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Effect of sintering on the fractal prefactor of agglomerates

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ABSTRACT

In a previous study different agglomerates composed by a variable number of primary particles corresponding to extreme and intermediate values of fractal dimension ($D_f = 1$, 2 and 3) were characterized to be used as reference shapes in a method for the determination of the fractal dimension of actual agglomerates. In that work, primary particles were assumed to be spherical and with no sintering or necking effects. In this work, the geometrical effect of processes such as coalescence, sintering, flattening, or surface growth is considered to evaluate the impact of these phenomena in the morphological parameters of fractal-like agglomerates. A sintering coefficient is firstly defined. Afterwards, the moment of inertia and radius of gyration of the agglomerate are determined and finally the prefactor of the power–law relationship is obtained as a function of the number of primary particles and the sintering coefficient. The equations proposed are used in a geometrical method to determine the fractal dimension of soot agglomerates, showing that sintering increases the prefactor significantly, which leads to a slight decrease in the fractal dimension of the agglomerates.

1. Introduction

Agglomerates formed in technologies involving solid colloidal suspensions are often formed by primary particles (monomers) with shapes close to spherules, whose diameters are very uniform in size. This is the case of diesel soot agglomerates, among others [1]. In modelling studies, assuming uniform diameter for primary particles is very common [2–6], since it has been proven that polydispersity does not affect significantly the morphological parameters describing the agglomerate [7]. However, this assumption has been recently refuted [8].

Primary soot particles are incepted from the gas phase at the nucleation zone of the flames and grow by both coagulation and surface growth, or shrink and burn up. In the post-nucleation zone, the size of these particles increases only by surface growth, the shape of primary particles not being substantially affected [9]. Flow displacement along the combustion chamber together with Brownian movement lead to collisions and therefore agglomerates begin to adopt a fractal-like geometry. Immediately after this initial stage of agglomeration with no coagulation, particles can be assumed to be in point contact. Surface growth continues, leading to agglomerates composed of primary particles interconnected by areas. This growth may not be distributed uniformly but concentrated around the contact area, as suggested by Morgan et al. [10]. Consequently, images of sampled particles always display contacts between primary particles which appear to be areas, smaller or larger, with approximately circular section, corresponding to the intersection of the two contacting spheres. These contacts are termed as "coagulational contacts" by Mikhailov et al. [11], or simply "neck" by others [12–15]. This geometry may also be a consequence of partial coalescence, flattening or sintering, with or without posterior surface growth. Agglomerates are finally arranged with a variety of different shapes and mass from one to another. They can be considered as fractal-like structures and it is accepted that, in case of being composed by a sufficient number of primary particles, they can be described by means of the power law relationship, with the fractal dimension and the prefactor as the characterizing parameters [16].

The geometrical effect of any of the mentioned processes is often termed as "sintering" in the soot literature [11,17,18], despite sintering is not really as relevant for soot agglomerates as it is in the case of aggregates (particles connected by chemical bonds) formed by inorganic materials. Sintering is a term belonging to the metallurgy terminology, and consists of particle morphology changes derived from material surface diffusion, vapour transport, grain boundary diffusion, plastic viscous flow or fusion under high temperature [19–21]. Through sintering, agglomerates can be converted into aggregates and, with enough time, coalescence could take place [22,23]. The geometrical effect of sintering is also often termed "overlap" [24,4,25], but this term is not precise either, since overlap is often referred to the optical effect of particles hidden one behind the other, as occurring in projected images regardless having point contact or area contact. Finally, the term "penetration" has also been used [26], but it does not realistically describe the deformation observed, since interpenetration of matter between the contacting primary particles does not necessarily occur. Therefore, none of the terms being satisfactory, the term "sintering" was adopted for this study, since it is the most commonly used in the literature. However, it

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Notation

A	projected area
a	correlation coefficient
b	correlation coefficient
c	circle or correlation coefficient
D	dimension
d	diameter, displacement between the geometrical centre and the centre of gravity.
h	factor included in the expression of the simplifying functions μ, η, ν
J	coordination number
i	numeral of the primary particle in the agglomerate
I	moment of inertia
k	prefactor
m	mass
N	number of elementary structures
n	number
r	radius or distance from the centre of gravity
V	volume
X,Y,Z	orthogonal coordinates
z	height
α	function that affects the mass of a sintered particle
β	function affecting the moment of inertia of a single sintered sphere
δ	sintering coefficient
γ	function affecting the centre of gravity of a (multi) sintered sphere
ρ	density
μ	function relating n_{p_o} and i_n for the cases where $D_f = 2, N = 1$
η	function relating n_{p_o} and i_n for the cases where $D_f = 2, N = 2$
ν	function relating n_{p_o} and i_n for the cases where $D_f = 2, N = 3$

Subscripts

f	fractal
G	centre of gravity
g	gyration
mss	multiple sintered sphere
n	number
o	geometrical centre
p	agglomerate
p_o	primary particle
s	sintering
sc	spherical cap
sss	simple sintered sphere

has to be noted that the effect studied here is a purely geometrical three-dimensional effect with a variety of possible origins.

