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Developing breakage models relating morphological data to the milling behaviour of flame synthesised titania particles

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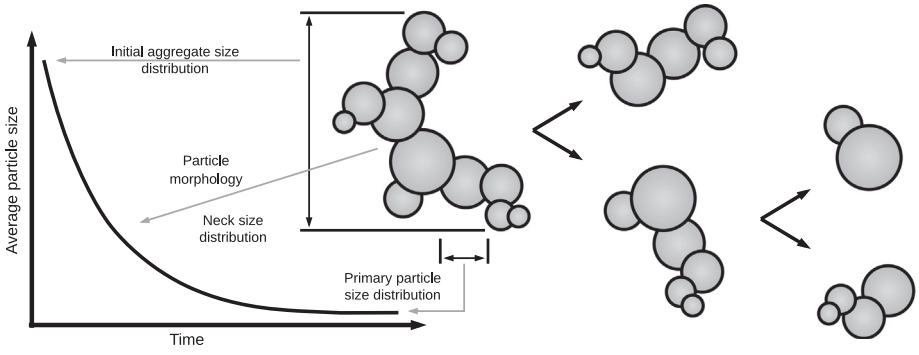
HIGHLIGHTS

- A hot wall titania reactor is simulated using a detailed population balance model.
- Breakage models are developed utilising morphological data from the particle model.
- Models are used to relate reactor conditions to the milling behaviour of particles.

GRAPHICAL ABSTRACT



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ABSTRACT

A detailed population balance model is used to relate the reactor conditions of flame synthesised titanium dioxide particles to their milling behaviour. Breakage models are developed that utilise morphological data captured by a detailed particle model to relate the structure of aggregate particles to their size-reduction behaviour in the post-synthesis milling process. Simulations of a laboratory-scale hot wall reactor are consistent with experimental data and milling curves predicted by the breakage models exhibit features consistent with experimental observations. The selected breakage model considers the overall fractal structure of the aggregate particles as well as the neck size between neighbouring primary particles. Application of the model to particles produced under different reactor residence times and temperatures demonstrates that the model can be used to relate reactor conditions to the milling performance of titanium dioxide particles.

1. Introduction

Titanium dioxide (titania, TiO_2) particles are an important industrial product. The functionality of the product is strongly influenced by the size, shape, morphology and crystalline phase of the particles. The oxidation of titanium tetrachloride ($TiCl_4$) in a flame or oxygen plasma is a key route for the industrial manufacture of TiO_2 particles. Although the industrial manufacturing process is widely used, optimisation remains largely empirical. In many cases, the product is milled in order to control the final particle size distribution (PSD). This imposes an additional time and energy cost.

Detailed population balance models provide a tool to investigate how process conditions affect the particle properties (Shekar et al., 2012a,b). Such models are, within reason, able to include an arbitrarily detailed description of each particle. This facilitates the simulation of quantities that are directly comparable to

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experimental observations. Most importantly, it also enables the option to include key physical details in the model. For example, models where the particle growth is a function of the aggregate composition (Celnik et al., 2008, 2009), or, as is the case in this work, where sintering and neck growth are resolved on the basis of individual pairs of neighbouring particles (Morgan et al., 2008; Sander et al., 2009, 2011).

Milling has been widely studied due to the high industrial demand for fine powders with tightly controlled properties. A lot of research has focused on identifying optimal milling parameters such as agitation speed, milling media size, filling ratio and suspension concentration. The effect of operational parameters on the milling performance of titanium dioxide has been investigated for fine grinding and dispersion of particles in wet stirred mills (Ohenoja et al., 2013; Bel Fadhel et al., 1999; Inkyo et al., 2006). Other work has studied the substructure and mechanical properties of titania agglomerates (Gesenhues, 1999), and the changes in fractal morphology of dense aggregates under wet milling (Jeon et al., 2015).

Population balance models have also been used to characterise the milling process, and identify breakage mechanisms in wet stirred media milling (Varinot et al., 1997; Berthiaux et al., 1996a; Hennart et al., 2009, 2012) by fitting Kapur's approximate first order solution (Kapur, 1970) to experimental data. More complex models consider non-linear effects and time-variant PBMs (Bilgili and Scarlett, 2005; Bilgili et al., 2006).

Over long milling times and for sub-micron sized particles more complex phenomena are typically observed. This includes time delays in breakage (Bilgili et al., 2006), and grinding limits due to a minimum obtainable particle size and agglomeration effects (Frances, 2004; Inkyo et al., 2006; Sommer et al., 2006; Hennart et al., 2012). Modelling multimodal particle size distributions with statistical laws has been used as an alternative method for obtaining the grinding kinetics (Bel Fadhel et al., 1999; Frances, 2004).

