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CARBON ATTRITION DURING THE FLUIDIZED COMBUSTION OF COAL

Quarterly Technical Progress Report for the Period
September 1–November 30, 1983

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Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

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SUMMARY

Batchwise fluidized bed combustion of a coal has been carried out to investigate the generation of elutriable carbon fines by attrition of the burning char. Differences between the purely mechanical attrition and the combustion assisted attrition of the char have been outlined. The time required to "activate" the char surface as regards attrition explains certain features of carbon elutriation curves. Attrition rate constants determined from these curves are compared with those previously found by continuous fluidized combustion of the same coal.

SCOPE

The generation of elutriable carbon fines in the fluidized combustion of a coal can be related to coal fragmentation, and to char attrition and combustion. Fragmentation is associated with devolatilization, and results in the break-up of coal into char particles of various sizes. Attrition is due to abrasion of these particles against bed material and the wall of the combustor, and produces fines which are rapidly entrained by the fluidizing gas because of their small size (mostly below 100 μm). Both combustion and, to a much lesser degree, attrition itself reduce char particles to sizes at which they are elutriated as unburnt residues from the bed (Beér et al., 1980). Within this framework, char attrition was successfully investigated by means of experiments of continuous fluidized bed combustion (CFBC) of a South African, bituminous, non swelling coal, continuously fed to a 140 mm ID unit (Donsi et al., 1981; Arena et al., 1983). These Authors found that under steady state conditions the attrition contribution to the elutriated carbon rate was proportional to the overall surface of char particles and to the excess of velocity above the minimum fluidizing velocity. A simple relationship of the type $E_c=k(U-U_o)W_c/\bar{d}$ was shown to hold between the elutriation rate of attrited carbon E_c, the amount of carbon in the char particles present in the bed, i.e. the bed carbon loading W_c, the average char particle size $\bar{d}$ and the fluidizing velocity excess $(U-U_o)$. The attrition rate constant k of the coal tested remained practically unvaried to changes of coal particle size, gas velocity, bed temperature, coal feed point location and air excess factor. It was significantly affected only by the size of the sand used as bed inert material.

It might be, however, that CFBC experiments are not the most suitable means for performing a detailed investigation of the attrition behaviour of any type of coal. Apart from the impossibility of separating fragmentation fines from attrition fines, continuous operation means that the measured rates of elutriated carbon integrate the contributions of attri-

ted fines from char particles whose residence times inside the bed cover the entire range from coal devolatilization to almost complete burn-out. More appropriate are batch fluidized bed combustion (BFBC) experiments which allow the separation of fragmentation and attrition effects, the time resolution of attrited fines generation, as well as the study of the influence of combustion on attrition by changing oxygen concentration in the inlet fluidizing gas. This includes the extreme case in which the bed, kept at the combustion temperature by external heating, is fluidized by inert gas so that rates of carbon fines separated from the exit gases are representative of purely mechanical attrition. This work aims at outlining the capabilities of the BFBC technique as resulted from its application to the South African coal already tested in continuous operation. The discussion of the mechanism of generation of carbon fines by attrition revealed by using this technique, and the presentation of a quick method for determining attrition rate constants based on batch combustion data, are within the scope of this work.

It should be noted that a number of works in the literature deal with the batch fluidized bed combustion of carbons and coals (Avedesian and Davidson, 1973; Borghi et al., 1977; Yates and Walker, 1978; Chakraborty and Howard, 1981; Pillai, 1981; Ross and Davidson, 1981; La Nauze and Jung, 1982). These, however, are directed to studying the role of phenomena controlling combustion, without taking into account attrition. Certainly, elutriation of attrited carbon concerns only a small proportion, mostly less than 10%, of carbon injected into the bed, but it is in fact this fraction which is of interest in the design of equipment required to make the fluidized combustion of coals efficient and environmentally acceptable.

CONCLUSIONS AND SIGNIFICANCE

The proposed BFBC technique is useful in investigating the attrition
behaviour of a coal under conditions typical of fluidized bed combustion.
Time resolution of elutriated carbon rates is high enough to separate
fragmentation from attrition effects and give details on the changes of
attrition rates during combustion. In particular, present BFBC results
definitely confirm the assumption (Arena et al., 1983) that, for the coal
in consideration, combustion and attrition of char particles inside the
bed occur in parallel. Moreover, they shed light on the enhancing effect
that combustion has on attrition. Two types of attrition have been out-
lined, depending on whether the bed is fluidized with an inert gas or an
oxygen containing gas: 1) a purely mechanical attrition, characterized
by the rapid decay of the elutriation of attrited carbon from an initial
high rate typical of angular solids to a lower stationary rate when
particles are rounded off (Vaux, 1978) and 2) a combustion assisted
attrition, where detachable asperities are continuously renewed by the
irregular movement of the combustion front. Some time is required to
fully "activate" the carbon particle surface in respect to combustion
assisted attrition. The rate of this type of attrition is broadly one
order of magnitude larger than that of purely mechanical attrition. These
phenomena combine with the progressive decrease of the surface of the
burning particle in determining the shape of attrition curves, with an
initial peak and a relative maximum located somewhere afterwards.

Working out BFBC data gives attrition rate constants k in fair agree-
ment with that previously found, as an average, for the same coal from
CFBC results (Donsì et al., 1981; Arena et al., 1983). In particular, the
relationship $E_c=k(U-U_o)W_c/\bar{d}$ holding for these results can be extended to
BFBC data in the form $e_c=k(U-U_o)w_c/\bar{d}$, where e_c, w_c and $\bar{d}$ are, respectively,
the instantaneous elutriated carbon rate, bed carbon loading and char
particle average size. A rapid procedure for determining k is based on the
regression straight line correlating data points of these variables collect-

ed at different times in a single BFBC run. This further confirms the usefulness of BFBC experiments as regards testing char attrition in fluidized combustion of coals. These experiments can be carried out rapidly and with small scale apparatus, and are therefore suitable for developing into a standard technique to compare different coals and evaluate attrition rate constants to be embodied in model calculations. A limit in scaling down the testing apparatus derives from the size of coal and bed material being considered. For given sizes, the diameter of the combustor should be sufficiently large to ensure thorough mixing of coal inside the fluidized bed solids.

EXPERIMENTAL

Materials

The coal used in this work is the South African, bituminous, non swelling coal whose attrition behavior has already been studied by means of CFBC experiments by Donsì et al. (1981) and Arena et al. (1983). The properties of the coal were reported in detail by these latter Authors. In particular, coal contents of fixed carbon, volatile matter and ash are about 60, 25 and 15%, respectively. Alternatively, char of the same coal, separately prepared in a fluidized bed at the temperature at which the attrition experiment is performed, has been used for comparison in some runs. Particle sizes of batches of coal and char tested are given in Table 1. Distributions of particle size of char formed inside the bed by fragmentation when using the various batches of coal are also given together with devolatilization times in this table. Batches of char did not show further fragmentation when injected into the bed. 0.4-0.3 mm sand was used as bed solids. Unexpanded bed height was about 100 mm.

Experimental apparatus and technique

The BFBC technique adopted for determining the rate of generation of carbon fines by fragmentation and attrition is based on the measurement of the rate of carbon fines elutriated from the bed and collected down-stream the combustor at given times after injecting a batch of coal (or char) into the bed. Attrition fines are generated throughout the combustion time of the batch from injection to burn-out; fragmentation fines only during the small fraction of time from injection to the end of devolatilization, and only when coal is used. An apparatus, consisting of a 40 mm ID and 1 m high combustor with two-exit head was specificly developed for these experiments. Carbon elutriation rates were supplemented with particle size distributions and carbon contents of the char present in the bed. These were obtained in parallel experiments with another combustor also of 40 mm ID but equipped with a basket made of a 0.6 mm opening net to allow the collection of char from the bed according to the

Andrei (1979) technique. The two-exit head combustor and the basket equip-ped combustor are presented in Figs. 1-I and II, respectively. Details about design and operation of these combustors are given elsewhere (Chirone et al., 1982). Only their main features are briefly described in the following.

The two-exit head combustor is operated by means of the three-way ball valve (11) in Fig. 1-I. The proper position of this valve allows the collection of fines in the filter connected to one of the exits during the substitution of the other filter. The connection is alternatively made with the two exits. Using several filters in sequence, carbon emission within the combustion time after coal (or char) has been charged into the bed through the hopper (5) could be conveniently time resolved. To keep oxidizing conditions substantially uniform during the combustion time , batches of only 3.4 g of coal (or 2.5 g of char) were used in each run , corresponding to the same amount w_{ci} of 2.0 g of fixed carbon charged into the bed. For given experimental conditions, operation was repeated with various batches of coal (or char) of the same size to allow, in each filter, the accumulation of an amount of fines large enough to make weighing and chemical analysis reliable. Knowing the amount of carbon collected in a given time interval of the combustion cycle and the number of repeated cycles, an instantaneous carbon elutriation rate e_c could be determined and assigned at the mean point of the time interval in consideration. To minimize post-combustion of carbon fines, the temperature in the freeboard was kept as low as possible by limiting the thermal insulation of the combustor only to a height equal to bed height. Neglecting post-combustion inside the bed and in the freeboard implies assuming that the rates of generation of carbon fines in the bed were equal to the rates of collection of carbon fines in the filters. At bed temperature of 850°C, the latter was up to 30% smaller, depending on the size of fines and oxygen concentration in inlet gas. This was shown by the results of a separate investigation carried out by measuring the degree of combustion

of carbon fines continuously fed to the bed of the combustor repor-
ted in Fig. 1-I. For given experimental conditions, burn-out time t_{bo}
was determined as the time at which CO_2 concentration dropped to zero
in exit gases. Known w_{ci} and the amount of carbon which had left the
combustor at a given time as CO_2 and CO, the bed carbon loading w_c, i.e.
the amount of carbon still present inside the bed at that time, could be
calculated.

The basket equipped combustor is operated by means of the basket
holder (1) in Fig. 1-II. It is moved up and down along the guide (2) and
pivoted around the axis (8) in order to locate the basket in the bed,
pull it out and discharge collected solids. Batches of coal (or char),
again 3.4 g (or 2.5 g), are injected in the bed and left there for a
given time, until combustion is interrupted by switching fluidizing gas
from the oxygen-nitrogen mixture to nitrogen. Char present in the bed at
that time is collected with the basket. Nitrogen issuing from a channel
between the basket holder and an outer tubing quenches the char and pre-
vents its further burning in the atmosphere. Weighing, sieving and ana-
lyzing the collected material for carbon content allows evaluation at
any time between coal (or char) injection and burn-out of: 1) the mass
fraction C of carbon in the char, ii) the bed carbon loading w_c, i.e.
the amount of carbon in the char particles found in the bed, and iii) the
fraction X_d of bed carbon contained in the char particle of size d and
the surface based average bed char particle size $\bar{d}=1/\sum X_d/d$. In parti-
cular, measurements on material collected at the end of devolatilization
time of each batch of coal gave the initial mass fraction C_i of carbon
and the initial distribution and average particle size $\bar{d}_i$ of the fragment-
ed coal reported in Table 1. The lower limit of this distribution reflects
the fact that only fragmented char coarser than 0.6 mm, i.e. coarser than
the net opening, could be collected with the basket. The amount of finer
fragments, however, accounted for less than 0.5% of w_{ci} as proved by
burning the amount of carbon left in the bed. Note that the initial size

distribution of fragmented coal was not affected by whether nitrogen or an oxygen-nitrogen mixture was used as fluidizing gas. Values of w_c determined with the basket technique and from gas analysis using the combustor of Fig. 1-I were equal to each other within an error of 3%.

Oxygen concentration in inlet gas, fluidizing velocities, and bed temperatures at which BFBC experiments were carried out are listed in Table 1. Differences between oxygen concentration in inlet and outlet gas changed during the combustion cycle from a maximum occurring soon after injecting coal (or char) into the bed to zero at $t=t_{bo}$. For given oxygen concentration in inlet gas, typical values of the minimum oxygen concentration in outlet gas are also reported in the table.

