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Acoustic emission during the solvent mediated cooling crystallization of citric acid

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ABSTRACT

The potential of Acoustic Emission (AE) for controlling crystallization processes is investigated. The sensing technology is successfully applied to monitor the batch cooling crystallization of citric acid (CA) in water. The solvent-mediated phase transition between the anhydrous and the monohydrated forms of CA is clearly detected from the recorded acoustic measurements. A tremendous amount of acoustic data is recorded by the equipment, and the analysis of the data is focused on the evaluation of AE as a new sensor for monitoring the basic steps of the crystallization processes (i.e., nucleation, growth, phase transition, etc.) A time- and frequency-domain analysis is presented which shows the wealth of the technique. It is finally concluded that AE allows very early detection of nucleation events, provides a means of monitoring the development of the crystallization process and allows monitoring phase transition phenomena obtained through cooling. It is thus suggested that acoustic emission could be valuable in the development of new crystallization monitoring and control strategies: this is all the more interesting that the acoustic piezo-sensor is non-intrusive and does not require any sampling of the slurry, two features which are of tremendous importance in the field of cooling crystallization processes.

1. Introduction

It is estimated that more than 80% of fine organic chemicals undergo at least one solid processing stage during their manufacture. In particular, as most active pharmaceutical ingredients (API) are processed and marketed in the solid form, solid particles elaboration and processing operations are essential in the fines chemical industry. In this particular industry as in other industries producing high value-added fine chemicals, crystallization is performed using batch processing which, owing to its unsteady-state dynamic features, requires continuous control during time. According to the products in question, crystallization can be essential as a solid-liquid separation, as a purification process, and also as a means of generating particles with specified end-use properties. Indeed, particle features such as the Crystal Size Distribution (CSD), crystal habit, chemical purity, crystallinity and polymorphic state are known to exert a significant impact on the end-use properties of the solid products (e.g., ease of downstream processing: filterability, behaviour on storage, and flowability) This is the reason why improving the control over batch crystallization operations remains a major theoretical, technological and economic issue.

As far as advanced process monitoring is concerned, it is clear that until today no faultless measurement technique is available that would enable quantitative evaluation of quality variables characterizing the solid particles. In particular, this lack is clearly problematic for measuring in-line the CSD as all existing technologies, among which laser diffraction sensors, FBRM (Focused Beam Reflectance Measurement [1, 2], image analysis) … exhibit major limitations depending on the basic features of the slurry (e.g. the solid concentration, and turbidity) and on properties of the particles (e.g. the particle shapes, the fines content, and roughness) This is the reason why in situ sensors are actively being sought that would provide relevant information about the time evolutions of the quality of the solid product in suspension; and about the overall advancement of the process. Moreover, it should be outlined that developing sensing approaches in crystallization processes is all the more difficult that crystallization slurries are necessarily in non-equilibrium conditions: this makes it complex to withdraw solid/liquid samples for reliable external analyses.

Even though its process application in crystallization was not reported, Acoustic Emissions (AE) has shown potential as an efficient process analytical technology (PAT) for monitoring many industrial organic processes, in particular solids elaboration processes. Indeed, changes in physical properties related to both the progress of the process and the time variations of the product quality are likely to generate acoustic emission. This is why, from an industrial point of view, AE offers

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valuable features which are all the more promising that the technique is non-intrusive, non-destructive, and rather easy to implement.

In the past AE has widely been used in many field of process engineering. As far as active acoustic measurement techniques are concerned, a general review paper was published by [3]. Meanwhile, rather few applications of passive AE measurement dedicated to the monitoring and control of industrial processes were reported [4]. To speak only of pharmaceutical processes, and without being exhaustive, the correlation between audible acoustic emission and particle sizes was investigated by [5]. Several case-studies and review papers present AE applications in many fields of pharmaceutical process engineering: grinding [6], end-point detection in drying [7–9,5], blending and mixing [10,11], drying [12,13], fluidized beds [14], granulation [12,15], tabletting [16–18].

The technique of AE uses a transducer acoustically coupled to a process in which materials are undergoing dynamic changes. The sensor detects the elastic energy of acoustic waves propagating from the physical source of AE. The latter arises from mechanical or physical phenomena (fracture, plastic deformation, phase transition, delamination, etc.). Because one single crystal, considered as a physical source of AE, can generate AE, the acoustic signal emitted by developing slurries consists of a mixture of many waves, stretching over several orders of magnitude. This is why the recorded acoustic emissions frequency spectra are generally complex. One can therefore reasonably expect that, depending on the phenomena of interest, relevant information can be extracted, e.g. through frequency and/or multivariate statistical analyses.

As already outlined, a major advantage of the AE technique is that the sensors do not need to be placed inside solids processing equipments (e.g., reactors, dryers, granulators, grinders, and crystallizers The technology can therefore be used in hard process conditions, for example in high temperature and/or high pressure conditions, corrosive media and outside environments where the growth of pathogenic organisms takes place. Another advantage of AE lies in the possibility of collecting a wide range of information in real-time.

