ATTRITION OF LIGNITE CHAR DURING FLUIDIZED BED GASIFICATION

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Abstract
Fragmentation and attrition phenomena occurring to lignite char particles during fluidized bed gasification by CO_2 have been studied in a lab-scale apparatus. The influence of bed temperature, fluidizing velocity and inlet CO_2 concentration on attrition and carbon conversion was investigated. Secondary fragmentation and attrition by abrasion of char particles during gasification were significant, suggesting a gasification-assisted attrition enhancement effect. This mechanism, associated to the low reactivity of the generated fines, made the loss of carbon by fines elutriation during char gasification more significant than that typically found under combustion conditions. Up to 10% of the carbon initially fed was lost in the elutriated fines. The carbon loss by elutriation increased with the fluidization velocity, and when the bed temperature and CO_2 concentration decreased. The effect of these last two variables was connected to their influence on the char gasification rate.

Introduction

Lignite is an abundant fuel and makes up approximately 40% of coal reserves in the world. Its commercial use is forecast to grow substantially [1]. However, lignite usually has high water and oxygen content, low energy density, and it is expensive to transport. All these characteristics have limited its utilization.

The urgent need to apply techniques to capture and sequester CO_2 emitted from the use of coal has triggered the development of new processes like chemical looping combustion and sorption enhanced gasification [2,3]. Both these processes require that fuel gasification is carried out at a relatively low temperature. This could limit the types of fuel that could be used to those with highly reactive chars, such as low-rank coals and biomass.

Fluidized bed (FB) gasification is acknowledged to have great flexibility in conversion of several solid fuels, including low rank coals, into synthesis gas [4]. This technology also allows the use of catalysts and sorbents directly in the reaction chamber for improving the gas quality [5,6]. The syngas can be directly used as a fuel or undergo further processing to yield H_2 or liquid fuels. Despite of its advantages over direct combustion, gasification faces several issues that have limited so far its widespread application. Among them, gasification is usually more capital-intensive and has often suffered for lack of reliability and availability. In addition, a typical drawback of FB gasification is the production of gas with a relatively high dust and tar content.

When injected in a hot FB, fuel devolatilization and primary fragmentation occur, and a fragile char particle is generated which further undergoes attrition and secondary fragmentation. All these phenomena are well known to affect the reliability and efficiency of FB combustion and gasification processes [7,8]. On the one side, attrition/fragmentation may significantly change the particle size distribution of the fuel in the bed, which influences the rate and the mechanism of fuel particle conversion, as well as particle heat and mass transfer coefficients. On the other side, they may cause the elutriation of fine material from the bed that results in the loss of unconverted carbon.

Several attrition studies have been carried out under fluidized bed combustion conditions, focused either on coal [8] or on alternative raw or pelletized fuels [7,9,10]. On the contrary, only very limited activity has been reported under FB gasification conditions [11-13], and no study could be found in the literature on attrition of lignite. A recent investigation [13] on the attrition behavior of fuel pellets during FB gasification showed that attrition of carbon fines from the char particles during gasification was extensive, especially at large carbon conversions. A gasification-assisted attrition mechanism was proposed to explain the experimental results, similar to the well known combustion-assisted attrition patterns already documented for coals under oxidizing conditions [8]. Noteworthy, the low reactivity of the generated fines under gasification conditions made the loss of carbon by fines elutriation much more significant than that typically found under combustion conditions.

In this work the fragmentation and attrition behavior of char from an Italian lignite, was studied under CO_2 gasification conditions in a lab-scale FB apparatus. Secondary fragmentation and attrition were characterized as a function of the char conversion degree. The influence of bed temperature, fluidizing velocity and CO_2 concentration on attrition and carbon conversion was investigated.

Experimental

An electrically heated stainless steel atmospheric bubbling FB combustor 40 mm ID and 1 m high was used for the experiments. Details of the apparatus are reported elsewhere [9].

Two different reactor configurations were used for the tests. The first configuration was used for char secondary fragmentation experiments. In this configuration the top section of the fluidization column was left open to the atmosphere, and the basket technique described by Chirone et al. [8] was applied. A bed of sand (0.2–0.3 mm, 180 g) was fluidized with pure CO_2 at 0.4 m/s and 850°C. During the run a stainless steel circular basket was inserted from the top to retrieve the particles from the bed. A basket mesh of 0.8 mm was used, so that the sand could easily pass through the net openings. In these experiments 3-4 pre-devolatilized char particles were fed into the bed from the top of the column. At definite times the char was retrieved from the bed with the basket and the fragments were weighed and photographed. The run ended when no more carbon was found in the basket, i.e. the fragments were consumed by gasification and attrition down to a size smaller than the mesh opening size.

Table 1. Properties of Sulcis lignite.