Unfortunately, investigation with bed sands of size coarser than 0.4 mm was impossible because these sands enhanced the set-up of piston-like fluidizations in the 40 mm ID combustor. This, in turn, determined severe segregations of char on the top of the bed. Moreover, it was unpractical to extend the experimental range of fluidizing gas velocities. Due to the limited free board height, the proportion of elutriated char particles coarser than d^*, the size of particles whose free fall velocity is equal to the gas velocity at the combustor exit, significantly increased at gas velocities above 110 cm s^{-1}. This made the evaluation of rates of generation of attrition fines from measured rates of carbon collected at the filters unreliable. Values of d* at the three levels of gas velocities tested are given in Table 1. Both these experimental limitations might be overcome by means of combustors of size larger than those used, but at the expense of some complication in experimental installations and procedures.

The granulometric analysis of carbon fines collected in the filters of the combustor of Fig. 1-I was made for one of the experimental conditions tested. The photographic technique used permitted to distinguish between ash and char of particle size as low as 3 μm.

EXPERIMENTAL RESULTS

The generation of elutriable carbon fines, i.e. of carbon particles finer than d*, is associated to fragmentation, which in turn depends on devolatilization, and to attrition. Devolatilization and fragmentation are not expected to occur when injecting char directly into the bed. Therefore, the differences in the amounts of carbon collected at the filters of the combustor of Fig. 1-I throughout the devolatilization time when charging coal and char, all other conditions remaining the same, account for the contribution of fragmentation fines. These differences are of about 10^{-3} g, i.e. less than 0.1% of fixed carbon w_{ci} charged into the bed. This confirms the negligible tendency of the coal tested to produce fragmentation fines during devolatilization.

Whatever the experimental conditions, carbon dioxide and carbon fines are simultaneously found throughout the time interval between injection and burn-out at the combustor exit. This is in agreement with the model suggested by Arena et al. (1983) which considers attrition as a side process of fluidized bed combustion. The yield in attrited carbon, however, is small, being at most about 10% of w_{ci} at low inlet oxygen concentration in fluidizing gas.

Following these general conclusions, average particle sizes and carbon contents of bed char obtained by means of the basket equipped combustor and instantaneous elutriation rates of attrited carbon, correspondingly obtained by means of the two-exit head combustor, will be presented and discussed separately. The whole data will be subsequently combined in testing attrition rate equations.

Char shrinkage curves

The progress of shrinkage of char particles is expressed in terms of the ratio $\bar{d}/\bar{d}_i$ of the actual average char size $\bar{d}$ to the initial average size $\bar{d}_i$ as a function of the fractional conversion $\zeta = (w_{ci} - w_c)/w_{ci}$ of fixed carbon injected into the bed (Fig. 2) and of

the ratio t/t_{bo} of the time t after injection to the burn-out time t_{bo}
(Fig. 3). Average sizes $\bar{d}_i$ are given in Table 1; burn-out times
t_{bo} in Table 2. Then, known w_{ci}, $\bar{d}_i$ and t_{bo}, values of w_c and $\bar{d}$ to be
used in attrition rate equations can be obtained from Figs. 2 and 3 at
any time for each experimental condition tested. The carbon contents C
of the char particles at time t after injection are reported as a function
of t/t_{bo} in Fig. 4.

Data in Figs. 2,3 and 4 are respectively compared with the follow-
ing expressions

$$\frac{\bar{d}}{\bar{d}_i} = (1 - \xi)^{1/3} \tag{1}$$

$$\frac{\bar{d}}{\bar{d}_i} = (1 - \frac{t}{t_{bo}})^{2/3} \tag{2}$$

$$C = C_i \tag{3}$$

derived from a carbon balance around the particle (Eqs. 1 and 3), and
between the particle and surrounding gas (Eq. 2).

In this latter equation C_i is the average initial carbon content of devo-
latilized coal. Equations 1 and 3 imply that conversion takes place at
constant mass fraction of carbon in the char, i.e. that the shrinking
particle model applies (Levenspiel, 1972; La Nauze and Jung, 1982; Jung
and La Nauze, 1983). Equation 2 assumes that, considering the coarse
size of particles over a large fraction of the time interval from inject-
ion to burn-out, the rate-controlling step is oxygen diffusion to carbon
(Levenspiel, 1972). Char shrinkages and carbon contents are approximately
represented by these equations for the majority of experimental conditions
tested. Note, however, that the validity of the shrinking particle model
described by Eqs. 1 and 3 refers to the behavior of the particle in its
entirity. Actually, oxygen somewhat penetrates inside the particle, de-
pending on the size of the pore, particle temperature and oxygen concen-
tration for reaction kinetics order different from one. In the average,

such penetration is likely to be small, but it is in fact the mechanical
structure of the cortical region of the particle which affects attrition.
In any case, consistently with the shrinking particle model, the instant-
aneous removal of ash from this region has been assumed.

Attrition curves

Influence of combustion on attrition. Curves of instantaneous elutriation
rates in Fig. 5 describe some features of char attrition under inert and
oxidizing conditions. Without oxygen, the e_c vs t curve (black circles) is
that typical of purely mechanical attrition of angular solids in fluidized
beds (Vaux, 1978). The peak value e_{ci} at t=0 is the initial attrition re-
lated to the detachment of asperities from the char surface. Rounding off
surface irregularities results in the decay of elutriation rate to a low
value of e_c after about 30 min of operation. Further decrease of e_c asso-
ciated with the reduction of exposed particle surface is very slow, due to
the long time required to significantly change particle size only by attri-
tion. A peak value e_{ci} is also found with 4.5% O_2 in fluidizing gas (open
circles of curve A), but in this case, after a temporary decay, e_c increases
rapidly again. It reaches a maximum e_c' at t=t' and eventually declines
slowly to reach zero at 60 min, which is the burn-out time t_{bo} of char
under the conditions tested. The maximum e_c', recently found in the attrition
curves of a number of other coals (Massimilla et al., 1983), may derive
from the opposite effects of two phenomena developing during the combustion
of the char particle: 1) the uneven progress of the combustion front,
which results in the generation and growing of detachable asperities and
2) the reduction of the surface of the burning particle, which reduces the
total number of asperities available for detachment. The "activation" of
char surface in respect to attrition induced by combustion was ascertained
by means of an experiment whose results are also shown in Fig. 5 (open
circles of curve B). At t=60 min, when the low value of e_c under inert
conditions had been reached, fluidizing gas was suddenly switched from
nitrogen to an oxygen-nitrogen mixture with 4.5% O_2. Combustion was respon-
sible for the rapid increase of e_c in this case. But apart from the initial

attrition which had been suppressed in the curve B by the pre-treatment of the char, the e_c vs t curves A and B are exactly the same.

Note that the rate of combustion assisted attrition is much larger than that of purely mechanical attrition. With reference to the left side of Fig. 5, e_c averaged over the 60 min between injection and burn-out is in the first case (open circles) about 5 times greater than in the second (black circles). A conceptual representation of purely mechanical and combustion assisted attrition is shown in Fig. 6.

Attrition curve shape and characteristic points. Attrition curves from experiments at 850°C and fluidizing velocity of 80 cm s^{-1} with 6.35-4.76 mm char and coal are respectively reported in Figs. 7 and 8. Changing from char to coal does not result in differences in the elutriation curve except as regards the effects of coal fragmentation fines on the initial peak value e_{ci} at t=0. Particle size distributions of carbon fines collected at various times for the run with coal feed and 4.5% O_2 in inlet gas are presented in Fig. 9. The distributions are expressed on numerical basis due to the difficulties of assigning a carbon density to relatively coarse char fines ($>$ 100 μm) whose micrographs present substantial intraparticle voids. These coarser particles, collected in larger proportion in the first minutes after injection, are probably the fragmentation fines or their unburnt residues.

Attrition curves similar to those of Fig. 8 are obtained feeding 4.76-4.00 and 9.00-6.35 mm coal (Fig. 10). The presence of the maximum e'_c depends on the severity of oxidation conditions as determined by both bed temperature and oxygen concentration in inlet gas. As shown in Fig. 11, at 750°C e'_c occurs at 2.5 min for 21% O_2 in fluidizing gas. At 850°C and the same oxygen concentration this maximum disappears. On the other hand, the values of e_c and the shape itself of the attrition curve at 950°C and 4.5% O_2 might have been influenced by significant post-combustion of attrited carbon under these conditions.

Table 2 gives the characteristic values of attrition curves for all the experimental conditions tested, namely: e_{ci}, e_c', the time t' at which e_c' appears, the carbon loading w_c' at t', the fraction $(w_{ci}-w_c')/w_{ci}$ burnt at t'. The fraction of unburnt carbon elutriated as attrited fines is related to carbon combustion efficiency η by the relationship:

$$1-\eta = \int_0^{t_{bo}} \frac{e_c}{w_{ci}}\, dt \qquad (4)$$

The losses of combustion efficiency $(1-\eta)$ due to char attrition are also reported in the table.

It is worth noting that for given coal feed size both t_{bo} and $(1-\eta)$ increase as oxygen concentration in inlet gas and bed temperature decrease. This is in accordance with the fact that, as observed by D'Amore et al. (1980), attrition being a side phenomenon in respect to combustion, the longer the burn-out time, the higher the loss of attrited carbon entrained in exit gas. $(O_2)_{in}$ less than 0.75% would result in $(1-\eta)$ larger than 0.108 , being as a limit case $1-\eta=1$ for 0% O_2. Results of present work suggest, however, that exposure time of the char particle in the bed is not the only variable determining the overall carbon elutriation by attrition. The amount of material effectively detached per each collision between the char particle and bed solids might also be important. For instance, the loss of combustion efficiency due to attrited carbon in experiments with 0.75% O_2 over the long exposure time of 360 min (Table 2) though high could have been somewhat limited by the low concentration of surface asperities. It is in fact possible that the conditions of the char surface in such a run were similar to those described in Fig. 6 for purely mechanical attrition.

ATTRITION RATE

Evaluation of rate equation constants

The attrition model is based on the assumption that the instantaneous rate of carbon fines detached from an individual char particle is proportional to the exposed surface as well as to the excess of gas velocity U above the minimum for fluidization U_o (Donsì et al., 1981). A similar assumption as regards the influence of fluidizing velocity was made by Merrick and Highley (1974) in their study on attrition of coal ashes in a fluidized bed combustor. With the further hypothesis that the shrinking particle model applies, the rate of loss of carbon by attrition experienced by a spherical char particle of diameter d is

$$\left(- \rho_c \frac{\pi}{6} \frac{dd^3}{dt}\right)_a = k'_a (U-U_o) \pi d^2 \tag{5}$$

where ρ_c is the carbon density of the char particle, i.e. the mass of carbon per unit particle volume, and k'_a is the attrition rate constant of the char. From Eq. 5 the attrition contribution to the shrinkage rate of the particle is obtained

$$\left(- \frac{dd}{dt}\right)_a = k_a (U-U_o) \tag{6}$$

in which

$$k_a = \frac{2 k'_a}{\rho_c} \tag{7}$$

Considering both diffusional and chemical kinetics control, and assuming complete mixing of gas in the particulate phase, first order reaction and conversion of carbon to CO_2, the combustion contribution to the shrinkage of the char particle is

$$\left(- \frac{dd}{dt}\right)_c = \frac{c_p}{\frac{d \rho_c}{2M_c Sh D_g} + \frac{\rho_c}{2M_c k_s}} \tag{8}$$

where c_p is the oxygen concentration in the particulate phase, ρ_c/M_c the carbon molar density of the char particle, Sh the particle Sherwood number, D_g the oxygen diffusivity and k_s the reaction rate constant at the particle effective temperature (Donsì et al., 1979). The overall shrinkage rate is

$$- \frac{dd}{dt} = (- \frac{dd}{dt})_c + (- \frac{dd}{dt})_a \tag{9}$$

which enters in the population balance equation of char particles in modelling a continuous fluidized bed combustor (Kunii and Levenspiel, 1969).

