Crystal Nucleation Control Using Microscopic Online Imaging

Tod Canty,
President

Jena Woodward,
Technical Support

J.M. Canty,
6100 Donner Road
Buffalo NY 14094

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ABSTRACT

Historically, imaging of crystallization processes has been limited by lighting capabilities, physical size restrictions created by high resolution optics, and the subsequent inaccuracies that occur due to post-process analysis. An innovative method of inline microscopic imaging has been developed to allow crystal viewing and measurement of size, shape, color, and concentration in batch or continuous lab reactors, pilot plant crystallizers and full production vessels at pressure (10,000 psi) and temperature (-450° to 800° F). The high resolution images presented will show how this technology successfully overcomes the limitations of other systems where particle resolutions are limited due to limitations of front lighting schemes, even though the optical lenses are capable of higher pixel resolution. The particle imaging system captures high resolution, 2-megapixel images down to .7 microns at camera shutter speeds as fast as 1/100,000 of a second, all while using fiber optic, back lighting. This intense illumination allows for viewing through a wide variety of fluids (crude oil, polymer, inks, paints, etc.) at velocities through10ft/sec. The software captures suspended particulate and analyzes for size and shape of particles, compiling the data to determine particle distribution by length, width, or volume along with PPM concentration. Process development personnel can employ lab based analyzer systems that allow the user to optimize the seeding process to provide best yield and filterability.

INTRODUCTION

In the chemical industry and beyond it is critical to monitor and control crystallization processes in order to improve quality and yield at minimum consumption of resources which ultimately leads to increased profitability. Historically, imaging crystallization has been restricted to post-process analysis. The lag between production and analysis can result in very costly losses when the crystal formation is not ideal. Sampling during the process run creates a different environment between sampled product and product remaining in the reactor. Differing conditions of temperature and pressure, for example, can lead to agglomeration of crystals. Turbidity is often used to measure the abundance of crystallization present, however it is extremely limited. This type of batch measurement lends no information about the nucleation process, nor does it reveal the size or shape of seed. Only an estimation of seed population can be extracted from turbidity data. Inverted microscopes have more ability to see down to one micron; however their inefficient lighting limits precision of measurement. The Canty Vision Systems offer online, real time analysis of crystallization and outputs invaluable particle size, shape, and distribution data, as well as concentration and visual verification. Using high resolution cameras in combination with unparalleled advanced lighting techniques, data can be collected down to .7 microns. Crystallization can be monitored from the point of nucleation up through full growth.

HISTORICAL BACKGROUND

Turbidity has been extensively used as a basic way of determining the degree of crystallization based on the reflectivity of the material being analyzed. This proves to be extremely limited however. While this type of batch crystallization analysis does indeed show degree of crystals formed, it does not provide any indication as to the size or polymorph of the seed being used in the nucleation process. Turbidity fails to identify the start of the nucleation process which is critical to controlling the seeding process. Particle Vision Measurement (PVM) and Focused Beam Reflectance Measurement (FBRM) offer improvements in analysis of crystallization in that they allow for analysis in-process. PVM involves a probe emitting six laser beams in the vessel which provides the user with real time image. FBRM involves a probe that emits a laser beam which in effect measures reflectivity back to the beam through a substance and translates this into a chord length. A series of chord lengths can then be created into a chord length distribution chart, the primary data derived from the FBRM method. Ineffective front-lighting weakens the efficiency of these methods as well by only showing a silhouette of particles. PVM and FBRM are limited when it comes to detecting particles in the low-resolution range, which inhibits the ability to detect the start of nucleation. Inverted microscopes have a greater ability to detect smaller particles, however they do not provide the most effective lighting and are not cost efficient. There has been a clear demand for a method of real time, online analysis of crystallization that can see below 1 micron and with no upper limit.

