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Fluidized bed combustion of single coal char particles at high CO_2 concentration

Fabrizio Scala*, Riccardo Chirone

Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche, Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

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ABSTRACT

Combustion of single coal char particles was studied at 850 °C in a lab-scale fluidized bed at high CO_2 concentration, typical of oxyfiring conditions. The burning rate of the particles was followed as a function of time by continuously measuring the outlet CO and O_2 concentrations. Some preliminary evaluations on the significance of homogeneous CO oxidation in the reactor and of carbon gasification by CO_2 in the char were also carried out. Results showed that the carbon burning rate increases with oxygen concentration and char particle size. The particle temperature is approximately equal to that of the bed up to an oxygen concentration of 2%, but it is considerably higher for larger oxygen concentrations. Both CO_2 gasification of char and homogeneous CO oxidation are not negligible. The gasification reaction rate is slow and it is likely to be controlled by intrinsic kinetics. During purely gasification conditions the extent of carbon loss due to particle attrition by abrasion (estimated from the carbon mass balance) appears to be much more important than under combustion conditions.

1. Introduction

Production of energy from fossil fuel combustion results in the emission of greenhouse gas species, with the most significant fraction being CO_2. The constant increase in greenhouse gas emissions has resulted in the development of new technologies with lower emissions and technologies that can accommodate capture and sequestration of carbon dioxide. Oxyfiring (or oxyfuel) technology can produce an almost pure CO_2 outlet stream, by using pure oxygen instead of air for fuel combustion [1]. Flue gas is partly recycled back into the furnace to control the combustion temperature. In this way the costs of CO_2 separation from the flue gas can be substantially reduced. Although most of the research activity in oxyfiring has concentrated on pulverized coal boilers [2], recently the application of this technology to circulating fluidized bed (CFB) coal boilers has been examined [3–7]. CFBs appear to be particularly suited for oxyfiring conditions because of the fuel flexibility and better temperature control (which allows to reduce the amount of recycled flue gas). The feasibility of CFB coal oxyfiring has been successfully demonstrated in pilot-plant tests, and no particular technological barrier appears to exist for implementing this technology in the near-term.

However, a number of issues still need to be addressed in more detail to obtain a more fundamental understanding of the changes between oxyfiring and conventional air-fired combustion [1]. One of these issues regards the combustion characteristics of coal char in an O_2/CO_2 atmosphere. The reactions that can occur during the oxy-combustion process are:

$$C(s) + O_2 \rightarrow CO_2 \tag{A}$$

$$C(s) + (1/2)O_2 \rightarrow CO \tag{B}$$

$$C(s) + CO_2 \rightarrow 2CO \tag{C}$$

$$CO + (1/2)O_2 \rightarrow CO_2 \tag{D}$$

where (A) and (B) represent the carbon combustion reactions, (C) carbon gasification by CO_2 and (D) homogeneous CO oxidation reaction. In fact, it has been suggested that under oxyfiring conditions (especially at the high temperatures experienced in pulverized fuel combustion) carbon gasification by CO_2 (reaction (C)) might contribute significantly to the char mass loss [1,2].

In this work, combustion of single large coal char particles in a lab-scale fluidized bed under simulated oxyfiring conditions was studied. The burning rate of the particles was followed as a function of time by continuously measuring the outlet CO and O_2 concentrations. Some preliminary evaluations on the significance of homogeneous CO oxidation in the reactor and of carbon gasification by CO_2 in the char particle at the relevant operating conditions are also reported.

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* Corresponding author. Tel.: +39 081 7682969; fax: +39 081 5936936.
E-mail address: scala@irc.cnr.it (F. Scala).