Taking into account Eq. 5, the elutriation rate E_c of attrited carbon from a continuous combustor is obtained by integrating the attrition contribution from all the char particles to be found in the bed at different stages from coal devolatilization to almost burn-out. If k'_a is the same for all the particles, i.e. if k'_a remains unchanged as each particle shrinks from its original size d_i to the elutriable size $d*$, it is

$$E_c = k'_a \pi (U-U_o) \int_{d*}^{d_i} d^2 P(d)dd \tag{10}$$

$P(d)$ being the bed char particle size distribution on a numerical basis. On the other hand, the overall bed char exposed surface $\pi \int_{d*}^{d_i} d^2 P(d)dd$ can be expressed as a function of bed carbon loading W_c and surface based average particle size $\bar{d}$. It is in fact

$$\bar{d} = \frac{1}{\int_{d*}^{d_i} \frac{P_w(d)dd}{d}} \tag{11}$$

where the size distribution on weight basis $P_w(d)$ is related to $P(d)$ and W_c by the relationship

$$P_w(d) = \frac{\frac{\pi}{6} \rho_c d^3 P(d)}{W_c} \tag{12}$$

Substituting between Eqs (10),(11) and (12), and putting

$$k = \frac{6k'_a}{\rho_c} \tag{13}$$

gives

$$k = \frac{E_c}{(U-U_o)\frac{W_c}{\bar{d}}} \tag{14}$$

Attrition rate constants were determined by Donsì et al. (1981) and Arena et al. (1983)by entering into this relationship with the values of the attrited carbon rates E_c, carbon loading W_c and average char particle size $\bar{d}$ from CFBC experiments and determining k as the slope of a regression straightline in the diagram E_c vs $(U-U_o)\frac{W_c}{\bar{d}}$. The value of k was invariable to changes in most operating conditions. Significant variations were only found when changing bed solids size. In particular, in view of further comparison with results from BFBC experiments, the value of k relative to all the runs with 0.2-0.4 mm sand for the entire experimental range of oxygen concentration in outlet gas $(0.5 < (O_2\%)_{out} < 7)$ is given in Table 3 together with values of k determined for sets of runs characterized by narrower ranges of $(O_2\%)_{out}$.

Although the e_c vs t curves from BFBC experiments fully describe the attrition behavior of the char in consideration, their use in predicting carbon loss by attrition from a continuous combustor is not straightforward even under the simplifying assumptions that coal feed is narrow size and

that fragmentation is negligible. In this case, if N is the number of coal particles used in the BFBC experiments, the instantaneous rate of attrited carbon lost by each char particle $(-\rho_c \frac{\pi}{6} \frac{dd^3}{dt})_a$ is $\frac{e_c(t)}{N}$, which can be converted into $\frac{e_c(d)}{N}$ due to the biunivocal relationship between t and d given by the char shrinkage curve. This leads to the equation for the rate of attrited carbon loss from the continuous combustor

$$E_c = \int_{d^*}^{d_i} \frac{e_c(d)}{N} P(d)dd \qquad (15)$$

Such equation is the counterpart of Eq. 10 used in working out results from CFBC experiments, but is difficult to handle because of the lack of knowledge on the size distribution P(d) of the char particles to be found in the bed. On the other hand, P(d) cannot be calculated separately because it is related within the char particle population balance equation to combustion and attrition itself through the shrinkage rates respectively given by Eqs. 8 and 6. These difficulties and, in particular, those arising when extending this procedure to multisize feed and fragmentable coal discourage the direct use of attrition curves in design application.

Alternatively, char shrinkage and attrition curves from BFBC experiments can be worked out together to give attrition rate constants defined, in similarity with Eq.14 , as $e_c/((U-U_o)w_c/\bar{d})$.Their averages over t_{bo}

$$k = \frac{\int_o^{t_{bo}} \frac{e_c}{(U-U_o)w_c/\bar{d}} dt}{t_{bo}} \qquad (16)$$

are given in Table 3 for the various BFBC runs. Inspection of data indicates that $e_c/((U-U_o)w_c/\bar{d})$ in Eq. 16 becomes practically constant at $t \geqslant t'$, so that an approximated value of k can be expressed within the time

interval $(t_{bo}-t')$ by means of the relationship

$$k = \frac{e_c}{(U-U_o) \dfrac{w_c}{\bar{d}}} \qquad (17)$$

The attrition rate constant is determined in this case as the slope of regression straight lines in the diagram e_c vs $(U-U_o) \dfrac{w_c}{\bar{d}}$ as shown in Fig. 12 and 13 for experiments with char and coal respectively. Data points in these figures are obtained by directly using the experimental values of e_c in the attrition curves, whereas w_c and $\bar{d}$ are the values interpolated in w_c vs t and $\bar{d}$ vs t curves at the corresponding times. Attrition rate constants k obtained by working out BFBC results according to this procedure are also given in Table 3.

The comparison between the various values of k shows the soundness of the BFBC technique in the characterization of the attrition behavior of the coal. In particular, the simple procedure based on data collected at t $\geqslant$ t' and use of Eq. 17 gives k which are in reasonable agreement with the value $1.86.10^{-7}$ given for the same coal and bed solids by Arena et al. (1983) as an average from results of CFBC experiments. The confidence range with which this attrition rate constant was given includes the majority of the values of k from BFBC experiments. The deviations found for runs at bed temperatures of 750° and 950°C and, to a lesser extent, at 50 and 110 cm·s^{-1} might reflect side effects, not yet completely clarified, related to changes in the degree of post-combustion of fines detached from char particles or in the features of attrition themselves. Differences in the degree of post-combustion might also explain the moderate increase of k found with 6.35-4.76 mm coal, at 850°C and 80 cm s^{-1} as $(O_2 \%)_{in}$ is reduced from 21 to 2.9. For further reduction from 2.9 to 0.75, k decreases from $2.14.10^{-7}$ to $0.86.10^{-7}$, to become $0.13.10^{-7}$ when fluidizing with nitrogen. This tendency which might be interpreted as the switching from the combustion assisted to the purely mechanical

attrition, does not immediately fit with k from CFBC data at different
oxygen concentration in exit gases. As shown in Table 3, these values of
k are very close to the average $1.86.10^{-7}$ for all the $(O_2\%)_{out}$. Had the
carbon been burnt inside the particulate phase and gas been completely
mixed in such phase, values of k from CFBC data at low $(O_2\%)_{out}$ should
have been comparable to those from BFBC experiments at low inlet (and
outlet) $O_2\%$. The discrepancy might depend on the fact that gas was not
thoroughly mixed in the particulate phase and that a substantial fraction
of carbon burned in the vicinity of the oxygen rich gas bubbles in CFBC
experiments. It should be finally noted that the reasonable agreement
between k determined by working out BFBC data according to Eqs. 16 or 17
reflects the limited generation of fines occurring during the fragmentation
of the coal tested and the relatively short time required to activate the
combustion assisted attrition. For other coals using Eq. 16 might result
more appropriate.

Application to design

The characterization of the attrition behavior of the coal from BFBC
experiments is conveniently made by evaluating the attrition rate constant
k. Using Eqs. 7 and 13, k is converted into k'_a and k_a, both required in
Eq. 10 for calculating the elutriation rate E_c of attrited carbon from a
continuous combustor. The value of k'_a enters directly into this equation;
that of k_a indirectly through the attrition contribution (Eq. 6) to the overall
char particle shrinkage rate (dd/dt). This in turn enters in the population
balance equation of char particles which determines P(d).

In this connection, it should be noted that attrition contribution to
(dd/dt) in Eq. 9 is small, being, in general, $(dd/dt)_a/(dd/dt)$ less than
0.1. The error induced on P(d) can be therefore strongly affected by the
uncertainties associated with the calculation of $(dd/dt)_c$, namely, by the
degree of gas mixing to be assumed in the particulate phase or, in the
case of complete mixing, by the oxygen concentration c_p in such phase. As

suggested by Eq. 10, uncertainties in P(d) directly propagate into E_c so that the occurrence of a poor contact between gas and solid inside the bed might result in elutriation rates of attrited carbon much higher than predicted even when a correct value of k is used. This fact should be taken into account when testing models for attrited carbon loss from fluidized bed combustors against results of operating units.

Finally, it should be borne in mind that values of k have been obtained from BFBC experiments intentionally designed to minimize post-combustion of carbon fines in the free board. Allowance for this effect must be made in model calculations of elutriation rates of attrited carbon from fluidized bed combustors where such conditions are not verified.

c_p = oxygen concentration in the particulate phase of the fluidized bed

C = mass fraction of carbon in the char

C_i = initial mass fraction of carbon in the char

$d, \bar{d}$ = particle and surface based average particle size of char in the bed

$d_i, \bar{d}_i$ = feed coal (or char) particle and initial surface based average particle size of char in the bed

$d*$ = size of the shrunken char particle with terminal velocity equal to gas velocity at the freeboard outlet temperature

D_g = oxygen diffusivity

e_c = instantaneous carbon elutriation (and attrition) rate in BFBC experiments

e_{ci} = initial carbon elutriation rate

e'_c = relative maximum of the carbon attrition curve at $t > 0$

E_c = carbon attrition rate in CFBC experiments

k, k_a, k'_a = char attrition constants

k_s = carbon reaction rate constant

M_c = carbon atomic weight

N = number of char particles in the bed

$P(d)$ = bed carbon particle size distribution on a numerical basis in CFBC experiments

$P_w(d)$ = bed carbon particle size distribution on a weight basis in CFBC experiments

Sh = char particle Sherwood number

t = time

t' = time at which e'_c occurs

t_{bo} = burn-out time

T = bed temperature

U = fluidizing gas superficial velocity at bed temperature

U_o = minimum fluidizing gas superficial velocity at bed temperature

w_c = bed carbon loading in BFBC experiments

w_{ci} = initial bed carbon loading

w'_c = bed carbon loading at t'

W_c = bed carbon loading in CFBC experiments

X_d = mass fraction of char particles of size d

X_{di} = mass fraction of char particles of size d at the end of coal devo-
latilization

η = carbon combustion efficiency

ζ = degree of conversion of injected carbon

ρ_c = carbon density of the char particle

LITERATURE CITED

Andrei, M., "Time Resolved Burnout in the Combustion of Coal Particles in
    Fluidized Bed",S.M. Thesis in Chem.Eng., MIT, Cambridge, MA, (1979)

Arena, U., M. D'Amore, and L. Massimilla, "Carbon Attrition During the
    Fluidized Combustion of a Coal", AIChE Journal, 29, 40 (1983)

Avedesian, M.M., and J.F. Davidson, "Combustion of Carbon Particles in a
    Fluidized Bed", Trans.Instn.Chem. Engrs., 51, 121 (1973)

Beér, J.M., L. Massimilla, and A.F. Sarofim, "Fluidized Coal Combustion:
    the Effect of Coal Type on Carbon Load and Carbon Elutriation", Interna-
    tional Conference on Fluidised Combustion. Systems and Applications,
    Institute of Energy Symp. Ser. No 4, IV-5-1, London,(1980)

Borghi,G.G.,A.F. Sarofim, and J.M. Beér, "A Model of Coal Devolatilization
    and Combustion in Fluidized Beds", AIChE 70th Annual Meeting, New York,
    November, 1977

Chakraborty, R.K.,and J.R. Howard, "Combustion of Single Carbon Particles
    in Fluidized Beds of High-Density Alumina", Journal of the Institute
    of Energy, 55, March (1981)