As far as crystallization is concerned, thanks to the large amount of collected data, one can reasonably expect AE to help designing new approaches for gaining a new point of view on basic crystallization phenomena (i.e. nucleation, growth, agglomeration …), to increase process understanding and provide a basis for innovative online monitoring and control applications. Wade [19] proposed that during crystallization in solution local physicochemical changes are induced in the suspension, yielding release of energy. AE waves would be thus generated and propagate in the liquid medium. It is clear, for example, that when crystal particles are generated, the elastic properties of dispersed phase change. Inter-particles and/or particles-wall frictions can also occur and generate size-dependent acoustic emission. Other particle properties such as shape, hardness or brittleness can also affect the elasticity of the dispersed phase and its kinetic energy.

In such a context this work aims at evaluating the potential for using acoustic emission to monitor batch cooling solution crystallization processes. In particular the ability of the AE technology for detecting specific event such as nucleation phenomena or phase transition is assessed. With this aim in view, the cooling crystallization of citric acid (CA) in water was selected as a model-system. Contrary to a previously reported study performed with ammonium oxalate in water [20], the present system offers the possibility of working with highly concentrated suspensions and to study solvent mediated phase transition phenomena occurring around ambient temperature.

2. Introduction to acoustic emission

The AE equipment consists of a piezoelectric sensor fixed on the wall of the crystallizer [21,22]. The sensor is connected to a fast data acquisition system dedicated to the processing of the many recorded pseudo periodic acoustic signals [23]. The latter are generated by the numerous crystals in suspension which are assumed to behave like tiny physical sources of emission. The acoustic signals propagate via the solution, the crystallizer wall and the heating/cooling external fluid, to the sensor where they are converted into electronic information. For further data processing, the electronic signal is converted into numerical information.

Acoustic emission waves appear as a sequence of a considerable number of "bursts" which are schematically illustrated in Fig. 1. Some important features of the waves are explained in Fig.1. In order to differentiate significant hits from unavoidable noise, a reference level of energy (about 600 a-Joules) and a threshold power ratio value (40 dB) have to be determined first from "blank" measurements performed to evaluate the level of insignificant signals emitted e.g. by the electromagnetic environment, the stirring system and the flow of coolant fluid in the jacket of the crystallizer.

Rather than recording the many raw acoustic measurements (several Go/h), global AE parameters can be computed to avoid recording too large a number of data. For example, a given acoustic wave can be characterized after integrating the output signal exceeding a given threshold or after computing its average and/or the number of counts *n*. (see Fig. 1). Such global parameters characterizing the waves are called descriptors. The integrated Absolute Energy (IAE) is a measure of the true energy derived from the integral of the squared voltage signal emitted by the sensor, divided by the reference resistance (10 kΩ) over the duration of the AE signal. Another basic parameter used to characterize the level of acoustic signals in the time domain is the root mean square value (RMS) defined as the integral over time of the square of the pressure magnitude, p(t), of the acoustic wave. Working with descriptors is made easier than working with raw pseudo-periodic data, and less CPU time is spent because the descriptors can be processed without requiring prohibitory amounts of data. Some definitions of important descriptors are introduced in the following.

As displayed in Fig. 1, $p(t)$ is actually evaluated from the electrical voltage $u(t)$ emitted by the acoustic transducer and amplified by the sensing device, such that: $u(t) \propto p(t)$.

The amplitude AdB is defined as the maximal voltage of the AE signal divided by the reference voltage of the sensor which, in our case, is equal to 1 μV. It is thus defined as follows:

$$A_{dB} = 20\log(u_{\max}/u_{ref}) \tag{1}$$

The average frequency $\overline{f}$ is defined as the average ratio between the number of counts n and the duration of the burst:

$$\overline{f} = n/d \tag{2}$$

The peak frequency *f*, expressed in kHz, is defined as the point in the power spectrum at which the peak magnitude is observed, and the

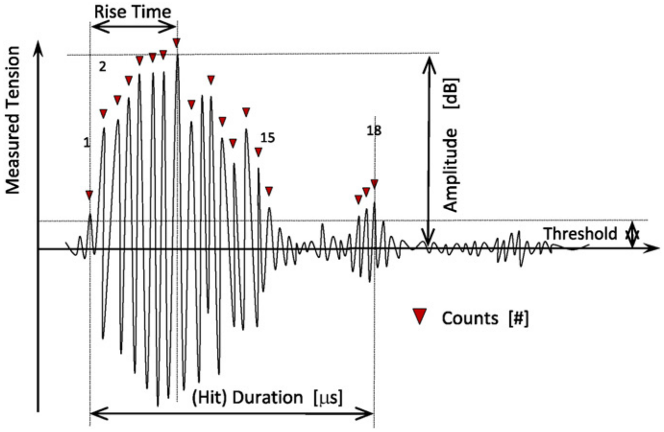

Fig. 1. Main characteristic parameters of a typical AE burst.