

OXIDATION-INDUCED FRAGMENTATION OF CARBONACEOUS MATERIALS AT LOW AND INTERMEDIATE TEMPERATURES

S. Vaccaro*, M. Sirignano**, A. D'Anna**

svaccaro@unisa.it

* Dipartimento di Ingegneria Industriale, Università di Salerno

**Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale -
Università degli Studi di Napoli Federico II

Abstract

Oxidation of carbonaceous materials in flames is a key phenomenon in determining the final emission of these compounds in the atmosphere both in terms of concentrations and particle sizes. Oxidation is generally considered as a surface process able to subtract carbon atoms from the particles reducing their size. However, fragmentation of particles can also occur if the oxidizing species is able to penetrate the particles and remove C atoms from weak points causing the break-up of the particles. This process can be referred to as oxidation-induced fragmentation and can be seen as particular events of oxidation. It produces a huge number of very small size particles increasing their subsequent burn-out.

Recent experimental data obtained in flames have shown the importance of oxidation-induced fragmentation and have individuated O_2 as the main responsible for particle fragmentation because of its relatively slow oxidation rate and the capability to penetrate the particles. Fragmentation can involve large aggregates containing a large number of individual particles leading to smaller aggregates, but also primary particles where internal burning fragments single particle into smaller clusters.

In order to have more insights on the process of oxidation-induced fragmentation of soot, the oxidation of various carbonaceous materials has been carried out in a quartz tubular flow micro reactor electrically heated to controlled temperatures ranging from 800 to 1300K. Continuous analysis of CO and CO_2 concentrations allowed the evaluation of carbon conversion at varying temperatures and material characteristics. Measurements of specific surface area of the fresh carbon materials and of the samples after partial carbon conversion have also been carried out.

Results showed a huge increase of the specific surface area as the carbon conversion proceeds. The increase was more evident in the low temperature range where the specific surface area was increased up to 800%. Analysis of the data have shown that fragmentation of the particles occurs particularly at lower temperatures where molecular oxygen is able to penetrate the pores to internally oxidize the particle causing their break-up. A fragmentation kinetic constant has been retrieved from the experimental data and compared with literature data

obtained in flame conditions.

Introduction

The capability of using an efficient process to clean combustion exhausts from carbon particles has increased in the last years but the complete achievement of this goal is not reached yet. Indeed, oxidation of carbonaceous materials still remains a major problem [1]. Different approaches have been adopted to study systematically this issue. Great part of the work has been conducted analyzing soot sampled from real combustion systems [2-6]. Particular attention has been devoted on soot coming from diesel engines, being this a relevant concern for the environment. However, also soot produced from laboratory flames and other similar materials have been studied [7-10] and among these, carbon blacks [11] because they often exhibit reactivity and morphological characteristics similar to soot.

The oxidation process has been studied in several different reactors [2-6]. However, the studies conducted on soot burn out in different environments led to contrasting conclusions. On the one hand the burning rate at high temperature ($>1000^{\circ}\text{C}$) agreed with a shrinking-core [9, 12-13] model where the soot was considered made of spherical non-porous particles shrinking as the oxidation proceed while at relatively low temperature the burning rate is somewhat underestimated by that model. In this situation, in fact, the reactivity calculated by that model, which is related to the surface area, does not reach the experimental values and the burn out of the soot is not correctly predicted [9, 12-13]. However, looking at the studies conducted on the structure of soot and carbon black, it has been found that, when subjected to heating at moderate temperatures ($400\text{-}500^{\circ}\text{C}$), a porous structure forms, which is responsible for the large specific surface area experimentally found. Actually, for particles from 30nm to 80nm, typical size of single primary particles, the surface area calculated from spherical approximation and considering a density of 2000 kg/m^3 , ranges from 37.5 to $100\text{ m}^2/\text{g}$, whereas the experimental values measured after heating at moderate temperatures easily reaches several hundreds of m^2/g . This excess of surface area is due to pores whose dimension is of the order of 1nm. This surface area should be available for the oxidation process if the diffusion of the oxidant within the pores does not become the controlling step of the process. The real availability of these pores has been under debate for quite a long period. One of the hypotheses is based on the presence of tarry material absorbed on the soot surface which volatilizes at the beginning of the process making available the pores [1]. This suggestion does not overtakes some issues such as the absence of this tarry material in pre-treated soot and carbon black for which high burning rates are found [1].