Chirone, R., A. Cammarota, M. D'Amore, and L. Massimilla, "Fragmentation
    and Attrition in the Fluidized Combustion of a Coal", Proc. of 7th
    International Conference on Fluidized Bed Combustion, U.S. Department
    of Energy, Washington D.C., 1023 (1982)

D'Amore, M., G. Donsi, and L. Massimilla, "Bed Carbon Loading and Particle
    Size Distribution in Fluidized Combustion of Fuels of Various Reacti-
    vity", Proc. of 6th International Conference of Fluidized Bed Combustion,
    U.S. Department of Energy, Washington D.C., 675 (1980)

Donsi,G.,L.Massimilla,M.Miccio,G.Russo,and P.Stecconi,"The Calculation of
    Carbon Load and Axial Profiles of Oxygen Concentration in the Bed of
    a Fluidized Combustor", Combustion Science and Technology, 21, 25 (1979)

Donsi, G., L. Massimilla, and M. Miccio, "Carbon Fines Production and
    Elutriation from the Bed of a Fluidized Coal Combustor", Combustion
    and Flame, 41, 57 (1981)

Jung, K., and R.D. La Nauze, "Sherwood Numbers for Burning Particles in Fluidized Beds", in Fluidization IV, 4th International Conference on Fluidization, Kashikojima, Japan, 6.3.1 (1983)

Kunii, D., and O. Levenspiel, "Fluidization Engineering", J.W. Wiley, New York (1969)

La Nauze, R.D.,and K. Jung,"The Kinetics of Combustion of Petroleum Coke Particles in a Fluidized-Bed Combustor", Proc. of 19th Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh Pa., 1087 (1982)

Levenspiel, O., "Chemical Reaction Engineering", J.W. Wiley, New York, (1972)

Massimilla, L., L. Borriello, A. Cammarota, R. Chirone, and A. Mazza, "Carbon Attrition During the Fluidized Combustion and Gasification of Coal", DOE Quarterly Technical Report No. DOE/PC40796-7, U.S. Department of Energy, Washington D.C. (1983)

Merrick, D., and J. Highley, "Particle Size Reduction and Elutriation in a Fluidized Bed Process", AIChE Symp. Ser., No 137, Vol.70,366 (1974)

Pillai, K.K., "The Influence of Coal Type on Devolatilization and Combustion in Fluidized Beds", Journal of the Institute of Energy, 142, September (1981)

Ross, I.B., J.F. Davidson, "The Combustion of Carbon Particles in a Fluidised Bed", Trans.Instn. Chem. Engrs., 59, 108 (1981)

Vaux, W.G., "Attrition of Particles in the Bubbling Zone of a Fluidized Bed", Proc.of the American Power Conference, Vol.40,793 (1978)

Yates, J.G.,and P.R. Walker, "Particle Temperatures in a Fluidi ed Bed Combustor", in J.F. Davidson and D.L. Keairns "Fluidization", Cambridge University Press (1978)

TABLE 1. - EXPERIMENTAL CONDITIONS

Operative Variables of the Combustors

Bed temperature, °C	750,850,950
Fluidizing velocity, cm s^{-1}	50 (d*=120 μm), 80 (d*=179 μm), 110 (d*=200 μm)
O_2% in inlet and outlet gas (*)	0, 0.75(0.58), 1.4(1.1), 2.9(2.2), 4.5(3.5), 21(16.7)

Size Distribution of the Batches of Coal and Char Tested

Coal feed

Feed size d_i,mm	Devolatilization time t_{dev}, s	Char from coal fragmentation d_i,mm	X_{di},%	$\bar{d_i}$,mm
4.76-4.00	20	4.76-4.00	92.26	4.25
		4.00-3.00	6.80	
		3.00-2.00	0.54	
		2.00-0.60	0.40	
6.35-4.76	25	6.35-4.76	85.64	4.84
		4.76-4.00	5.54	
		4.00-3.00	4.23	
		3.00-2.00	2.11	
		2.00-0.60	2.48	
9.00-6.25	30	9.00-6.35	54.02	5.36
		6.35-4.76	28.62	
		4.76-4.00	5.21	
		4.00-3.00	6.51	
		3.00-2.00	2.45	
		2.00-0.60	3.19	

Char feed

d_i, mm	$\bar{d_i}$, mm
6.35-4.76	5.56

(*)O_2% in outlet gas (in parenthesis) is the minimum oxygen concentration read at the analyzer during the combustion of the batch of coal.

TABLE 2.- CHARACTERISTIC VALUES OF ATTRITION CURVES

Coal feed

d_i mm	U cms^{-1}	T °C	$(O_2)_{in}$ %	t' min	t_{bo} min	e_{ci} 10^{-3}gmin^{-1}	e'_c	w'_c g	$\dfrac{w_{ci}-w'_c}{w_{ci}}$	$1-\eta$
4.76-4.00	80	850	4.5	4.5	46	2.2	2.9	1.54	0.25	0.029
6.35-4.76	50	850	4.5	10.0	68	3.7	1.2	1.38	0.32	0.021
6.35-4.76	80	750	21	2.2	18	6.6	4.7	1.35	0.34	0.010
6.35-4.76	80	750	4.5	7.2	68	13.4	3.5	1.44	0.29	0.063
6.35-4.76	80	850	21	-	15	6.7	-	--	--	0.010
6.35-4.76	80	850	4.5	6.8	56	3.8	2.9	1.44	0.29	0.037
6.35-4.76	80	850	2.9	10.8	84	5.6	2.7	1.54	0.25	0.056
6.35-4.76	80	850	1.4	18.3	160	7.6	1.6	1.60	0.22	0.061
6.35-4.76	80	850	0.75	32.8	360	9.0	1.4	1.53	0.25	0.108
6.35-4.76	80	850	0	--	-	3.4	-	--	--	1
6.35-4.76	80	950	4.5	2.5	54	4.0	1.3	1.80	0.12	0.019
6.35-4.76	110	850	4.5	5.9	52	12.2	4.6	1.46	0.29	0.054
9.00-6.35	80	850	4.5	5.7	68	3.0	2.8	1.66	0.19	0.043

Char feed

d_i mm	U cms^{-1}	T °C	$(O_2)_{in}$ %	t' min	t_{bo} min	e_{ci} 10^{-3}gmin^{-1}	e'_c	w'_c g	$\dfrac{w_{ci}-w'_c}{w_{ci}}$	$1-\eta$
6.35-4.76	80	850	21	2.5	18	1.8	2.2	1.28	0.37	0.007
6.35-4.76	80	850	4.5	6.8	60	2.3	2.9	1.52	0.25	0.037
6.35-4.76	80	850	1.4	20.2	160	4.9	1.5	1.50	0.27	0.058
6.35-4.76	80	850	0	--	-	2.9	=	--	--	1

TABLE 3.- EVALUATION OF THE ATTRITION RATE CONSTANTS OF THE COAL TESTED FROM RESULTS OF CFBC AND BFBC EXPERIMENTS.

		Feed size mm	Bed sand size, mm	U,cm s^{-1}	T, °C	O_2, % Inlet	Outlet	$k \cdot 10^7$ from Eq. (14)	(16)	(17)
based on CFBC data	coal	1-0.4;3-1 6-3 ;9-6	0.4-0.2	80-160 80-160 80-160 80-160	650-950 650-950 750-950 650-950	21 21 21 21	0.5-7 0.5-1 1-3 3-7	1.86 1.82 2.05 1.88		
based on BFBC data	char	6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76	0.4-0.3	80 80 80 80	850 850 850 850	21 4.5 1.4 0	16.8 -21 3.6 - 4.5 1.1 - 1.4 0		1.44 1.33 1.28 --	1.84 2.02 1.17 0.18
	coal	4.76-4.00 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 6.35-4.76 9.00-6.35	0.4-0.3	80 50 80 80 80 80 80 80 80 80 80 110 80	850 850 750 750 850 850 850 850 850 850 950 850 850	4.5 4.5 21 4.5 21 4.5 2.9 1.4 0.75 0 4.5 4.5 4.5	3.2 - 4.5 3.6 - 4.5 17.3 -21 3.5 - 4.5 16.7 -21 3.5 - 4.5 2.2 - 2.9 1.1 - 1.4 0.58- 0.75 0 3.3 - 4.5 3.3 - 4.5 3.7 - 4.5		1.99 1.38 3.25 2.77 1.90 2.30 2.69 0.76 0.78 -- 1.09 2.10 2.60	1.82 1.30 3.52 2.41 1.81 2.07 2.14 1.02 0.86 0.13 0.86 2.26 2.28