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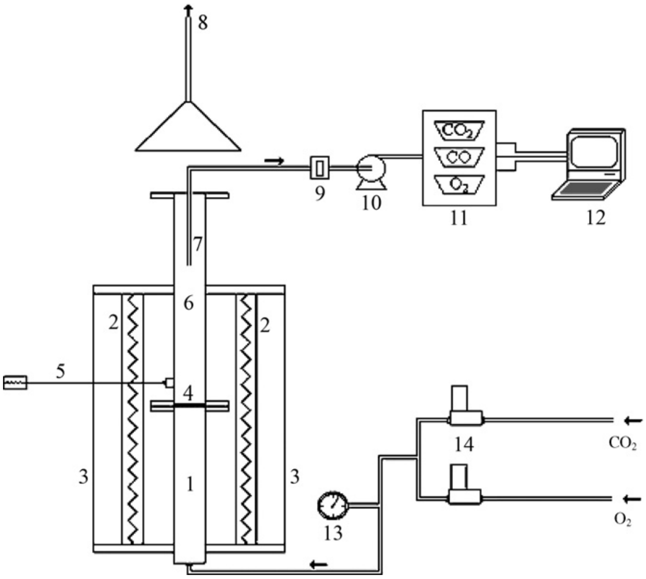

Fig. 1. Experimental apparatus: (1) gas preheating section; (2) electrical furnaces; (3) ceramic insulator; (4) gas distributor; (5) thermocouple; (6) fluidization column; (7) gas suction probe; (8) stack; (9) cellulose filter; (10) membrane pump; (11) gas analyzers; (12) personal computer; (13) manometer; (14) digital mass flowmeters.

2. Experimental

2.1. Apparatus

A circular stainless steel atmospheric bubbling fluidized bed reactor 40 mm ID and 1 m high was used for the experiments (Fig. 1). The gas distributor was a 2 mm thick perforated plate with 55 holes 0.5 mm in diameter disposed in a triangular pitch. A 0.6 m high stainless steel column, containing a number of steel nets for gas preheating and mixing, was placed under the distributor. The fluidization column and the preheating section were heated by two semicylindrical electric furnaces. The temperature of the bed, measured by means of a thermocouple placed 40 mm above the distributor, was kept constant by a PID controller. Temperature variations during the runs were always within ±1 °C of the set point.

Gases were fed to the column via two high-precision digital mass flowmeters/controllers (accuracy ±1% full scale). Each flowmeter/controller was calibrated with a bubble flowmeter. Gases were supplied from two cylinders containing carbon dioxide and oxygen.

The top section of the fluidization column was left open to the atmosphere and the exit gas was sucked by a hood. A stainless steel probe was inserted from the top of the column to convey a known fraction (0.06 m^3/h) of the exit gas directly to the gas analyzers. A high efficiency cellulose filter was inserted in the line to avoid dust entrainment into the analyzers. The probe, 2 mm ID, was positioned 0.6 m above the distributor, approximately at the axis of the column. The absence of any gas leakage and/or suction to/from the surrounding environment in the sampling probe and line was carefully checked.

Table 1
Properties of Snibston coal.

Proximate analysis, % (as received)	
Moisture	14.6
Ash	4.0
Volatile matter	35.2
Fixed carbon	46.2
Ultimate analysis, % (dry and ash free basis)	
Carbon	81.3
Hydrogen	5.3
Nitrogen	1.6
Oxygen	10.8
Sulphur	1.0
Char density (kg/m^3)	1040

A NDIR analyzer (accuracy ±1% full scale) was used for on-line measurement of CO and CO_2 and a paramagnetic analyzer (accuracy ±2% full scale) for O_2 concentration in the exhaust gases. The measuring range of the O_2 analyzer was 0–10% (v/v), for CO 0–1000 ppmV and for CO_2 0–100% (v/v). Data from the analyzers were logged and further processed on a PC.

2.2. Materials

A Snibston bituminous coal was selected as the test fuel. Table 1 reports the fuel properties. Char from this coal has been reported to have the lowest propensity to attrition and fragmentation among the coals studied in previous investigations [8]. The fuel particles were first devolatilized by dropping them in the fluidized bed with N_2 at 850 °C. After 5 min, char particles were retrieved from the bed, cooled down in N_2 and machined (by hand with abrasive paper) into almost spherical particles with an average size of ~6–7 mm (Fig. 2a). The particles were further pre-processed in air for 8 h in the fluidized bed at ambient temperature and 0.3 m/s to smoothen the particle surface.

The bed material consisted of 180 g of quartz sand, corresponding to an unexpanded bed height of 0.1 m. Sand was double sieved in the 500–600 μm particle size range. The minimum fluidization velocity was 0.13 m/s. The particle density of the quartz sand was 2560 kg/m^3, and the bed voidage at minimum fluidization was 0.44.