Proximate analysis, % (as received)	
Moisture	6.3
Ash	16.9
Volatile Matter	49.7
Fixed Carbon	27.1
Ultimate analysis, % (dry and ash free basis)	
Carbon	71.7
Hydrogen	5.7
Nitrogen	1.8
Oxygen	13.1
Sulphur	7.7
LHV, kcal/kg	5137

t_0=0min	t_1=30min	t_2=50min	t_3=70min	t_4=90min	t_5=110min
X_{C0}=0%	X_{C1}=35.9%	X_{C2}=56.3%	X_{C3}=71.2%	X_{C4}=81.0%	X_{C5}=86.2%

Figure 1. Snapshots of char particles extracted at different gasification times during a secondary fragmentation experiment (t = gasification time, X_C = carbon conversion degree). T=850°C, U=0.4 m/s, 100 % CO_2.

In the second configuration, used for char attrition experiments, a two-exit brass head was fitted to the top flange of the column. By operating a valve it was possible to convey flue gases alternately to two removable sintered brass filters. Batches (~1.0 g) of pre-devolatilized char were fed to the bed (0.3–0.4 mm sand, 180 g). The bed was fluidized with a N_2-CO_2 mixture with a CO_2 concentration in the range 20-100%. The fluidization velocity was varied in the range 0.2-0.6 m/s, and the bed temperature in the range 800-900°C. Elutriated fines were collected by means of the two-exit head by letting the flue gas flow alternately through sequences of filters for definite periods of time. The difference between the weights of the filters before and after operation, divided by the time interval during which the filter was in operation, gave the average fines elutriation rate relative to that interval. Fines collected in the filters were further analyzed to determine their fixed carbon content. A NDIR analyzer was used for on-line measurement of CO and CO_2 concentration in the exhaust gas.

The fuel used in the experiments was an Italian lignite (Sulcis) whose properties are reported in Table 1. The lignite particles were pre-devolatilized in N_2 in a FB operated at 850°C. The obtained char particles were sieved in the nominal particle size range 6.3-8.0 mm.

Results

Secondary fragmentation experiments were carried out by injecting a batch of char particles in the bed of sand fluidized by 100% CO_2. At pre-set time intervals the fluidization gas was switched over to nitrogen in order to quench gasification. The char particles were retrieved from the bed, photographed and then re-injected in the bed for further conversion. Parallel CO gas concentration measurement at the exhaust enabled the calculation of carbon conversion during the run.

Figure 1 reports the results of a fragmentation test on the lignite char. It can be noted that only limited secondary fragmentation occurs at low carbon conversions, while significant shattering is evident at conversions larger that 50%. Since char gasification in the present operating conditions is controlled by intrinsic kinetics, internal reaction progressively weakens the structure inside the particle, enhancing particle fragmentation. Small fragments detaching from the particle surface are subject only to limited conversion in the fluidized bed because of the low reactivity of char towards CO_2, and consequently are mostly collected by the basket during the experiments.

Figure 2A shows the rates of carbon fines elutriation measured during batch attrition experiments under gasification conditions with the lignite char at three bed temperatures. The carbon elutriation rate (E_C) was normalized with respect to the initial amount of fixed carbon fed to the reactor (W_{C0}). The curves show a significant peak in the carbon elutriation rate at some point during particle conversion. The presence of such a peak in the carbon elutriation rate indicates that carbon consumption in the particles progressively weakens the char structure by pore enlargement, much like the combustion-assisted enhancement mechanism typically observed during FB combustion of coal [8].

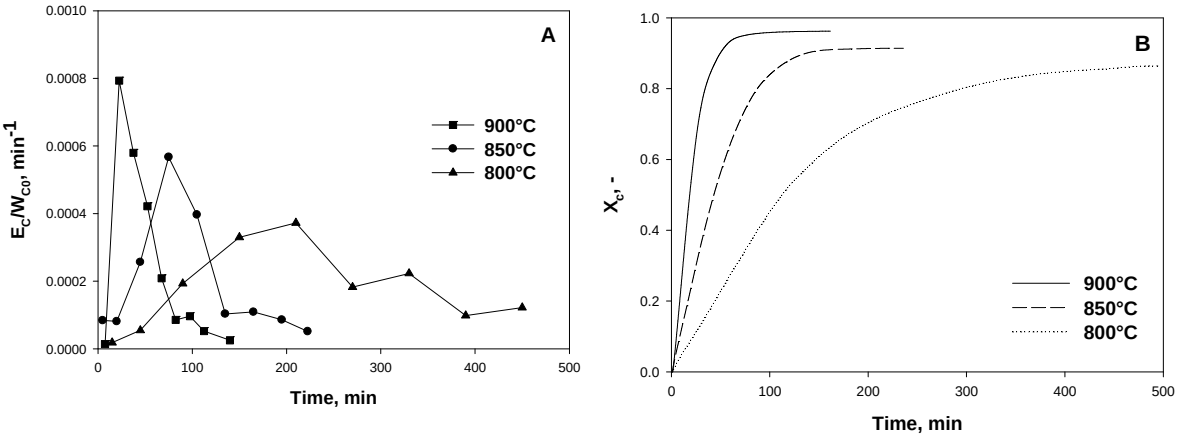

Figure 2. Results of char attrition tests under gasification conditions at three different bed temperatures. A: normalized elutriation rate. B: carbon conversion degree. U=0.4 m/s, 100 % CO_2.