In the medium temperature conditions no systematic experiments have been conducted to prove or evidence the increase of number concentration of small particles. However, the increase of total surface area could be explained through the fragmentation approach and the increase of numerical concentration of smaller particles.

Recently this approach has been implemented in a multi sectional method to predict the behavior in diffusion laminar flame, finding that the inclusion of fragmentation is mandatory to predict the burnout of soot [14].

This work takes place from an experimental investigation on oxidation of carbon black particles in a fixed bed reactor, conducted at constant temperature and oxygen partial pressure. Morphological characterization of carbon black suggested that the material is suitable to be compared to soot in terms of structure and burning rate. Surface area data at different conversion of the mass are available. A simple model for the mass consumption has been implemented to predict the burn out and the surface area evolution. Both constant and variable number concentration of particles is considered to simulate the behavior with and without taking into account the fragmentation of the particles.

Experimental set up

The carbonaceous material used in the tests was a sample of a commercial amorphous carbon black (CB-330, DEGUSSA). The BET specific surface area of CB-330 was 86 m²/g. The bulk density of both materials was 375 kg/m³.

The apparatus for the tests comprises a quartz tubular flow reactor 300 mm height and 20 mm internal diameter, heated by an electrical furnace. The reactor temperature was controlled by a programmer-controller (Ascon). Cylinder air and nitrogen (99.999 % purity) were mixed downstream of mass flow controllers (HI-TECH) to obtain different oxygen partial pressures in the gas entering the reactor. Exhaust gas concentrations were determined by Hartmann & Braun continuous analysers: URAS 10E (for carbon monoxide and carbon dioxide) and Magnos 6G (for oxygen). Signals from the analysers were acquired and processed by a personal computer which also performed the control of the experiment. Carbonaceous materials were diluted with 180-350 mm quartz particles up to a mass ratio between carbonaceous material and quartz of 0.01, to avoid localized temperature rises during the tests. The diluted mixture was loaded in the quartz flow reactor, filling about 3 cm in length of its central zone. The remaining part of the reactor was filled with 700-2000 mm quartz particles. The temperature in the reacting zone was detected by a type K thermocouple. Tests of carbon combustion were carried out at constant temperature and pressure.

The test was started by raising the temperature to the desired value in nitrogen flow. The gas feed to the reactor was turned to the oxidising stream to start the oxidation. Carbon burn-off was followed by monitoring, through the continuous analysers Uras 10E, the carbon monoxide and dioxide produced during gasification. Carbon mass balance was verified within a 5% tolerance range for all tests. In all the runs parameters were kept at values such to allow the reactor working under differential conditions. The feed gas flow rate was 500 Ncm³/min and the operating pressure 101 kPa. The initial mass of carbonaceous matter was changed in the range 3-15 mg. Two temperature conditions were chosen to be investigated: a high temperature condition (T=1273K) and a low temperature

condition ($T=833K$).

Model Prediction in Diffusion Flames

A simple model has been implemented in order to predict the evolution of carbon black particles in the oxidative environment set up. The influence of diffusion of the oxygen from the bulk to the surface of the particle has not been considered. This approximation should not affect the general consideration on the role of fragmentation, although a more detailed model should be provided. On this hypothesis the oxygen concentration becomes a constant in the model.

Carbon clack particles have been defined by the total mass and the total number. These parameters allow to follow the evolution of the mass and the surface of the carbon black both considering and neglecting the fragmentation process. In fact for the simulation in which the fragmentation has not been considered the total number of the particles did not change and the total surface area is just depending by the progress of the surface reaction and thus the consumption of the initial particles. When fragmentation process is accounted for the total number of particles has been considered variable with the total mass, i.e. with the progress of the reaction. This hypothesis follows the consideration that fragmentation occurs when a certain mass of the particles is lost and the forces that held the particles together become weak enough to let them break apart. This represents a first approach to follow the fragmentation process

The mass and number concentration balances on the analyzed material as a function of time are:

$$\frac{dM}{dt} = K_L T^{-0.5} e^{\left(\frac{-E_A}{RT}\right)} (\pi N)^{1/3} \left(\frac{6M}{\rho}\right)^{2/3} P_{O_2}$$

$$\frac{dN}{dt} = 10 \frac{N_0}{e^{\left(\frac{M}{M_0}\right)}}$$

where M and M_0 are the mass at time t and at the beginning of the process, respectively, N and N_0 the current and the initial number of particles (calculated on the experimental initial diameter of the particles), T is the temperature, P_{O_2} is the partial pressure of oxygen (here hypothesized constant), E_A and K_L are the activation energy and the frequency factor for the surface oxidation reaction developed by Lee et al. [9].