2.3. Procedures

In all the tests performed in this experimental campaign the inlet oxygen concentration was lower than 10% (v/v), because these are the relevant local O_2 concentrations near a burning particle in a fluidized bed under oxyfiring conditions. If low oxygen concentrations are used (<2%, v/v), it is known that the particle temperature can be assumed approximately equal to that of the bed [9]. Since some tests were performed with a higher O_2 concentration, in these tests a thermocouple was inserted inside the particle to measure its

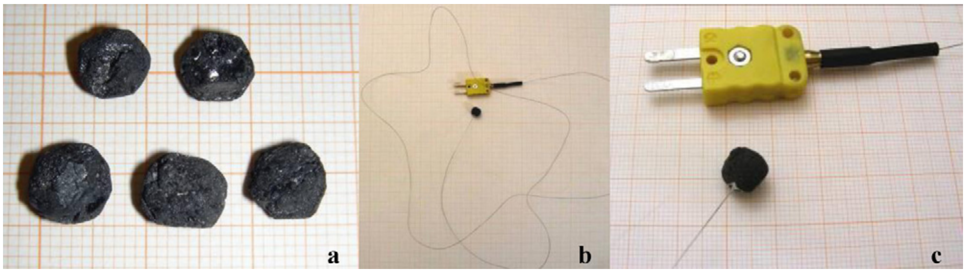

Fig. 2. (a) Coal char particles used for the experiments; (b and c) char particle with thermocouple inside at two different magnifications.

temperature. A long (1.5 m) and thin (250 μm OD) thermocouple was fitted and cemented inside a hole drilled through the particle (Fig. 2b and c). The thermocouple tip was placed approximately at the center of the particle. The thermocouple was sufficiently thin and flexible not to restrict appreciably the free motion of the particle inside the bed. This was confirmed by repeating the same experiment with similar char particles with and without the thermocouple: the carbon burning rate as a function of the particle diameter was practically the same for both runs.

The experiments were performed in a fluidized bed at 850 °C, atmospheric pressure, with a fluidization velocity of 0.3 m/s, which corresponds to bubbling/slugging conditions [10]. An inlet gas mixture was introduced made of CO_2 and O_2 in the combustion tests and 100% CO_2 in the gasification tests; O_2 concentration in the combustion tests was fixed at 1, 2, 4.5 or 8% (v/v). Each test consisted in the injection of one char particle, of known mass and diameter, in the fluidized bed and in the continuous measurement of CO and O_2 concentrations at the outlet. To obtain the char burning rate during the tests, mass balances on oxygen (Eq. (1)) and carbon (Eq. (2)) in the reactor were carried out, under the pseudo-stationary assumption:

$$\dot{m}^{\text{in}}_{O_2} + \frac{32}{44}\dot{m}^{\text{in}}_{CO_2} = \dot{m}^{\text{out}}_{O_2}(t) + \frac{16}{28}\dot{m}^{\text{out}}_{CO}(t) + \frac{32}{44}\dot{m}^{\text{out}}_{CO_2}(t) \qquad (1)$$

$$\frac{12}{44}\dot{m}^{\text{in}}_{CO_2} + \dot{m}^{\text{consumed}}_{C}(t) = \frac{12}{44}\dot{m}^{\text{out}}_{CO_2}(t) + \frac{12}{28}\dot{m}^{\text{out}}_{CO}(t) \qquad (2)$$

where $\dot{m}^{\text{in}}_i$ and $\dot{m}^{\text{out}}_i$ are the mass flow rates of species i that enter and exit the reactor in the gas flow, respectively, and $\dot{m}^{\text{consumed}}_{C}$ is the carbon consumption rate by reaction, all in kg/s. Combining these two equations gives:

$$\dot{m}^{\text{consumed}}_{C}(t) = \frac{12}{32}\left[\dot{m}^{\text{in}}_{O_2} - \dot{m}^{\text{out}}_{O_2}(t)\right] + \frac{3}{14}\dot{m}^{\text{out}}_{CO}(t) \qquad (3)$$

By integrating the curve obtained with Eq. (3) between time zero and the end of the test (t_f) it is possible to calculate the total mass of carbon consumed by reaction during the test:

$$m^{\text{consumed}}_{C} = \int_0^{t_f} \dot{m}^{\text{consumed}}_{C}(t)\,dt \qquad (4)$$