In this case, however, fines post-conversion in the reactor is much less important, since the gasification reaction has a significantly lower rate than combustion. The decreasing part of the curves at the right of the peaks is obviously caused by the progressive decrease of the carbon loading in the bed that overtakes the attrition enhancement at late stages of carbon conversion.

Figure 2B reports the related curves of carbon conversion during the gasification experiments (the curves do not end at 100% conversion because of the significant carbon loss due to elutriation). At the end of the tests, the fluidizing gas was passed to air, and the remaining unreacted carbon was estimated from the $CO+CO_2$ concentration measurement at the exhaust during burn out. Table 2 reports for each experiment the fraction of the initial carbon fed with the fuel char that was cumulatively elutriated and the fraction that was converted to CO, and also the residual carbon burned out at the end of the run.

Table 2. Percentage of the initial carbon fed with the fuel char cumulatively elutriated and converted during the experiments.

Experimental conditions:	**Gasification time (min)**	**Gasified carbon (%)**	**Elutriated carbon (%)**	**Unconverted carbon (%)**
T = 800°C; U = 0.4 m/s; [CO_2] = 100%	480	86.4	8.9	4.7
T = 850°C; U = 0.4 m/s; [CO_2] = 100%	240	91.4	4.8	3.8
T = 900°C; U = 0.4 m/s; [CO_2] = 100%	160	96.2	3.4	0.4
T = 900°C; U = 0.2 m/s; [CO_2] = 100%	240	97.1	1.8	1.1
T = 900°C; U = 0.6 m/s; [CO_2] = 100%	120	92.9	5.9	1.2
T = 900°C; U = 0.4 m/s; [CO_2] = 20%	300	85.4	10.0	4.6
T = 900°C; U = 0.4 m/s; [CO_2] = 50%	200	91.8	5.2	3.0

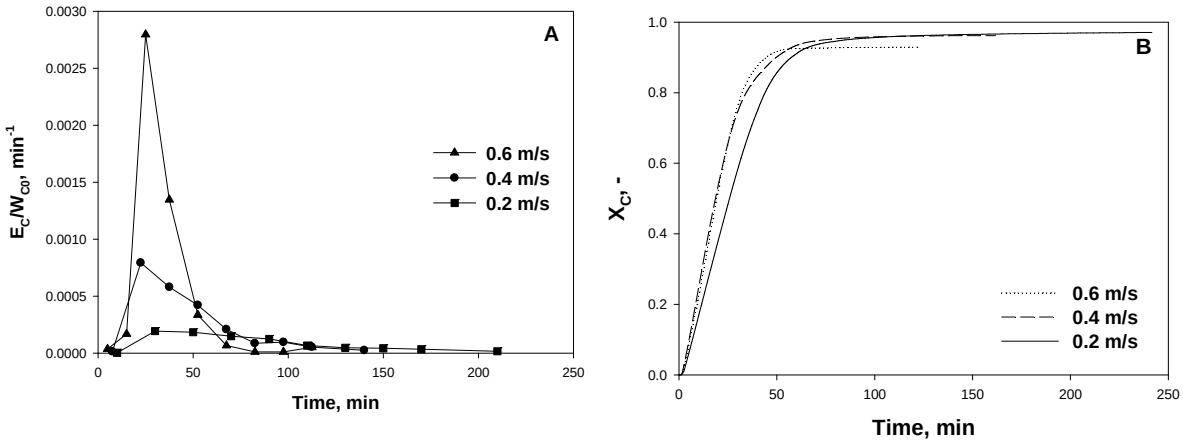

Figure 3. Results of char attrition tests under gasification conditions at three different fluidization velocities. A: normalized elutriation rate. B: carbon conversion degree. T=900°C, 100 % CO_2.