Results

Figure 1 and 2 show the evolution of the surface area versus the conversion factor for the high and low temperature conditions, i.e. 1000°C and 560°C, respectively.

In the same figures modelling results with and without considering the fragmentation process are compared with experimental data.

The experimental results for the high temperature conditions (1000°C) show an increase of the surface area respect to the initial value by a factor of 2. The model predicts well the trend although it slightly underestimates the maximum value (Fig.1). This behavior suggests that the reaction on the surface occurs really fast and the fragmentation is a process of minor relevance. In the case in which the fragmentation is not considered (dotted line in Fig.1) the surface area globally decreases during the particle burn-out.

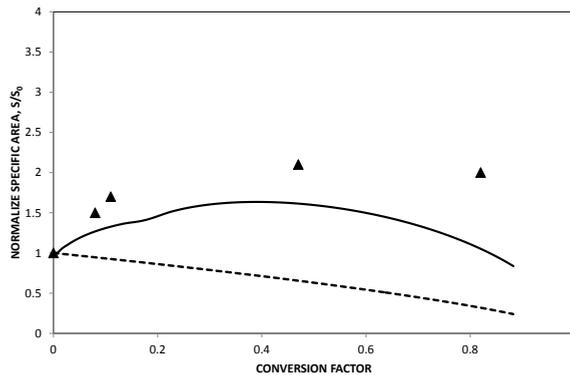


Figure 1. Modelling results (lines) compared with experimental data for normalized total surface area with (full line) and without (dotted line) considering fragmentation for the 1000°C condition.

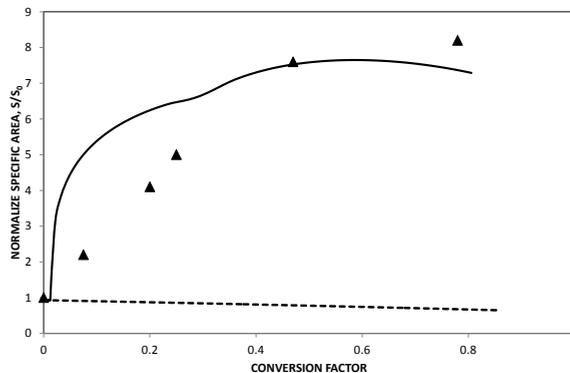


Figure 2. Modelling results (lines) compared with experimental data for normalized total surface area with (full line) and without (dotted line) considering fragmentation for the 560°C condition.

A similar situation is found for the low temperature condition (560°C) reported in Fig. 2. In this case a strong increase of the surface area is experimentally detected and numerically predicted when fragmentation is considered. The agreement

between the model and the experimental data is good although the model over predict the surface area for small conversion factor, i.e. in the beginning of the burn-out process. Vice versa, without considering the fragmentation process the global surface area is always decreasing with respect to the initial value.

Specific surface area of soot or carbon black particles strongly increases during oxidation process at relatively low temperature; this increase, which goes up to about ten times the initial values, is hardly to be explained only with the presence of the pores on the particles. For this behavior two explanations have been suggested through years. The first hypothesis is that these pores are enlarged by the oxidation process: the consumption of the material leads to the formation of larger pores that consumes the particles inside, basically following a shrinking-core model. In this case the mean size of the particles remains unvaried, whereas the density decreases [1]. The second hypothesis follows the suggestion of Sarofim group in the 80's, recently updated with new experimental data [7-8]. The idea is that aggregates of particles and particles can fragment forming smaller aggregates and/or smaller particles when a critical mass is loss in weak points of the structure. Their studies are conducted at flame temperature, generally higher than other studies, where the reaction rates are higher. However, also in these conditions the diffusivity of oxygen in the pores is fast enough compared to the surface reaction. This leads to the consumption of the particles in the weak points provoking the break apart of the structure. Fragmentation increases the number of particles present in the flame and also their surface area, making available the inner part of the structure. This behavior has been hypothesized after the finding of the increase of the fraction of smaller particles during the oxidation process. In particular, from large aggregates, 80nm and more, before the complete burn out takes place, particles as small as 2-4nm can be formed in concentration 2 orders of magnitude higher than the initial one. This behavior cannot be explained with the shrinking-core model neither with the surface oxidation.