Assuming that the spherical particle burns according to a constant-density shrinking-particle model [9], the char particle diameter as a function of time is given by:

$$d(t_1) = \left(\frac{6\left(m^{\text{initial}}_{C} - \int_0^{t_1} \dot{m}^{\text{consumed}}_{C}(t)\,dt\right)}{\pi\rho_{\text{char}}}\right)^{1/3} \qquad (5)$$

3. Results and discussion

3.1. Char combustion tests

Fig. 3 shows the typical concentration profiles of CO and O_2 at the exit of the bed, for a combustion test with 2% O_2 at the inlet. Similar profiles were obtained at the other oxygen concentrations. It can be noted that just after char particle injection a peak in CO concentration was measured. This peak was most likely caused by O_2 adsorbed on the particle at ambient conditions before the test. The peak was considered for carbon mass balance calculations, but was discarded for char burning rate analysis. The absence of other significant peaks or sudden changes in the slope of the CO profile confirmed that no particle fragmentation occurred during char conversion. Using the data from these curves together with Eqs. (3) and (5) it was possible to determine the variation of the particle diameter with time, under the assumption of a constant-density shrinking-particle conversion pattern.

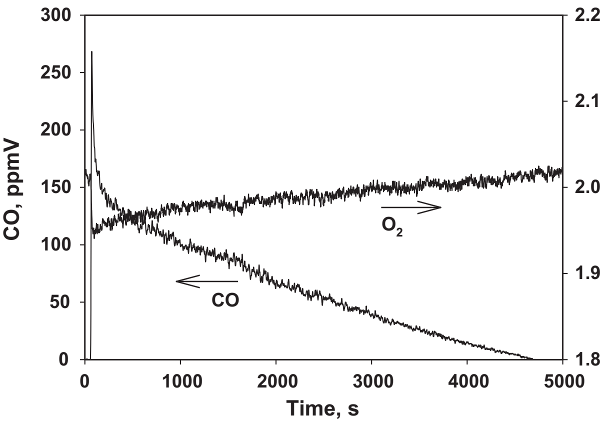

Fig. 3. CO and O_2 concentration profiles during a typical oxyfiring char combustion test, T = 850 °C, O_2 = 2% (v/v).

Fig. 4 reports the carbon burning rate (calculated with Eq. (3)) as a function of the particle diameter for the oxyfiring combustion tests at different O_2 inlet concentrations. Results show that the combustion rate increases as the concentration of O_2 in the bed increases. This result can be expected both in the case of kinetically controlled and diffusion controlled combustion. Fig. 4 also shows that the combustion rate increases almost linearly with the particle diameter, indicating that diffusion of oxygen through the particle boundary layer is likely to be the most important mechanism controlling the burning process, as it was the case during air combustion of the same char [9]. This result justifies the assumption of a constant-density shrinking-particle conversion model for this char. Only data for d > 1 mm are reported in Fig. 4 since for smaller particle sizes the particle burning rate is not likely to be controlled (at least predominantly) by external diffusion. When comparing these burning rate data with those obtained in combustion tests with the same char in O_2/N_2 atmospheres under the same operating conditions and in the same apparatus (as reported in [9]), it was noted that under oxyfiring conditions a slightly higher (∼30–40%) burning rate was measured for all particle diameters and oxygen concentrations. This result is consistent with those reported by Rathnam et al. [2] for pulverized coals, and was explained by these authors as a possible contribution of the carbon–CO_2 gasification reaction at temperatures above 1030 K.

As stated previously, some of the combustion tests were performed with a thermocouple inserted in the char particle to

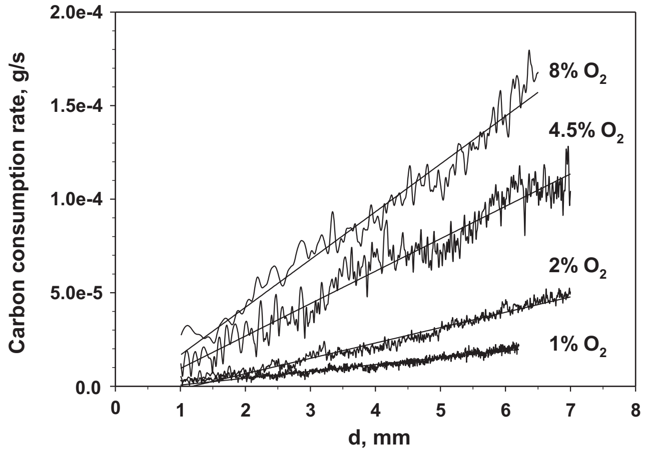

Fig. 4. Carbon consumption rate as a function of particle diameter during oxyfiring char combustion tests at different O_2 concentrations, T = 850 °C.

