



Investigation of rate-limiting steps during granulation with a chemically reactive binder



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ABSTRACT

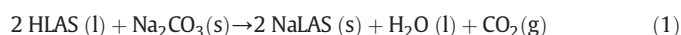
The system of dodecyl-benzenesulfonic acid as a binder and sodium carbonate powder as primary particles is considered in this work, motivated by the so-called dry neutralization process used in the manufacture of powder detergents. The measurement of dry neutralization kinetics in a laboratory-scale mechanically agitated reaction vessel is described. The volume of evolved carbon dioxide, which is a by-product of the neutralization reaction, has been used for following the reaction kinetics, and the effect of selected key parameters on the progress of the reaction has been investigated. These include process temperature, size distribution (thus specific surface area) of the primary particles, agitation rate and the binder/solids ratio. The overall conversion of the reaction and the properties of the formed granules (size distribution, internal structure and porosity) have been evaluated in each case. Hypotheses about the rate-limiting steps in each stage of the process – which can be the rate of binder spreading, the availability of fresh solid surfaces, the diffusion rate of reaction components near the interface, or the intrinsic reaction kinetics – have been proposed based on kinetic parameters evaluated using a mathematical model. Knowledge of the rate-limiting step is a pre-requisite for making rational process control decisions.

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1. Introduction

Binders used in wet granulation can be grouped according to the mechanism by which they solidify as solution binders (e.g. aqueous solutions of polymers or water itself), melt binders, and reactive binders [1–3]. While the kinetics of binder setting in the former two cases can to a large extent be controlled by the process parameters directly (drying rate or cooling rate) [4], in the reactive case the rate of phase change is more or less spontaneous and driven by the kinetics of local reaction–diffusion processes near the binder–particle interface. Investigation of granulation-related phenomena such as binder spreading, particle collisions, nucleation and granule growth [5] is thus further complicated by the simultaneously occurring chemical reaction and the change of physicochemical properties of the binder that are associated with it. A two-way coupling exists between granulation and reaction kinetics: the evolving structure of the granules being formed influences the solid–liquid contact area to which the overall reaction rate is proportional, and the reaction influences the viscosity and other properties of the binder, which control its spreading on primary particles and ability to dissipate the kinetic energy of inter-particle impacts.

An industrially important technology involving a chemically reactive binder is the production of sodium dodecyl-benzenesulfonate (NaLAS) for powder detergents [6–9]. NaLAS is currently one of the most common anionic surfactants thanks to its favorable physicochemical properties, biodegradability [10] and compatibility with other formulation components [11]. Industrially it is produced by a reaction of dodecyl-benzenesulfonic acid (HLAS) with a neutralizing agent, which is sodium carbonate (Na_2CO_3) in the case of granulation. The chemical reaction is then called dry neutralization since the base is in the solid phase and the stoichiometric equation of the reaction can be written as:



During dry neutralization in a reactive granulator (often a horizontal axis mechanically agitated vessel) [8,12] the drops of the acid are sprayed into an agitated bed of Na_2CO_3 primary particles. The acid wets and spreads over these particles creating a viscous layer in which the neutralization reaction occurs (see Fig. 1). This layer absorbs the kinetic energy of other particles during collisions and helps create larger agglomerates. Therefore the acid acts not only as a reactant but also as a binder. Since the physico-chemical properties of this binder change as a function of conversion during the reaction, there is a close coupling between the reaction kinetics and the kinetics of granulation. The progress of the chemical reaction has a direct influence on the granule properties such as composition, particle size distribution, porosity, or strength,

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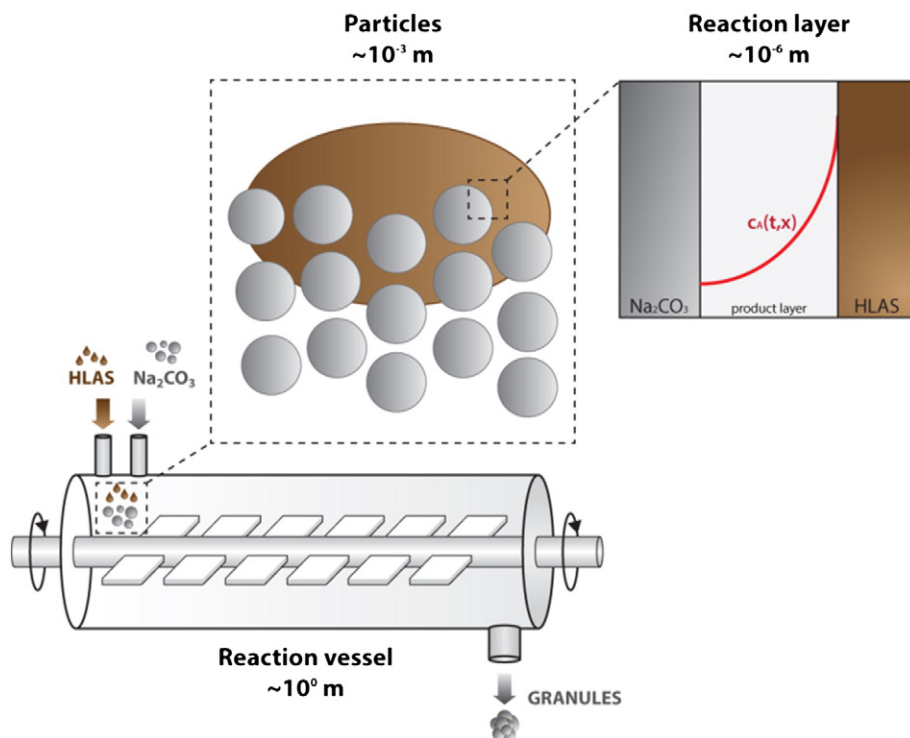