Figure 1-I. Fluidized bed two-exit head combustor used
in attrition experiments.
A) The apparatus. 1) Air preheater; 2a and
2b) Electric furnaces; 3) Fluidization
column; 4) Two-exit head; 5) Hopper; 6a
and 6b) Flue gases filters; 7) Pump; 8)
O_2, CO, CO_2 analyzers.
B) Two-exit head front view. 9) Brass tube;
10) Conical shaped duct; 11) Three ways
ball-valve; 12) Pipes to filters; 13)
Brass filters; 14) Pipes to analyzers.
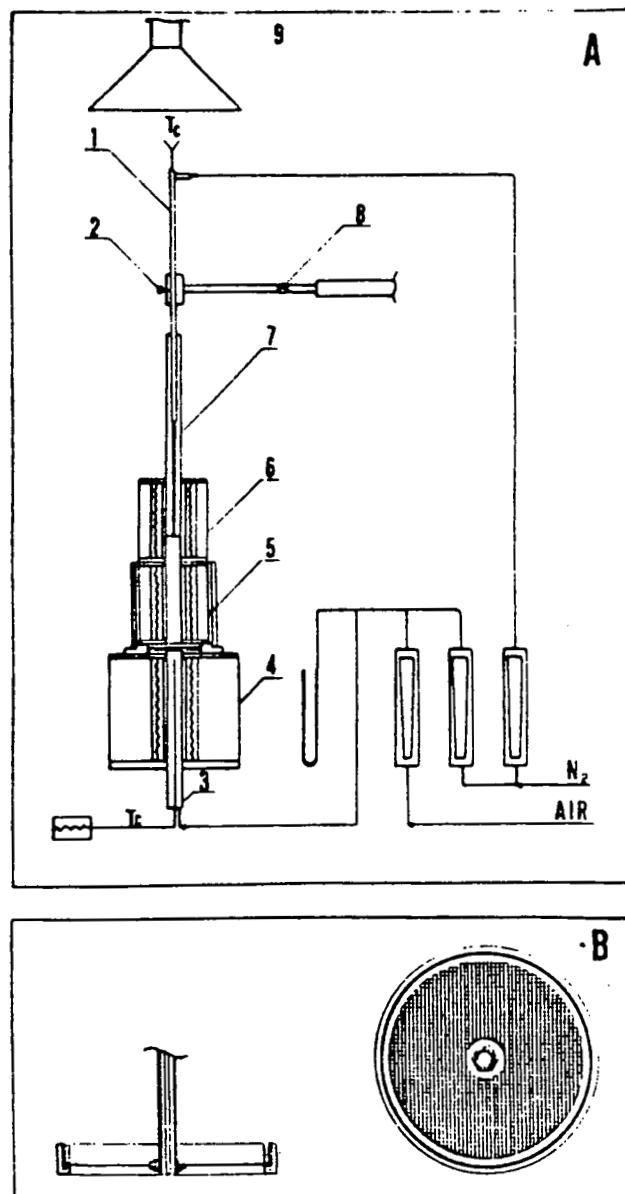
Figure 1-II. Fluidized bed combustor used in fragmentation
           experiments.
           A) The apparatus. 1) Basket holder; 2) Basket
              holder guide; 3) Air pre-heater; 4) Pre-he
              ater electric furnace; 5,6) Fluidization
              column electric furnaces; 7) Quartz tube;
              8) Spherical pivot for basket holder; 9)
              Stack.
           B) Basket front and top views.
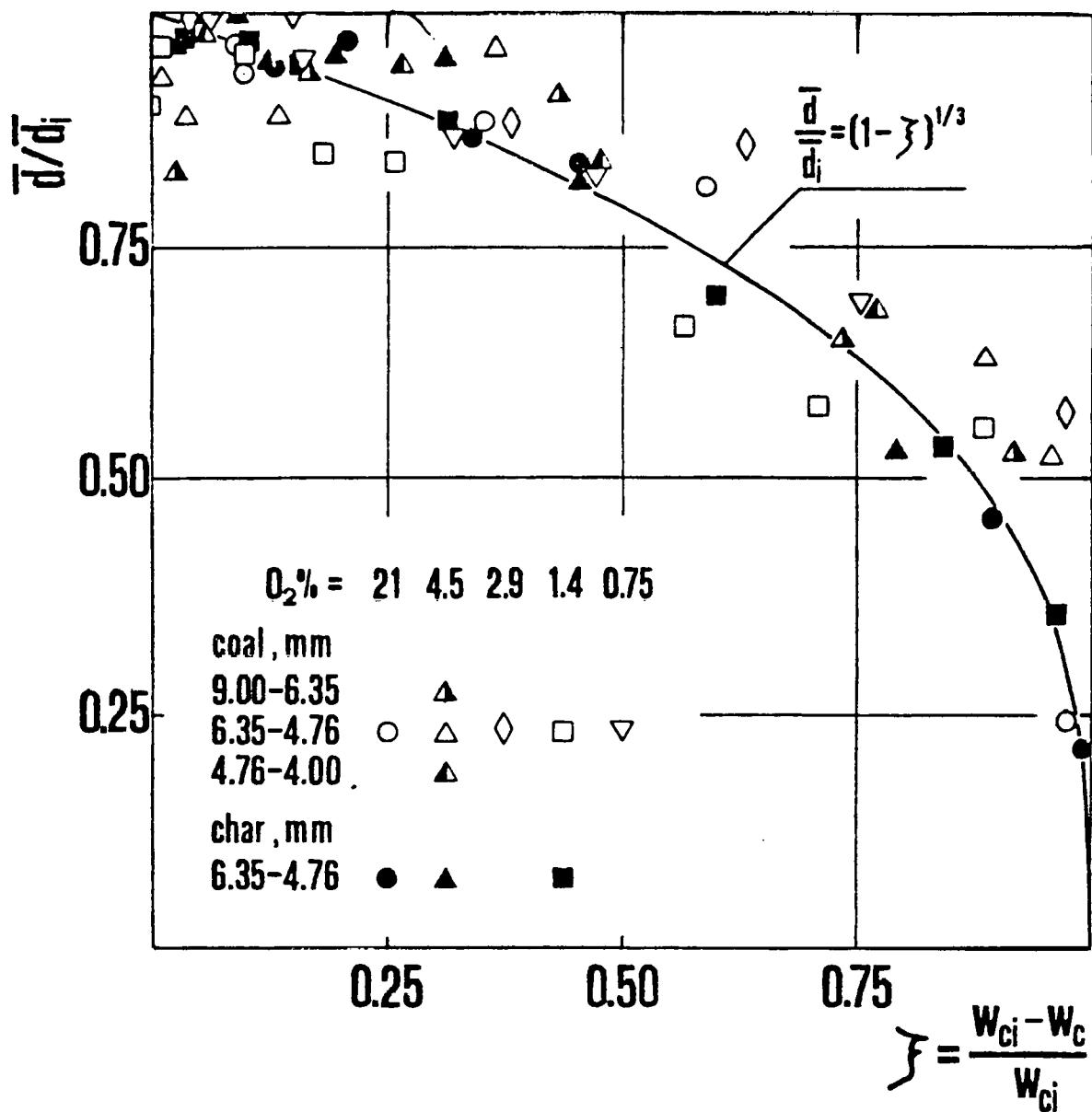
Figure 2. Char particle shrinkage as a function of fractional conversion of carbon.

U = 80 cm s^{-1}; T = 850 °C.

The figure shows a plot of $\overline{d}/\overline{d_i}$ versus t/t_{bo} with the equation:

$$\frac{\overline{d}}{\overline{d_i}} = \left(1 - \frac{t}{t_{bo}}\right)^{2/3}$$

Legend:

$O_2\% =$	21	4.5	2.9	1.4	0.75
coal, mm					
9.00–6.35		△			
6.35–4.76	○	△	◇	□	▽
4.76–4.00		△			
char, mm					
6.35–4.76	●	▲		■	
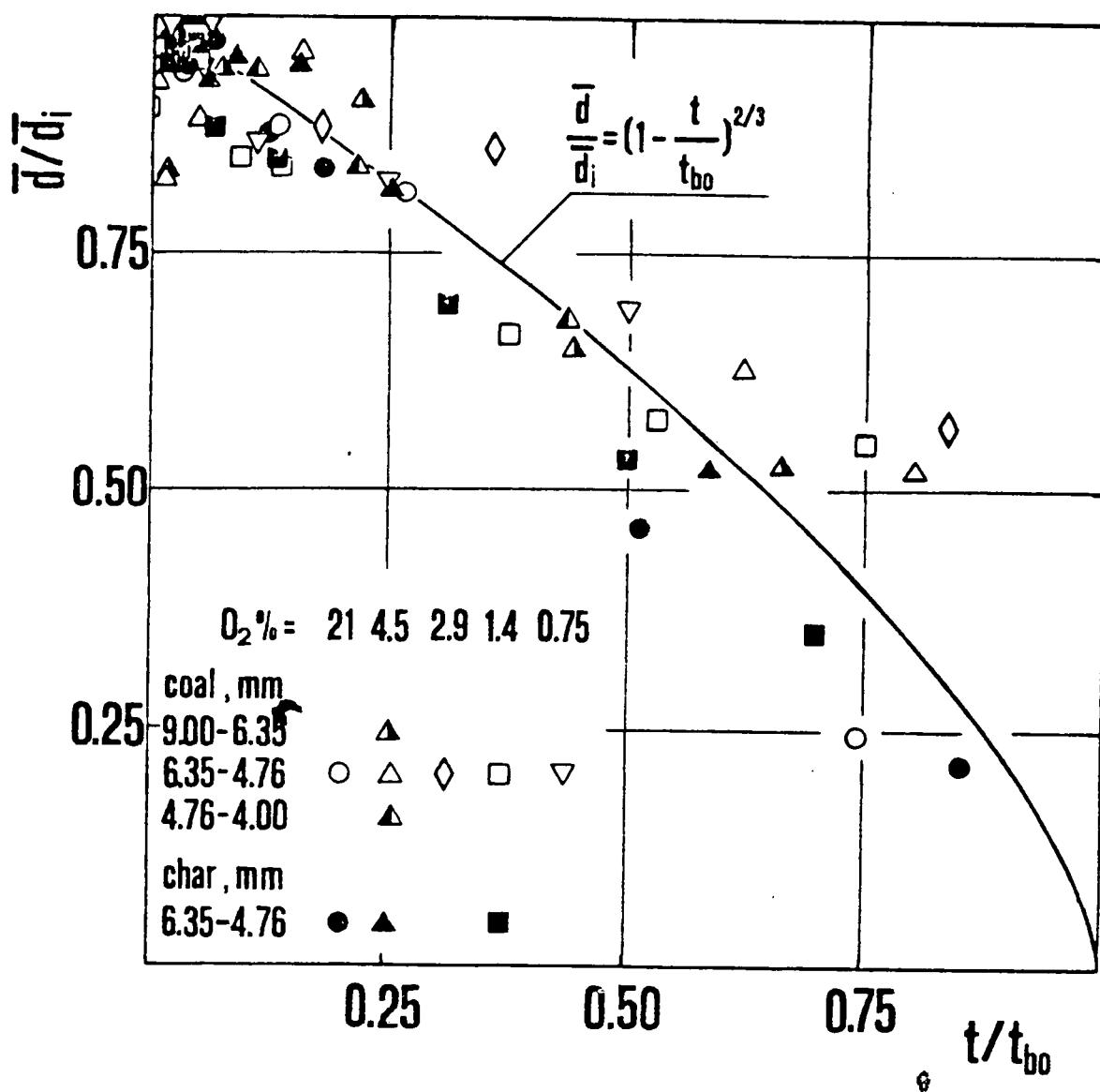
Figure 3. Char particle shrinkage as a function of time.
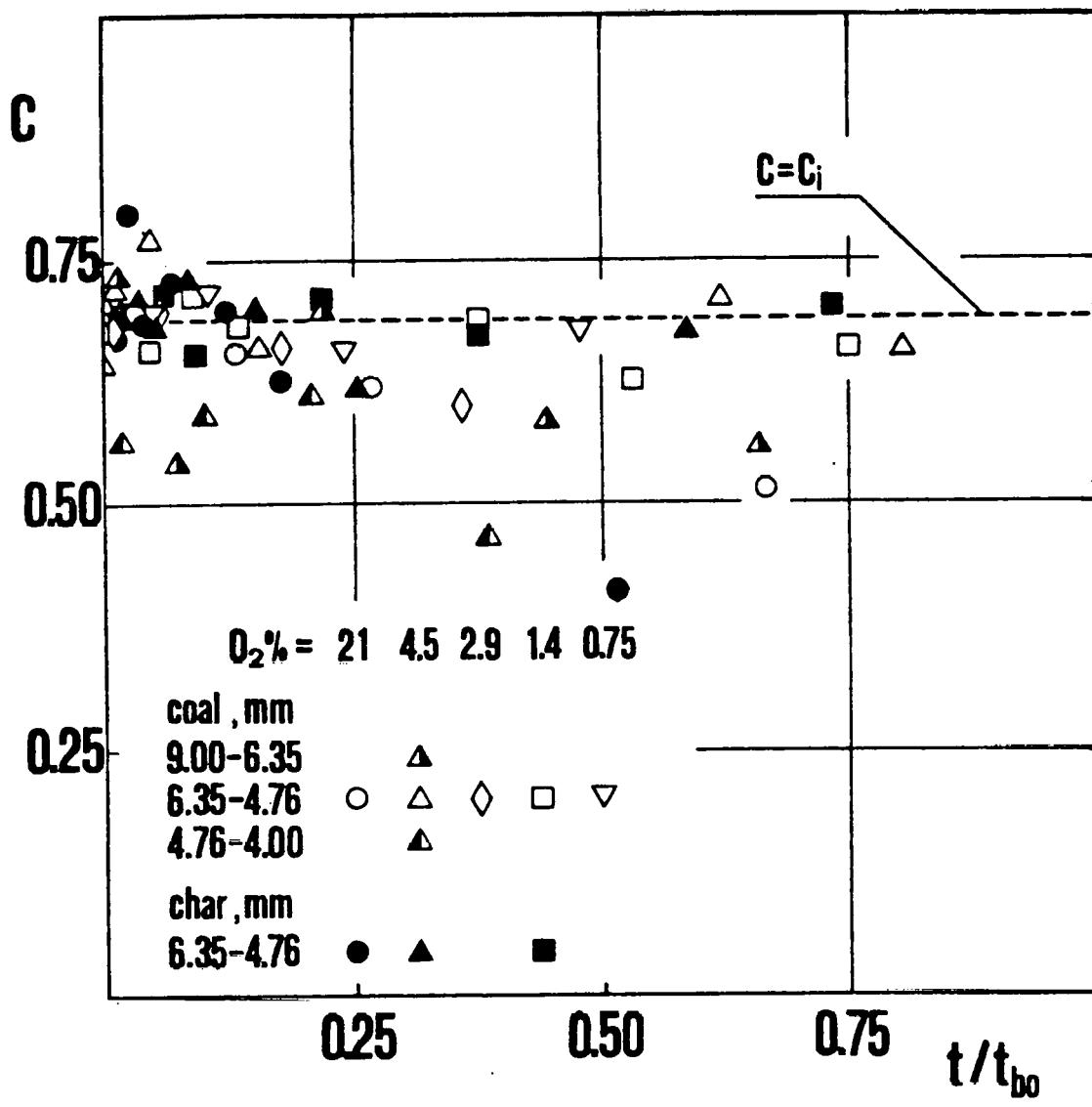
$U = 80$ cm s^{-1}; $T = 850$ °C.