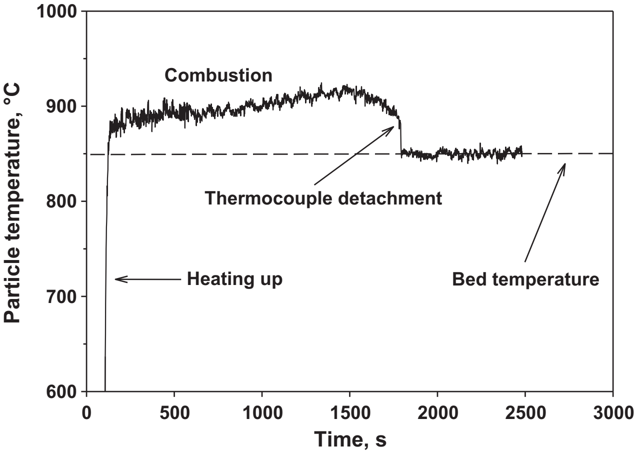

Fig. 5. Particle temperature profile during a typical oxyfiring char combustion test, $T = 850\,^\circ\mathrm{C}$, $O_2 = 8\%$ (v/v).

measure its temperature during the test. Fig. 5 reports a typical plot of the particle temperature measured by the thermocouple during a test (8% O_2 at the inlet). Just after injection in the bed the particle temperature rapidly increases to a temperature larger than that of the bed. During char combustion the particle temperature remains approximately constant, slightly increasing with time, until at some point (about 98% carbon conversion for this run) the thermocouple detaches from the particle, rapidly reaching the bed temperature value. Qualitatively similar temperature traces were obtained at 2 and 4.5% oxygen inlet concentrations. Table 2 reports the results of these experiments in terms of the measured maximum temperature difference between the particle and the bed. It can be noted that for an oxygen concentration larger than 2% the error done by considering that the char particle has the same temperature as the bed is larger than 10 °C.

The carbon mass balance for the char particle was calculated by comparing the initial carbon mass in the particle and the total amount of carbon consumed during the test (Eq. (4)). For all the tests under simulated oxyfiring combustion conditions this balance had an absolute error which was always less than 5%.

3.2. *Char gasification tests*

Another series of tests was performed at 850 °C to quantify how important is reaction (C) during the tests. A typical outlet CO concentration profile obtained during a gasification test (100% CO_2) is shown in Fig. 6. Some experiments were also performed with an O_2 trap (outlet O_2 concentration <1 ppmV) in the gas feeding line to make sure that no oxygen impurity could enter the reactor, but results showed no difference with respect to the tests without the O_2 trap. Again, the sharp initial CO peak was most likely caused by O_2 adsorbed on the particle at ambient conditions before the test. The gasification tests clearly show a much longer reaction time with respect to that of the combustion cases. Fig. 6 also shows (right axis) the carbon consumption rate as a function of time for the same gasification test. For this test the curve was not plotted as a function of diameter, since in these conditions the constant-density shrinking-particle model (and in turn Eq. (5)) is likely not to apply anymore.

Table 2
Peak temperature difference between the char particle and the bed for different inlet oxygen concentrations.