The purpose of this paper is to develop a breakage model utilising the morphological data captured by a detailed particle model. This allows us to relate the reactor conditions during particle synthesis to the milling performance of TiO_2 particles. Particle synthesis is simulated using a detailed population balance model outlined in Section 2 that describes the time evolution of the internal structure of the fractal aggregates. The simulation results are post-processed using a breakage model developed in Section 3 to provide proof of concept that the morphological data in the detailed model can be related to milling behaviour. Five different breakage models are compared.

2. Computational details

A detailed population balance model coupled to a gas-phase kinetic model is used to simulate the synthesis of the TiO_2 particles. The kinetic model for the formation of TiO_2 particles from $TiCl_4$ is based on the mechanism proposed by West et al. (2009). It comprises 28 gas-phase species and 66 reactions. The dynamics of the population are described by the Smoluchowski coagulation equation with additional terms for particle inception, surface growth and sintering. The mathematical details of the model and methods are described in detail elsewhere (Shekar et al., 2012b), so only a brief summary is given here.

2.1. Particle model

The description of each aggregate in the population balance model (formally known as the type space) is illustrated in Fig. 1. Each aggregate is composed of primary particles, where neighbouring particles may be in point contact, fully coalesced or anywhere between. The model resolves the common surface area between each pair of neighbouring primary particles. The primary particle composition of an aggregate is polydispersed where each primary is described in terms of the number of TiO_2 units, from which the mass and volume are derived.

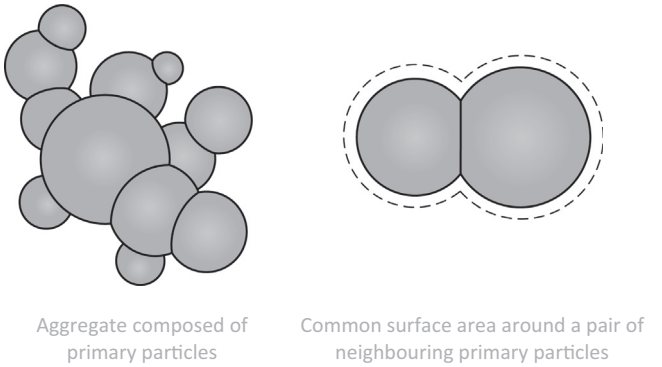

Fig. 1. An illustration of the type space of the detailed particle model showing an aggregate particle composed of polydispersed primary particles (left panel). The level of sintering between primary particles is resolved by a common surface area (dashed line in right panel) for each pair of neighbouring primaries.

2.2. Particle processes

2.2.1. Inception

Inception, modelled as per Akroyd et al. (2011), is assumed to be collision-limited and result from the bimolecular collision of gas-phase titanium oxychloride species

$$\mathrm{Ti}_{x_\alpha}\mathrm{O}_{y_\alpha}\mathrm{Cl}_{z_\alpha} + \mathrm{Ti}_{x_\beta}\mathrm{O}_{y_\beta}\mathrm{Cl}_{z_\beta} \rightarrow (x_\alpha + x_\beta)\mathrm{TiO}_{2(\mathrm{s})} + \left(\frac{y_\alpha + y_\beta}{2} - x_\alpha - x_\beta\right)\mathrm{O}_2 + \left(\frac{z_\alpha + z_\beta}{2}\right)\mathrm{Cl}_2, \quad x, y, z \geqslant 1, \tag{1}$$

where the molecular collision diameter is taken as 0.65 nm (West et al., 2009). An inception event creates a particle consisting of a single primary composed of $(x_\alpha + x_\beta)$ TiO_2 units.

2.2.2. Surface growth

Surface growth is treated as a single-step reaction as in Akroyd et al. (2011)

$$\mathrm{TiCl}_4 + \mathrm{O}_2 \rightarrow \mathrm{TiO}_{2(\mathrm{s})} + 2\,\mathrm{Cl}_2, \tag{2}$$

with the rate expression

$$\frac{\mathrm{d}[\mathrm{TiO}_2]}{\mathrm{d}t} = k_\mathrm{s} A_\mathrm{s} [\mathrm{TiCl}_4][\mathrm{O}_2], \tag{3}$$

where A_s is the surface area per unit volume of the TiO_2 population and k_s has an Arrhenius form

$$k_\mathrm{s} = A\ \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \frac{\mathrm{m}}{\mathrm{s}} \cdot \frac{\mathrm{m}^3}{\mathrm{mol}}, \tag{4}$$

with activation energy E_a and pre-exponential factor A. One surface growth event adds one unit of TiO_2 to the particle. Eq. (3) assumes fixed reaction orders with respect to $TiCl_4$ and O_2. Alternative models for the rate of surface growth are discussed by Shirley et al. (2011).

2.2.3. Coagulation

An aggregate is formed when two particles stick together following a collision. The rate of collision is calculated using the transition regime coagulation kernel (Patterson et al., 2006a)

$$K_\mathrm{tr} = \left(\frac{1}{K_\mathrm{sf}} + \frac{1}{K_\mathrm{fm}}\right)^{-1}, \tag{5}$$

where the slip flow and free molecular kernels are