Results of the experiments show, as expected, that the gasification rate increases with the bed temperature. Correspondingly, the gasification time increases when the bed temperature decreases. At high temperatures, carbon elutriation is characterized by a high initial peak rapidly decreasing with time. When the bed temperature is lowered, the height of the peak decreases, and the peak position shifts to longer times. This behavior is clearly connected to the lower carbon consumption rate at lower temperatures. Noteworthy, the total carbon cumulatively elutriated during the run (the integral of the curves reported in Fig. 2A) increases when the bed temperature is decreased (Table 2). Two reasons are likely to determine this behavior. First, at lower temperatures the residence time in the bed during which the particles are subject to attrition increases (from 160 min at 900°C to 480 min at 800°C). Second, the extent of in-bed conversion of the attrited fines before they are elutriated from the bed should increase with the bed temperature.

Figure 3A reports the rates of carbon fines elutriation measured during attrition experiments at three fluidization velocities. The corresponding carbon conversion curves are shown in Fig. 3B. Table 2 reports for these runs the fraction of the initial carbon cumulatively elutriated and that converted to CO. The char gasification rate was only slightly influenced by the fluidization velocity. This result was expected, since the reaction rate is controlled by intrinsic kinetics. On the other hand, carbon elutriation rate significantly increased with the fluidization velocity. This results can be easily explained by considering that higher fluidization velocities result into an enhancement of the turbulent motion of the bed particles and into more energetic particle collisions. This result is in line with those typically reported under combustion conditions [8]. Interestingly, the total carbon cumulatively elutriated during the run increased almost linearly with the fluidization velocity (Table 2).

Figure 4A shows the influence of the inlet CO_2 concentration on the rates of carbon fines elutriation measured during the attrition experiments. The corresponding carbon conversion curves are shown in Fig. 4B. Again, Table 2 reports for these runs the fraction of the initial carbon cumulatively elutriated and that converted to CO. The char gasification rate increased less than linearly with the CO_2 concentration. In particular, a change of the inlet CO_2 concentration from 50% to 100% produced only a slight increase of the char consumption rate. This result is well consistent to the typical kinetic expressions used for char gasification by CO_2 [14].

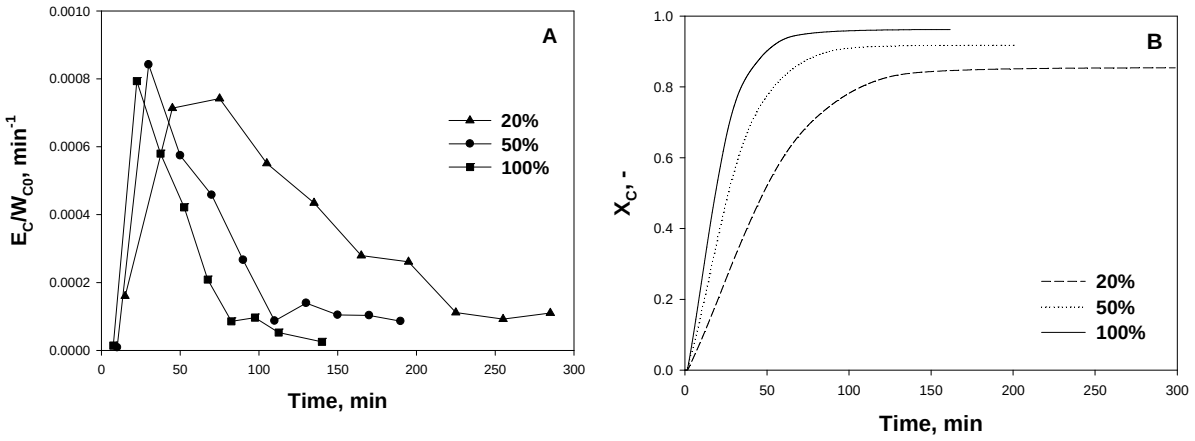

Figure 4. Results of char attrition tests under gasification conditions at three different inlet CO_2 concentrations. A: normalized elutriation rate. B: carbon conversion degree. T=900°C, U=0.4m/s.

It is well known, in fact, that the rate with respect to CO_2 concentration is approximately first order at low pressure but approaches zero order at high CO_2 partial pressures [14].

Carbon elutriation decreased at higher CO_2 concentrations. As before, at lower CO_2 concentrations the residence time in the bed during which the particles are subject to attrition increases (Table 2), and the extent of in-bed conversion of the attrited fines decreases. Also in this case the peak position shifts to longer times when the gasification rate decreases. The total carbon cumulatively elutriated during the run increased when the CO_2 concentration was decreased (Table 2). In particular, it is noted that at 20% CO_2 concentration 10% of the carbon was lost in the elutriated fines. This figure is the highest found in the present experimental campaign.

On the whole, these results show that the carbon loss by elutriation is certainly one of the critical factors during the gasification process, especially at high fluidization velocities and at low gasification rates (i.e. at low CO_2 concentration and bed temperature).

Acknowledgements

The experimental support of M. Troiano is gratefully acknowledged. S. Russo performed particle photographs.

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