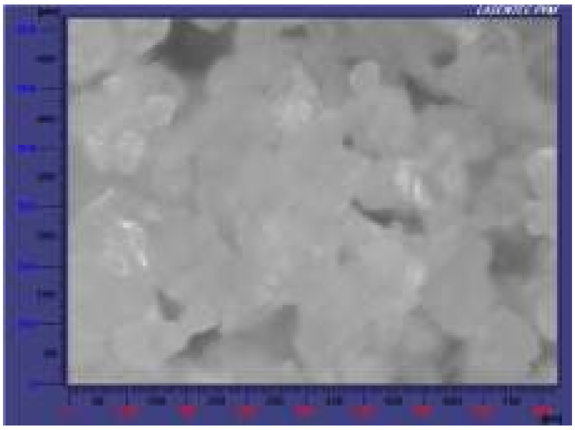

Figure 1, PVM data. Inability to analyze <50 microns, unable to capture individual particle parameters

INNOVATIVE ADVANCES

The way crystallization is observed was revolutionized with the advent of the SugarScope, a high speed video system that captures and displays live video images of sugar crystals in a sugar pan under process conditions. This enabled monitoring without disrupting pressure and temperature for sampling.

Figure 2, SugarScope

The fundamentals of the system include the fused glass lens technology together with high intensity illumination and high speed, high resolution video capability.

The fuseview lens creates a rugged, high pressure boundary for the camera and light to see through. The glass surface is polished to a mirror finish and because it seals flush with the metal lens tube (or front cap) there are no gasket sites where contamination can build and obscure the view.

Bright, consistent illumination is another vital component of the system. High speed video requires extreme illumination due to the brevity of the shutter opening. This enables the camera to clearly see particulate in a consistent manner so that results are also consistent from analysis to analysis. High speed, high resolution vision continues to develop and enhance the analysis capabilities of the system.

Figure 3, Glass Reactor Microscope

The SugarScope is still in use today, and is joined by two more recent advancements for particle analysis: the Glass Reactor Microscope and the InFlow particle analyzers. The Glass Reactor Microscope, or GRM, is designed for laboratory use and has the same measurement capabilities as the SugarScope and includes thermal control, mixing/agitation and access for additional instrumentation through the lid.

Development of this instrumentation has brought high powered optics to fruition as an inline tool for particle analysis. Accurate imaging of particles down to the wavelength of light is possible in real time. Such accurate technology allows for precise detection of the onset of nucleation, the determination of both the number and size of particles at that point, and most importantly allows the user to pinpoint the optimal level of seed needed for nucleation. Once seeding is controlled, the remainder of the crystallization process can be controlled more accurately.

A second benefit of the vision technology is the capability of the user, and/or the software, to image the size of the crystals formed. It is crucial that the user can clearly identify the shape of crystals from the immediate start. The software can be used to identify in real-time the quality of the crystalline structures that are growing in the reactor. Uniform crystals with a small dispersion of size distribution are ideal. The generation of fines and fractured or fragmented crystals are not desirable. When this occurs, changes in process parameters can be made or the batch can be shut down thereby saving the expense of continuing the production of bad product.

Thirdly, in order to provide reliable data the software must be quite adept at sizing particles as well as assessing shape. The shape information, which can be done accurately by vision technology, is what enables the software to sort through the various captured particles and discern good product from bad. This is done by using a variety of parameters recorded by the software.

Figure 4, Canty InFlow

Figure 5, CrystalScope

The software collects and records a multitude of shape features during analysis. The major and minor axis, as well as area and perimeter are generated. A maximum and minimum equivalent circle diameter is recorded for each particle, which interpolates the largest and smallest circle that could fill the particle, respectively. Centroid diameter is calculated, as well as fiber length which is an extensional calculation of each particle. Color values in a RGB scale are recorded. Aspect ratio is a particularly useful parameter that creates a ratio of major axis to minor axis. Perimeter gradient is a grayscale number between 0 and 255 which indicates the strength of the edge of each particle, and allows for easy filtration of background particles. Circularity is automatically generated, which is a calculation of (4*Pi*Area)/(Perimeter/Perimeter). All of these parameters can be controlled in the Particle Filters tab of the software and allows for custom analysis of a multitude of applications, see Figure 6. For crystallization, the user can determine which parameters will distinguish their ideal product from bad product, and filter accordingly.