Figure 4 . Mass fraction of carbon in the char as a function of time.
U = 80 cm s^{-1}; T = 850 °C.
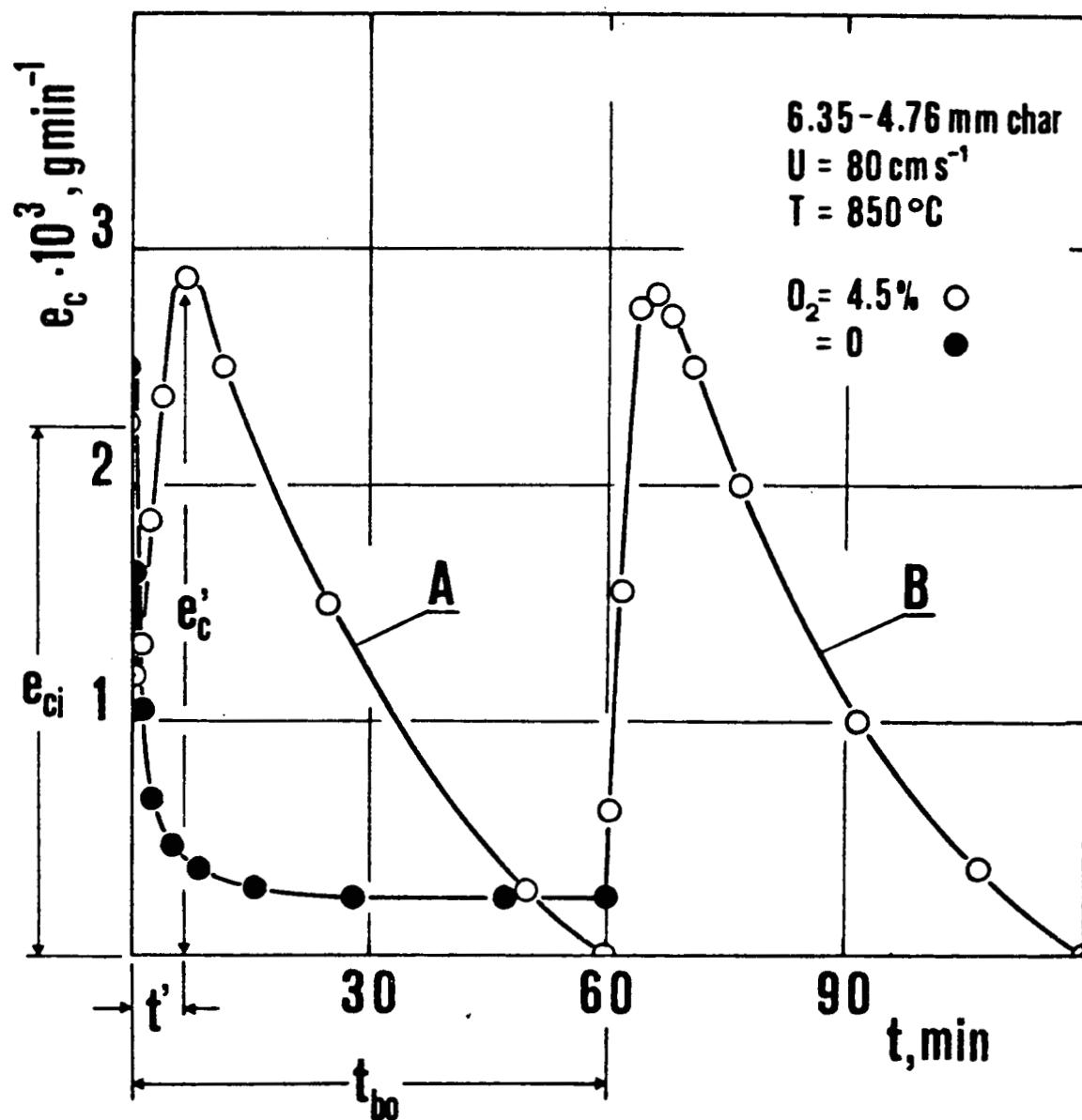
Figure 5. Carbon elutriation curves for purely mechanical (●) and combustion assisted (○) attrition.
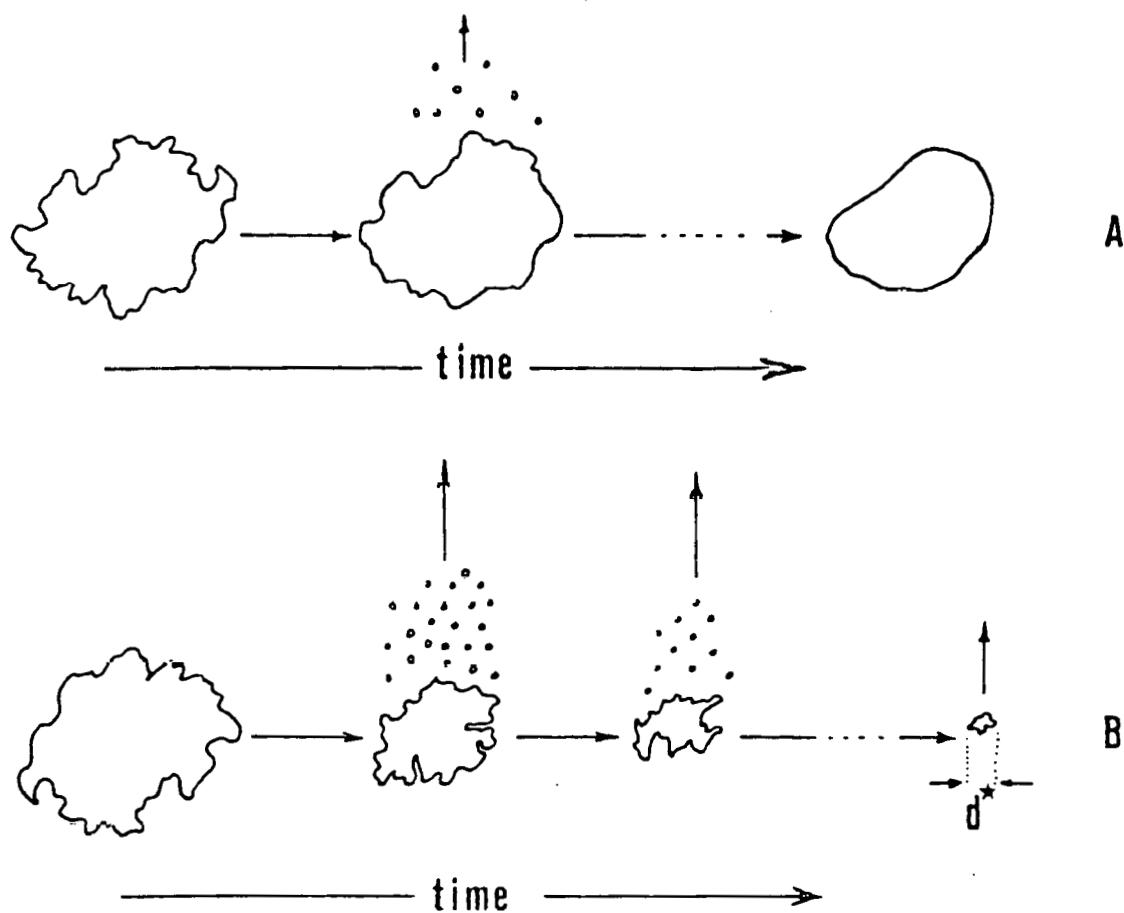
Figure 6. Model representation of purely mechanical (A) and combustion assisted (B) attrition.
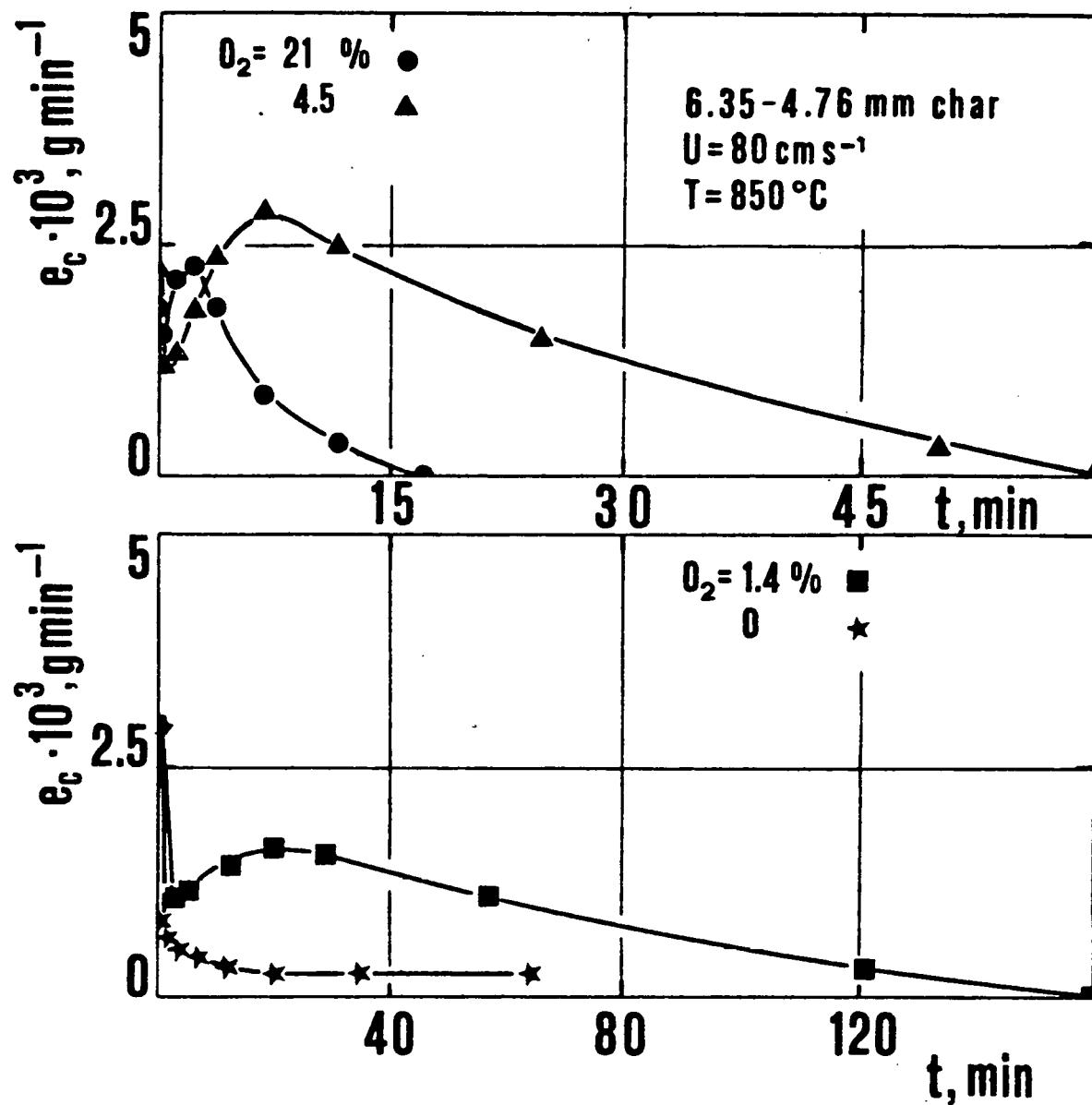
Figure 7. Attrition curves for char feed: the influence of oxygen concentration in inlet gas.