Inlet O_2 concentration (% v/v)	Peak temperature difference (°C)
2	15
4.5	36
8	68

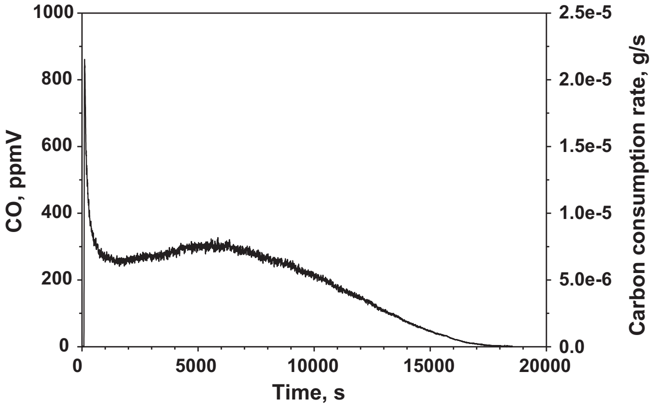

Fig. 6. Measured CO concentration and carbon consumption rate as a function of time during a typical char gasification test, $T = 850\,^\circ\mathrm{C}$, $CO_2 = 100\%$ (v/v).

By comparing Figs. 4 and 6 it can be clearly noted that the gasification reaction rate at 850 °C is always slower than the combustion rate (at least for oxygen concentrations larger than 1%) and that it is less dependent on the actual char particle mass (especially for the first half of the run, see Fig. 6), denoting a significant contribution of the intrinsic kinetics on the reaction rate. The presence of a maximum of the carbon consumption rate at intermediate burn-off has been often observed during gasification of different fuels under intrinsic kinetics control, and can be explained by the effect of pore widening and of the increase of accessible surface area by carbon consumption [11]. On the whole, the gasification rate under high CO_2 bulk concentrations at 850 °C is slow but not negligible, contrary to what happens under typical air combustion conditions [9]. In addition, it is important to note that for oxygen concentrations above 2% the particle temperature may be significantly higher than that of the bed, and this in turn would further increase the carbon gasification rate by CO_2.

The carbon mass balance calculation for the char particle in the gasification tests indicated that the error was of the order of 20% (the calculated consumed mass was always smaller than the initial mass of carbon). This suggests that particle abrasion by attrition is important during the gasification tests and that part of the char probably exited the reactor as elutriated material without reacting. This is consistent with recently reported results of carbon attrition of different fuel chars in fluidized bed under CO_2 gasification conditions [12]. It was shown that attrition of carbon fines from the char particles during gasification is extensive, due to a so-called gasification-assisted attrition mechanism, where carbon consumption in the particles progressively weakens the char structure by pore enlargement. The low reactivity of the generated fines under gasification conditions makes the loss of carbon by fines elutriation much more significant than that typically found under combustion conditions.

3.3. *Homogeneous CO oxidation tests*

In order to check if reaction (D) occurred in the reactor, several tests were done in which a mixture of CO, CO_2 and O_2 was introduced in the fluidized bed (without the presence of any char particle) first at ambient temperature and then at 850 °C. In particular, CO was separately introduced through a steel probe just above the gas distributor to avoid possible oxidation in the pre-heating section. Operating conditions were the same as in the combustion tests. Inlet CO concentration in the gaseous mixture was 500 or 1000 ppmV. It was observed that at 850 °C the concentration of CO at the exit significantly decreased when compared to ambient temperature. CO conversion was not dependent on the inlet CO concentration, but slightly varied with inlet O_2 concentration. About 61% and 53% CO conversions were measured for 2% and 1% inlet O_2 concentrations, respectively. In conclusion, these tests suggest that in the conditions of the present oxyfiring combustion tests reaction (D) is not negligible.

4. Conclusions

Results from preliminary experimental tests showed that during oxy-combustion of coal char in a bubbling fluidized bed at 850 °C, besides the heterogeneous combustion reactions, the CO_2 gasification reaction and the homogeneous CO oxidation reaction are not negligible, and should be taken into account in analyzing the reaction rate data.

During coal char oxyfiring the carbon burning rate increased with oxygen concentration and char particle size, and particle conversion closely followed the constant density-shrinking particle conversion pattern. These results suggest that diffusion of oxygen through the particle boundary layer is likely to control the burning process. The temperature of the particle was approximately equal to the bed temperature up to an oxygen concentration of 2%, for higher concentrations the temperature of the particle was considerably higher than that of the bed.

The CO_2 gasification reaction was slower than the combustion reaction (at least at oxygen concentrations larger than 1%), and intrinsic kinetics was likely to control the gasification rate. During gasification conditions particle attrition phenomena appeared to be more important than under combustion conditions, leading to a significant loss of carbon by elutriation.

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