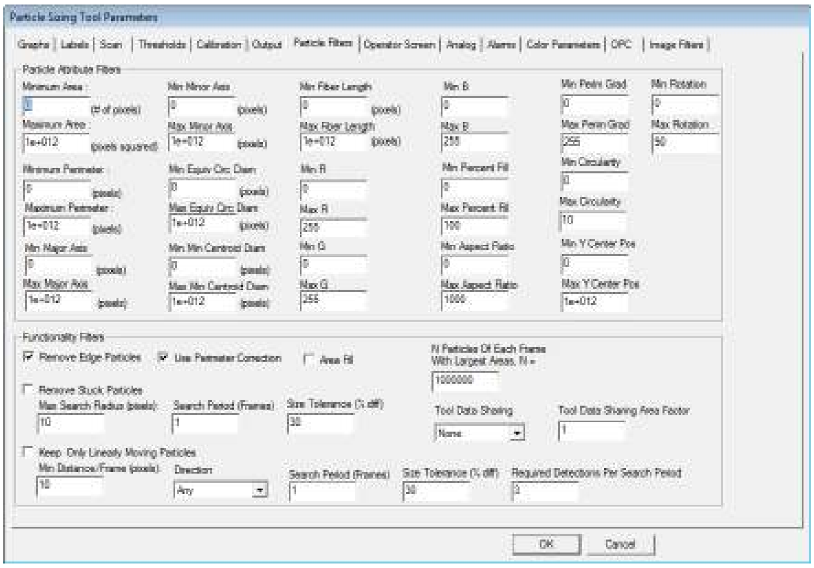

Figure 6, Particle Sizing Tool Parameters

Data is displayed in graphs, bin analysis, and tables through the software. Data can also be outputted through a 4-20 mA connection, OPC interface, Modbus, to a database, and various other options. The different vision system options allow for both batch and continuous analysis options. The vision based system has the ability to continuously measure the size and shape of the production. This measurement enables efficient process control so that optimal product streams are produced. Better process control leads to cost savings as less oversized or undersized product is made.

SUCCESSFUL APPLICATIONS

Examples of successful implementation of vision technology to the crystallization process are now presented to illustrate the capabilities. The first application presented is a process development exercise carried out in a lab-based reactor system. The issue needing resolution was the determination of seeding levels required for a range of process parameters. By simulating the process conditions variable seed rates were tested to determine the initial point of nucleation and the subsequent addition rates to yield an optimum product quality. A second example is shown progressively in Figures 8-10 where the crystal growth is seen at a very early state, through mid-development and up to final crystal formation. This example was conducted in an in-process setting.