Fig. 1. Characteristic length-scales of elementary rate processes taking place in reactive granulation.

but at the same time the granule properties – in particular the solid–liquid contact area – have an influence on the reaction rate.

In order to design and control the reactive granulation process, it is important to have both qualitative understanding and quantitative description of the elementary processes (i.e. binder spreading on primary particles and binder setting due to chemical reaction) taking place during reactive granulation. The wetting of model primary particles by pre-neutralized HLAS mixtures was described in detail by Germaná et al. [13,14]. The kinetics of the reactive wetting of a static sodium carbonate pellet by a macroscopic dodecyl-benzenesulfonate acid droplet was recently investigated by Schöngut et al. [1]. One of the main conclusions from that work was that the chemical reaction proceeds long after the formation of a product layer (NaLAS with H₂O) at the carbonate surface, which means that the reaction components are capable of diffusing through the liquid crystalline “passivation” layer [15]. In a follow-up work that considered reactive granulation in a mechanically agitated powder bed [2], a reaction kinetic model of dry neutralization has been developed and compared with experimental data with a very good agreement.

The aim of the present work is to investigate the parametric sensitivity of the reactive granulation process with a view of identifying the rate-limiting step. In general, the progress of the neutralization reaction can be limited by the intrinsic reaction kinetics (the rate-constant was shown to follow Arrhenius dependence on temperature [1]) or by the availability of fresh surface area of the carbonate particles, which depends on the binder spreading kinetics (spontaneous due to capillary forces or forced by mechanical agitation) and on the particle size. The extent to which the above parameters influence the conversion of the neutralization reaction and the final granule properties (size distribution and porosity) has been investigated by using narrow sieve fractions of sodium carbonate powder as the primary particles, and in each case systematically varying temperature and agitation rate in order to control the specific surface area, intrinsic reaction kinetics and binder spreading kinetics, respectively. Inferences about the rate-limiting step in each case can be drawn on that basis.

2. Materials and methods

The measurements of neutralization kinetics during reactive granulation were carried out in a flat-bottom Erlenmeyer flask (55-mm base diameter, 120-ml volume) with agitation provided by a magnetic stirrer (50-mm length) and heating provided by a heating plate. The experimental set-up is shown schematically in Fig. 2 and the physical properties of the reaction components are given in Table 1.

Two narrow size fractions of sodium carbonate powder were prepared from a commercial material (purchased from Lach-Ner, Czech Republic) using a set of laboratory sieves: fine (25–56 μm) and coarse (71–100 μm) in order to study the effect of surface area on reaction kinetics. The mean particle sizes for the fine and the coarse particles were 40.5 and 85.5 μm , respectively. The SEM images of the primary particles are shown in Fig. 3 and their specific surface area, calculated from the mean particle size assuming the equivalent sphere approximation, was 27.6 $\text{m}^2 \text{kg}^{-1}$ and 58.4 $\text{m}^2 \text{kg}^{-1}$ for the coarse and fine fraction, respectively (i.e., approximately 100% difference). A constant batch size of 20.0 g of sodium carbonate was used in each experiment, resulting in an initial bed depth of approximately 20 mm in the reaction vessel. Before the addition of HLAS acid, the acid as well as the powder bed were pre-heated to the desired temperature (20, 60 or 100 $^\circ\text{C}$) by a heating plate and maintained at that temperature for the remainder of the experiment. The CO₂ evolved during the reaction was collected in a graded cylinder and its volume as function of time evaluated from time-lapse images of the liquid level in the cylinder. This method was validated by generating known quantities of CO₂ using a homogeneous (liquid phase) neutralization reaction. Although the reaction is exothermic, the heat capacity of the batch and the glassware was such that no significant temperature rise occurred as a result of the reaction.

Dodecyl-benzenesulfonic acid (purchased from Acros Organics, a mixture of C₁₀–C₁₃ isomers) was added drop-wise using a medical syringe with its needle diameter of 0.9 mm to maintain a good balance between flow of the highly viscous acid and droplet size for good binder distribution. The syringe was always pre-heated in a water bath to the

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