The mass, apparent density, optical properties [15,25,27], thermal properties [28], aero-dynamical properties [29] and diffusional properties [3,12,14] of the agglomerates are affected, not only by their different arrangements but also by the type of contact between primary particles. Oh and Sorensen [4] investigated this geometrical effect (which they denoted as overlap) and concluded that overlap retained the fractal character of the agglomerates, as defined by the power–law relationship, and observed that both the fractal dimension and the prefactor increased with the degree of overlap, indicating densification of the cluster. Also Brasil et al. [24] studied the effect of overlap between monomers and concluded that overlap was not dominant in the determination of the fractal parameters, although acknowledged a significant effect in reducing the surface area of the agglomerate. Both studies considered the primary particles as cut spheres resulting from detracting as many spherical caps as contacting points. On the contrary, Morgan et al. [10] proposed modified geometries derived from the growth of a conical frustum between couples of spheres.

Also Schmid et al. [30] investigated the effect of simultaneous coagulation and sintering and showed, from Monte Carlo simulations in which the radius of the primary particles was increased to preserve the mass, that the fractal dimension increased as the coagulation and sintering progressed, but the prefactor started to decrease when fractal dimension reached a value around 2.3. They also showed that not only coagulation but also sintering contributed to the surface area reduction. In a posterior modelling study from the same authors [17], they introduced surface growth simultaneously to coagulation and sintering, and observed that surface growth led to faster increases of the fractal dimension with respect to the case of coagulation and sintering only. In both studies the power–law relationship provided good fit to their data, proving that the fractality of the agglomerates remained.

Some other geometrical models, such as that proposed by Cho and Biswas [12] and that proposed by Xie [13] predicted the growth of the neck, length shrinkage and surface area reduction for equally [12] or differently [13] sized primary particles, but did not show the effect on the fractal parameters.

The geometrical study presented here is useful for the determination of the fractal dimension of individual agglomerates. This study follows that presented in Ref. [31], where primary particles were considered as perfect spheres in all cases, and provide solutions for the prefactor on the power–law relationship for integer values of the fractal dimension of agglomerates composed of sintered primary particles.

The prefactor of the power–law relationship has been also termed lacunarity [32,33,31], filling factor [3] or structural coefficient [34,35]. It is a key parameter for the morphological characterization of agglomerates. Agglomerates with similar size and fractal dimension may have different shapes, the difference being characterized by the prefactor. The prefactor expresses how the space is being filled up by the agglomerate mass, independently of its size, and how the primary particles are packed [2]. It has been associated with the lacunarity of the agglomerate [33], based on the definition of lacunarity given by Allain and Cloitre [36], as the mean square deviation of the autocorrelation probability function (function expressing how the probability of primary particles to occupy some space decreases as the distance from the agglomerate's centre of gravity increases) divided by its square mean. Successively updated literature reviews [2,31,37], and [38] have shown a very high dispersion of the values proposed, which demonstrates the need to consider the prefactor as a variable to be modelled, similarly as the fractal dimension. However, few studies can be found proposing variation rules for the prefactor [39,35,40], and none of them considers the effect of sintering on the prefactor.

2. Modelling approach, assumptions and coefficients

2.1. Modelling assumptions

Fractal agglomerates can be described, when composed of a large enough number of primary particles, by the power law relationship:

$$n_{p_o} = k_f \left(\frac{d_g}{d_{p_o}} \right)^{D_f} \tag{1}$$

where n_{p_o} is the number of primary particles, k_f is the prefactor of the power law, d_g is the diameter of gyration of the agglomerate, d_{p_o} is the diameter of a primary particle and D_f is the fractal dimension of the agglomerate. This equation has been used for the fractal analysis of soot agglomerates in [41] from their microscopic images. Although real agglomerates are anisotropic, irregular and have non-integer fractal dimension, isotropic, symmetric agglomerates with integer