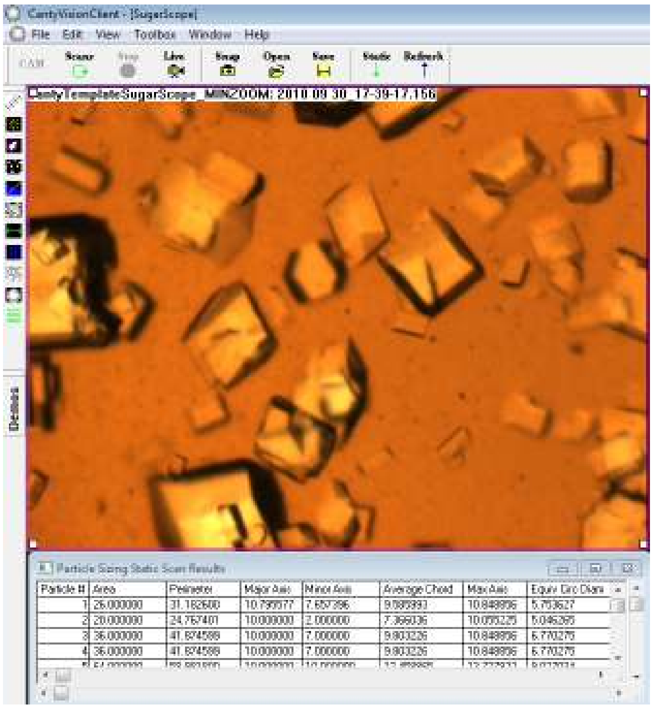

Figure 7, crystal analysis in the software

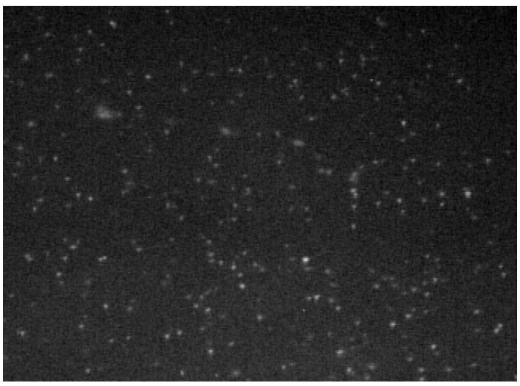

Figure 8, primary nucleation

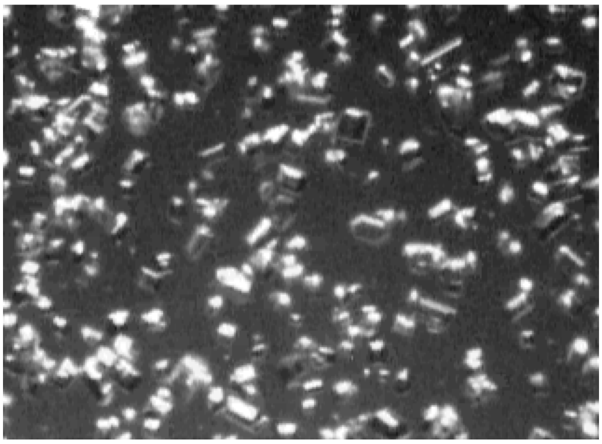

Figure 9, crystal growth

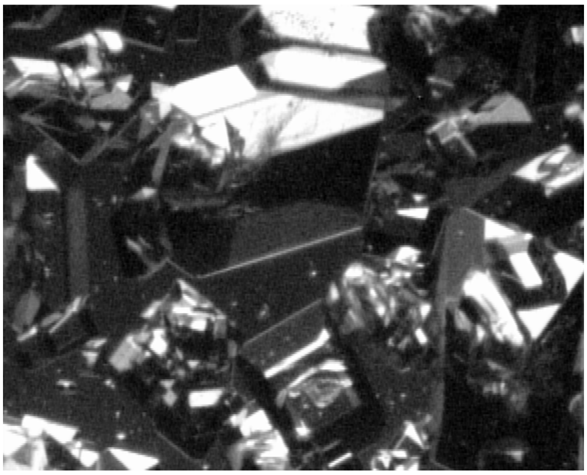

Figure 10, final crystal formation

CONCLUSION

Vision based systems that present 2-D particle size analysis offers the best and most accurate data for the crystallization process. This type of in-process analysis allows for improved quality and yield of product. Previous technologies lack sophisticated lighting and utilize front lighting, which limits their ability to image very small particles. Particle imaging systems capture high resolution images down to .7 microns, allowing one to identify the precise moment nucleation begins. Fiber optic backlighting allows for the most accurate and efficient imaging. The software is able to analyze particles based on a myriad of parameters and outputs particle distribution by length, width, volume, or ppm concentration. This system allows the user to optimize the seeding process and control nucleation, which in effect enhances filterability and yield.