_2/CO_2 environment, which was then integrated into circulating fluidized bed reactor computation software.

Based on these studies of the fuel combustion process, as well as other data obtained previously on hydrodynamics and heat transfer in a CFB reactors, a mathematical model and subsequent eng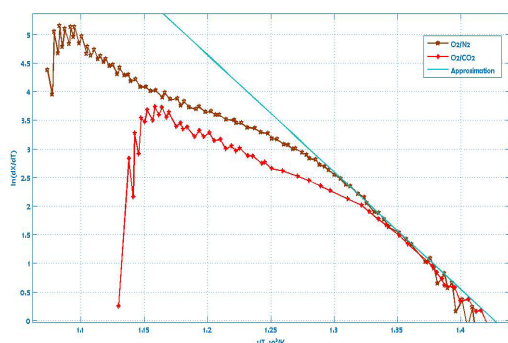ineering method were developed for calculating the basic regime and performance characteristics of units with oxyfuel-based CCS technology. This technique was then used for detailed analysis of feasibility and advisability of shifting the CFB boiler at the Novocherkassk TPP unit №9 to an oxyfuel mode.

Conclusions

TGA experiments aimed at discovering specific features of coal combustion under an O_2/CO_2 medium were performed for comparison with an O_2/N_2 environment. Pyrolysis tests revealed essentially identical behavior of DTG curves, with a somewhat lower decomposition rate and slightly higher total mass loss in O_2/CO_2. The former was attributed to the lower thermal diffusivity of CO_2 and the latter was assumed to be a result of initiation of a gasification reaction in the higher temperature region during sample decomposition in a CO_2 atmosphere. Combustion tests were conducted with chars obtained under these atmospheres as well as with chars generated under standard routine conditions. Both tests revealed lower oxidation rate of chars in an O_2/CO_2 medium, which was attributed primarily to a lower binary diffusion coefficient of oxygen in CO_2 than in N_2.

The char-CO_2 gasification reaction contributed to the conversion process and was particularly noticeable at temperatures above 750 °C, as well as under an internal diffusional controlled regime (zone II), implying displacement of oxygen out of the char particle pore volume and subsequent free reaction of CO_2 on the developed pore surface. Non-isothermal kinetic analysis revealed no particular difference in intrinsic kinetics of the oxidation reaction in O_2/CO_2 compared to O_2/N_2 medium, at least when the char-CO_2 reaction was inhibited. Both tests revealed two distinctive linear regions of the reaction rate logarithm versus the inverse temperature plot. Within these regions that apparently corresponded to internal kinetically and diffusionally controlled regimes, both curves had slopes related as $166/79 \approx 2.1$, which agrees well with known features of the observed reaction activation energy within a diffusionally controlled regime, which is two times lower than the true value due to so-called diffusional falsification. The only difference between the curves obtained in O_2/CO_2 and O_2/N_2 was a slightly earlier transition to the internal diffusion mode in O_2/CO_2 compared to O_2/N_2, which was attributed to lower oxygen diffusion activity in the CO_2 medium.

The obtained data were used to develop a coal combustion model under O_2/CO_2 conditions, which was then incorporated as a combustion module into circulating fluidized bed (CFB) computation software.

Fig. 8. Conversion curve semilogarithmic plot comparison in O_2/N_2 and O_2/CO_2 in the low temperature region.

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