Conclusion

In this work the oxidation process of carbon black particles have been investigated in order to study the evolution of the surface area during the burn out. Experimentally, measurements were performed in a fixed bed reactor at relatively high and low temperature. Numerically, a simple model was implemented to track the total mass and the total number of the particles. When fragmentation was not considered in the model, the total number of the particles has been considered constant. Fragmentation was successively taken into account by considering the total number as a variable and defining a variation law. The evolution of the particle total number was defined dependent on the conversion factor according to hypothesis on fragmentation process present in literature. Comparison of the modeling results with experimental data clearly show that fragmentation was necessary to predict the increasing of the total surface area. Moreover the fragmentation process is more evident when the reaction is slow, i.e. at low

temperature, and the surface consumption of the particles is less effective.

References

- [1] Stanmore, B.R., Brilhac, J.F., Gilot, P., The oxidation of soot: a review of experiments mechanisms and models, *Carbon*, 39 2247-2268 (2001).
- [2] Lahaye J, Boehm P, Chambriou P, Ehrburger P, Influence of cerium oxide on the formation and oxidation of soot, *Combust Flame*, 104,199–207 (1996).
- [3] J.P.A Neeft, T.X Nijhuis, E Smakman, M Makkee, J.A Moulijn, Kinetics of the oxidation of diesel soot, *Fuel*, 76,1129–1136 (1997)
- [4] Neeft JPA, Makkee M, Moulijn JA, Diesel particulate emission control, *Fuel Proc Technol*,471–69 (1996).
- [5] Ciambelli P, Corbo P, Parrella P, Scialo M, Vaccaro S., Catalytic oxidation of soot from diesel exhaust gases. 1. Screening of metal oxide catalysts by TG-DTG-DTA analysis, *Thermochim Acta*;16283–9 (1990).
- [6] G de Soete Catalysis of soot combustion by metal oxides *Western States section meeting*, Salt Lake City, 21–22 March, The Combustion Institute (1988)
- [7] K.G Neoh, J.B Howard, A.F Sarofim, Effect of oxidation on the physical structure of soot, *Twentieth international symposium on combustion*, The Combustion Institute, Pittsburgh 951–957 (1984).
- [8] Echavarria, C.A., Jaramillo, I.C., Sarofim, A.F., Lighty, J.S., Studies of soot oxidation and fragmentation in a two-stage burner under fuel-lean and fuel-rich conditions, *Proceedings of the Combustion Institute* 33, 659-666 (2011)
- [9] K.B Lee, M.W Thring, J.M Beér, On the rate of combustion of soot in a laminar soot flame, *Combust Flame*, 6 137–145 (1962).
- [10] A Garo, G Prado, J Lahaye, Chemical aspects of soot particles radiation in a laminar methane–air diffusion flame, *Combust Flame*, 79, 226–233 (1990).
- [11] P Ciambelli, M d’Amore, V Palma, S Vaccaro, Catalytic combustion of an amorphous carbon black, *Combust Flame*, 99, 413–421 (1994).
- [12] T Ishiguro, N Suzuki, Y Fujitani, H Morimoto, Microstructural changes of diesel soot during oxidation, *Combust Flame*, 85 1–6 (1991).
- [13] P Gilot, F Bonnefoy, F Marcucilli, G Prado Determination of kinetic data for soot oxidation. Modeling of competition between oxygen diffusion and reaction during thermogravimetric analysis *Combust Flame*, 95 87–100, (1993).
- [14] Sirignano, M., D’Anna, A., Modeling Formation and Oxidation of Soot in non-Premixed Flames, *Energy Fuels* 27 (4) 2303-2315 (2013).