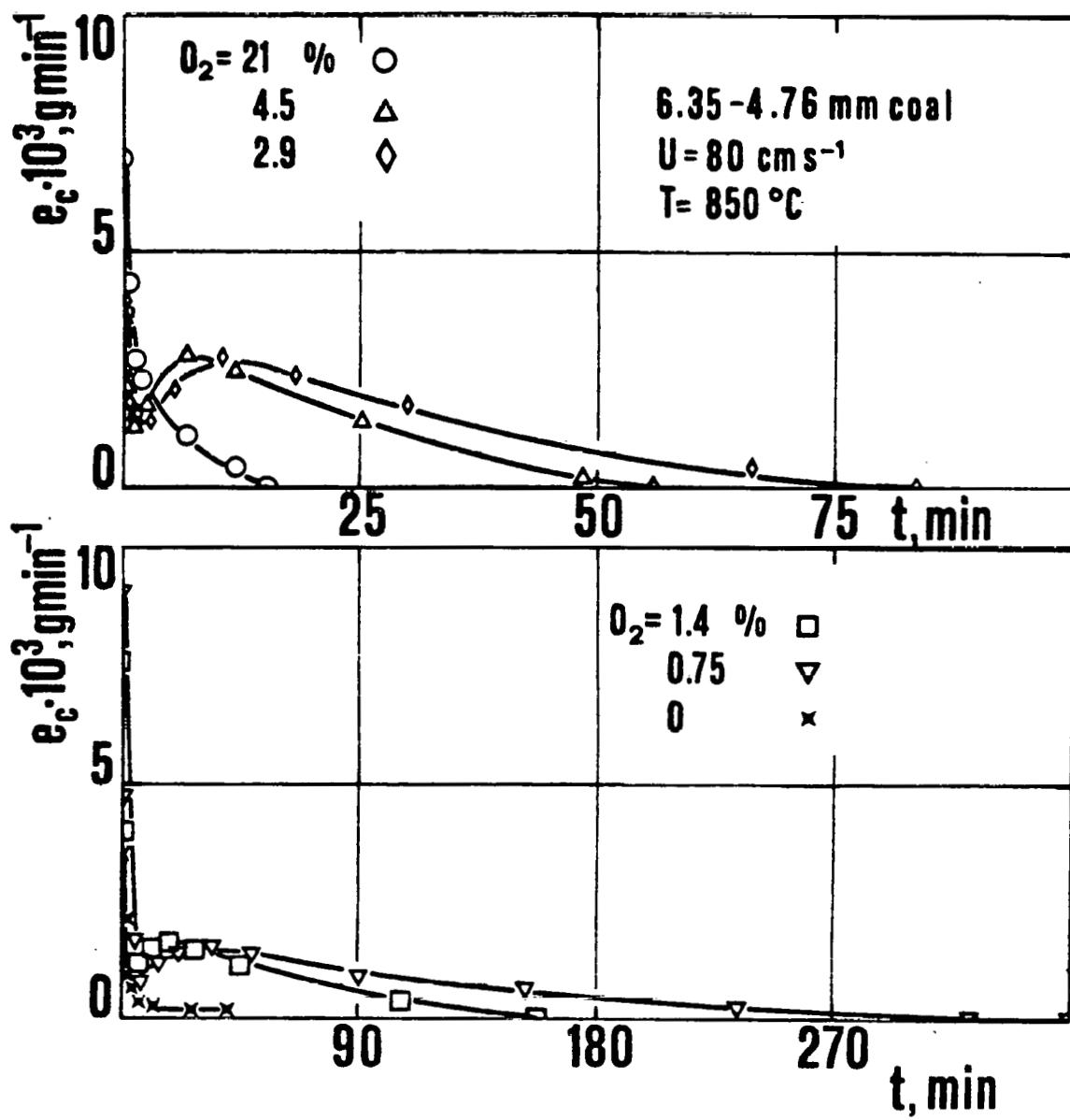
Figure 8. Attrition curves for coal feed: the influence of oxygen concentration in inlet gas.
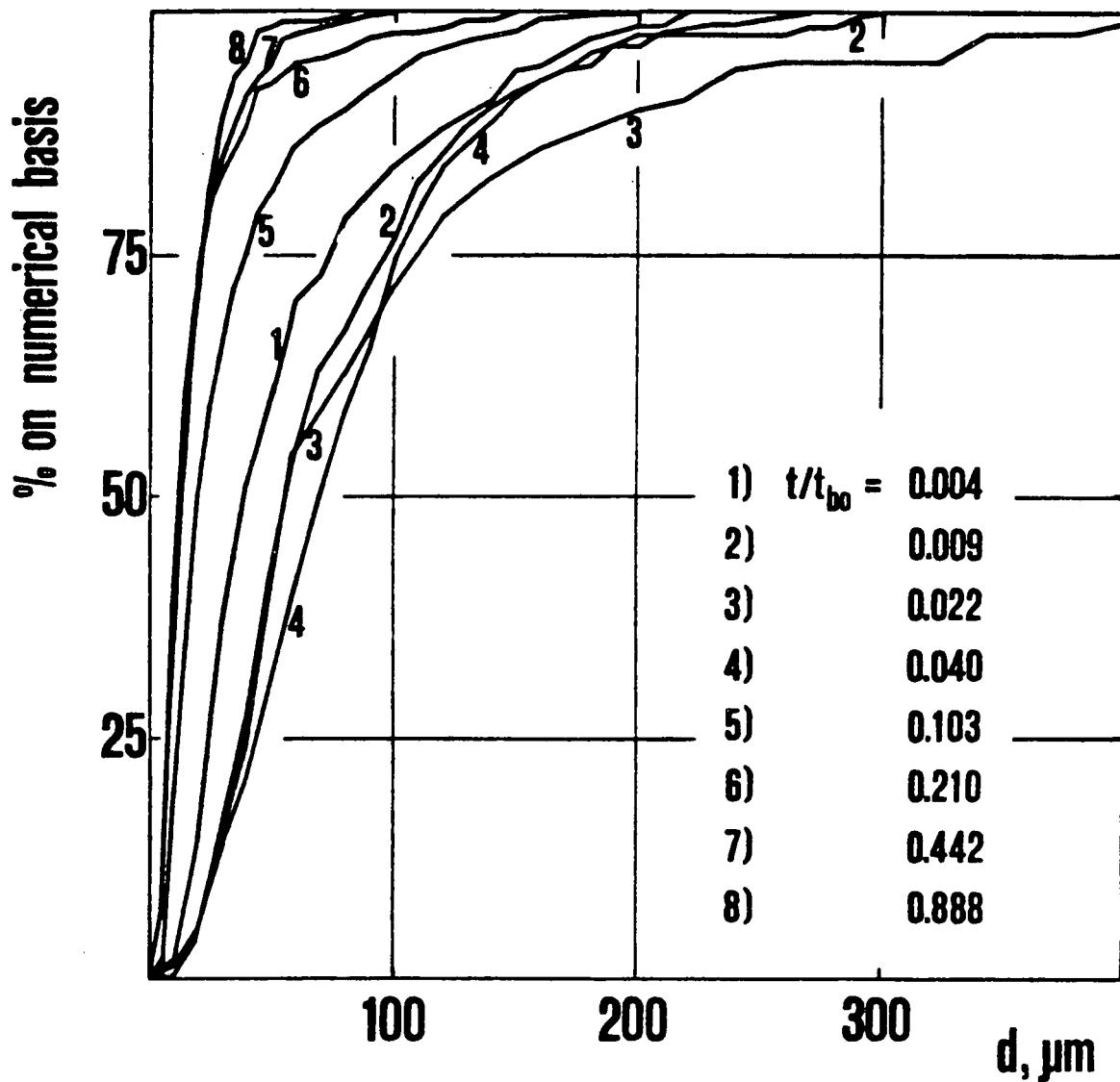
Figure 9. Cumulative particle size distribution of carbon fines collected
at the filters during the time interval between injection and
burn-out.
6.35-4.76 mm coal; U = 80 cm s^{-1}; T = 850 °C; O_2 in inlet gas =
4.5% ; t_{bo} = 56 min.
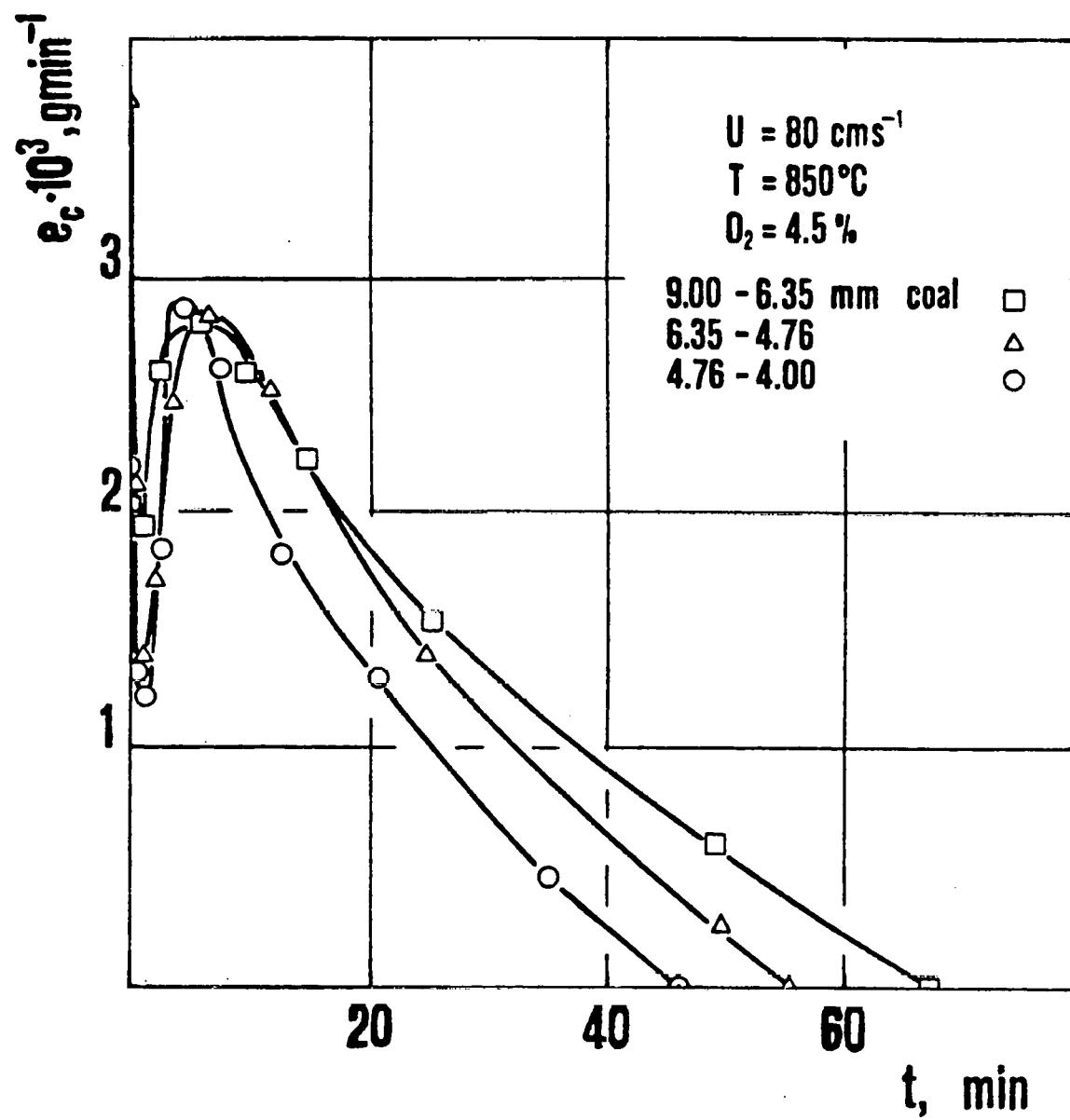
Figure 10. Attrition curves for coal feed: the influence of feed size.
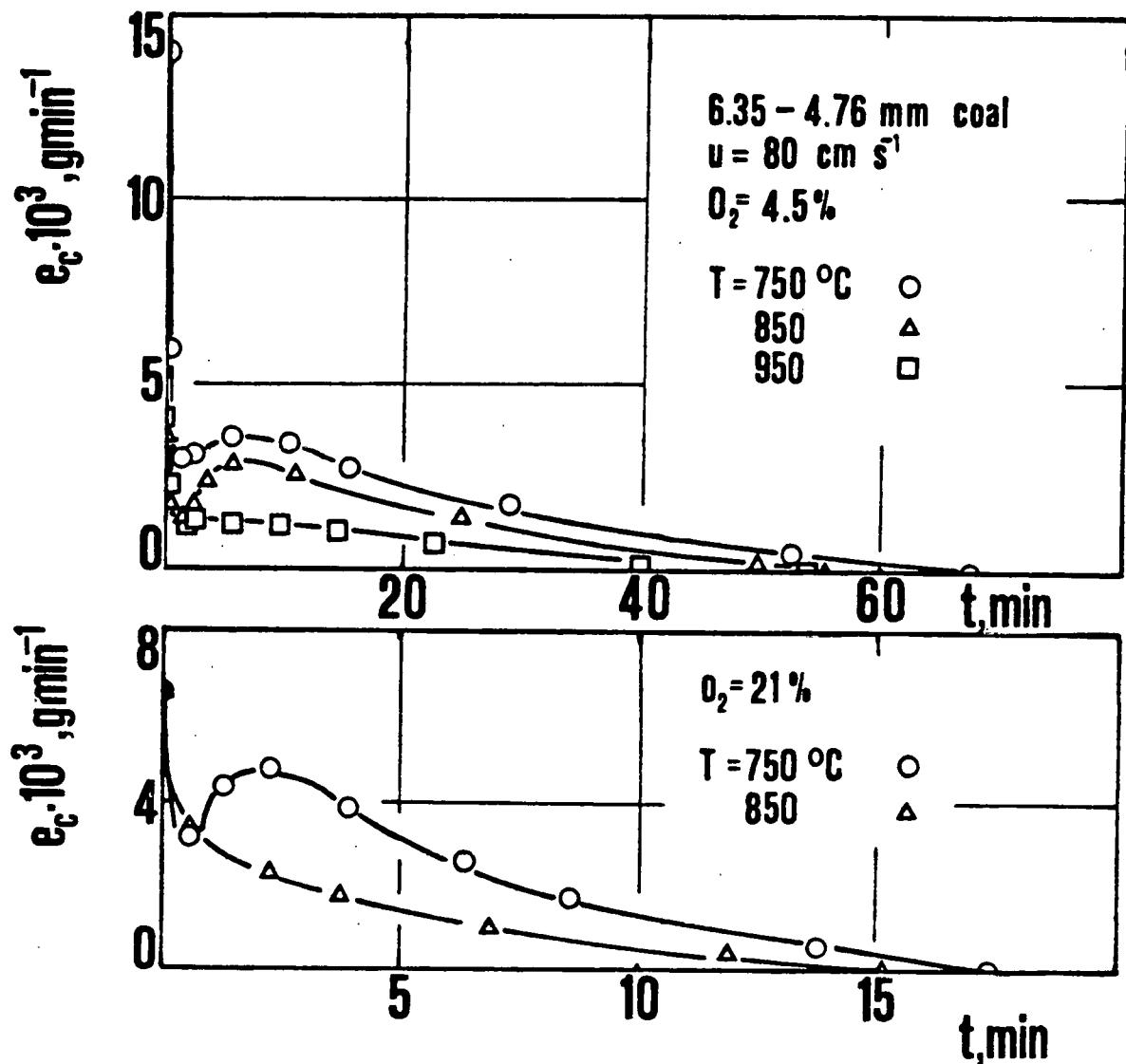
Figure 11. Attrition curves for coal feed: the influence of bed temperature
at two levels of oxygen concentration in inlet gas.
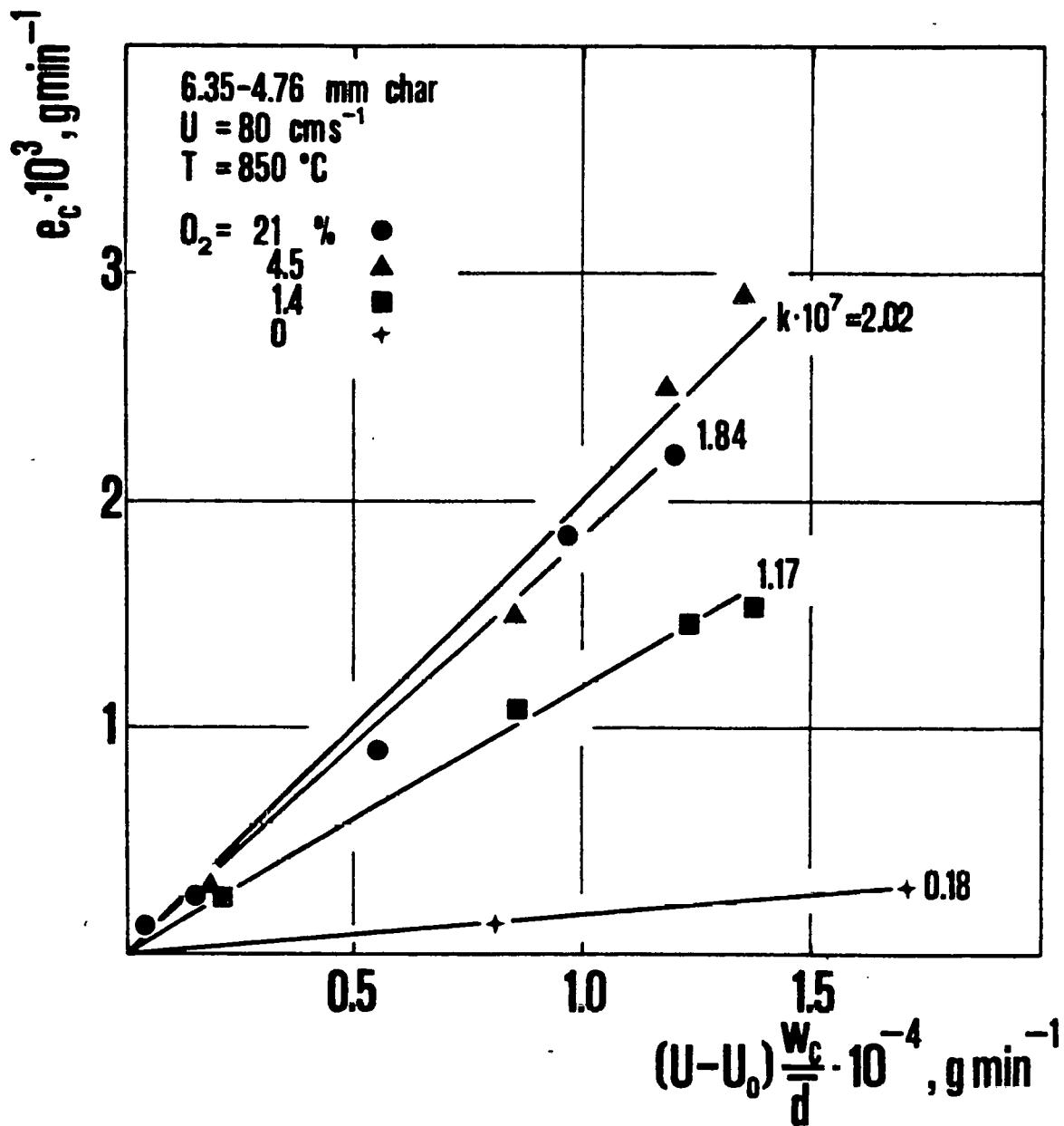
Figure 12. Evaluation of the attrition rate constants based on Eq. 17 for char feed.
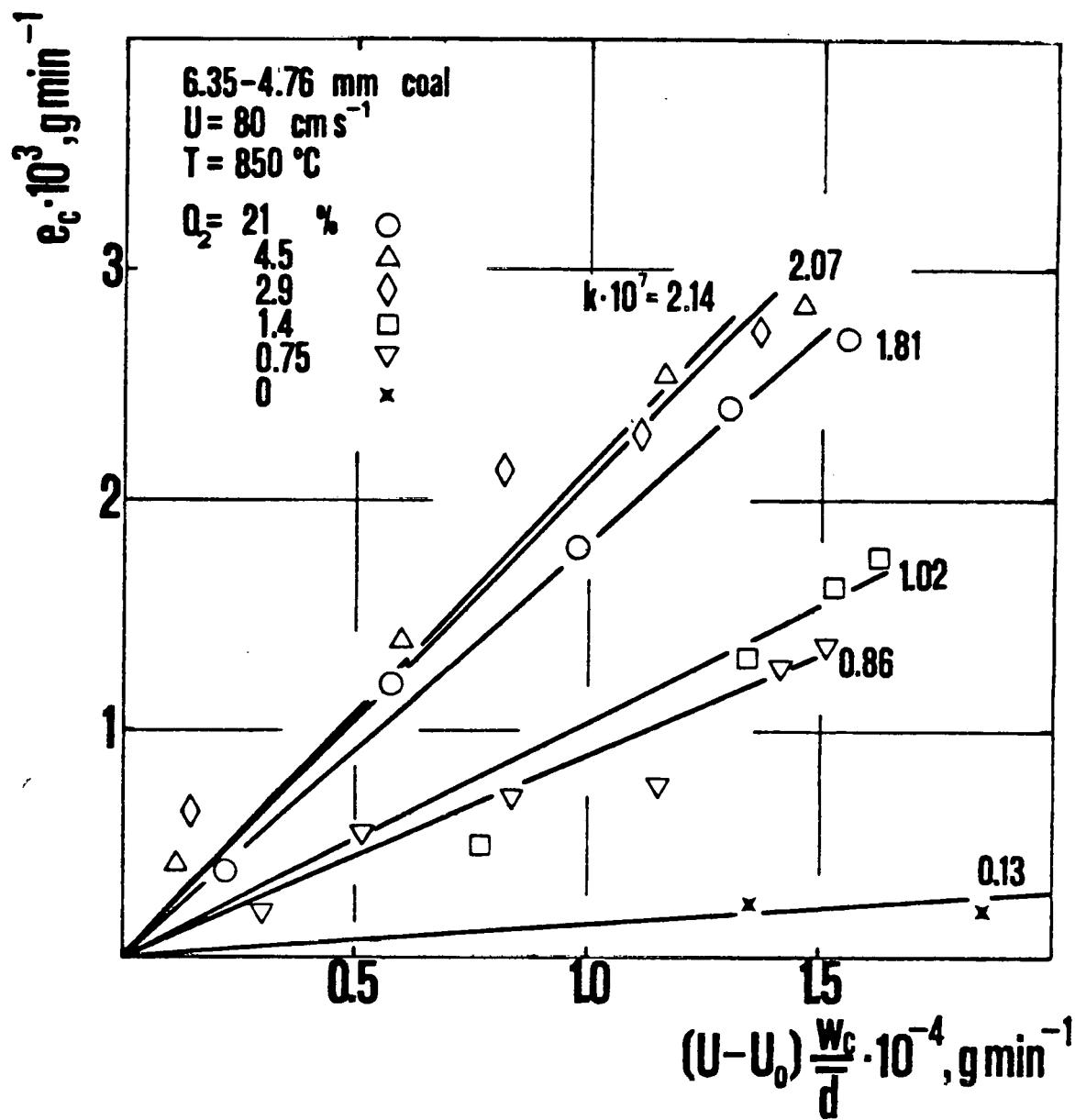
Figure 13. Evaluation of the attrition rate constants based on Eq. 17 for coal feed.