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POWDER & BULK SOLIDS

Practical Low-Temperature Size Reduction

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Size reduction of solid materials may be one of the most important technologies in the modern world. Coal that is pulverized to the size of talcum powder fuels the generators that supply over 45% of the electric power in the U.S. and over 40% worldwide. Size reduction is a key process step in making cement and extracting metals from their ores. Rocks are crushed to create the gravel used to build roads. A variety of biological products are ground to make powders, such as flour and spices. Size reduction is also a key step in the production of modern, high-tech ceramics and pigments, such as titanium dioxide, used in paints and coatings. Additionally, organic compounds, including dyes and inks, drugs, and polymers are routinely pulverized.


Size reduction lab

Size reduction presents the technologist with two significant challenges. First, the physical properties of many materials are not conducive to size reduction at ambient temperatures. Examples of these materials include many biological products, such as spices or food additives; materials made from polymers, such as powder coatings, recycled rubber, and many rotational molding compounds; and organic materials with melting points that are close to ambient temperature. Many biological materials with high levels of hydrocarbon materials, such as waxes or oils, cause buildup in size reduction machines that will quickly block a hammermill's screens and stop production. Rubber and other polymers can be especially difficult to pulverize at ambient temperatures because of the viscoelastic nature of their physical properties.

The second challenge is that size reduction is a relatively inefficient consumer of energy. A majority of the mechanical energy supplied to a size reduction machine is converted into heat. This heat may damage heat-sensitive materials or even result in undesirable reactions. For example, the heat generated from grinding can cause spices to lose their essential oils, distort their aroma and flavor profiles, and alter their color, all of which reduce the quality of the spices.

Cooling the size reduction process is an accepted technology for overcoming these challenges. In many cases, the size reduction process must be cooled to a temperature that is substantially below ambient temperature. For example, Luff and Kazarnowicz teach that a temperature range of -130˚F to -256˚F should be used for pulverizing thermoplastic coated fabrics in US Patent 4,483,488.[1] Singh and Goswami found that cumin ground at temperatures below -76˚F retained higher amounts of volatile oils than cumin ground at temperatures of -40˚F and higher.[2]

Liquid nitrogen is a convenient and economical source of the refrigeration required to achieve these low temperatures. Liquid nitrogen can be used to cool materials being ground, the size reduction equipment, or both. For example, pre-cooling an oily biological product using liquid nitrogen will eliminate product buildup in the pulverizer. This will allow production to proceed without interruption and may even facilitate an increase in production rates.

Process Implementation

Liquid nitrogen offers a number of features that are attractive to processors trying to grind challenging materials. Liquid nitrogen looks like water but is much colder. Liquid nitrogen has a boiling point of approximately -320˚F at one atmosphere pressure compared to the 212˚F boiling point of water. This means that liquid nitrogen can be used to cool materials that require very low processing temperatures. Nitrogen is inert and does not react with other substances or support combustion under normal conditions, so adding nitrogen to a size reduction operation can help make the operation safer.[3]

Liquid nitrogen can be supplied in portable, double-walled vacuum insulated stainless steel containers known as dewars. Dewars are typically used to supply laboratory and pilot-scale operations. Liquid nitrogen can also be supplied from a vacuum insulated storage tank located on the processing site. This tank would be refilled by the liquid nitrogen supplier via a tank truck and is suitable for production-scale requirements.

Figure 1 is a simplified diagram of a continuous, pilot, or production-scale system for low-temperature pulverization. This system consists of the following major pieces of equipment:

- Liquid nitrogen supply system. The diagram is for a production-scale system that uses enough liquid nitrogen to require an on-site liquid nitrogen storage tank. Insulated piping between the tank and the pulverizing equipment would also be required.

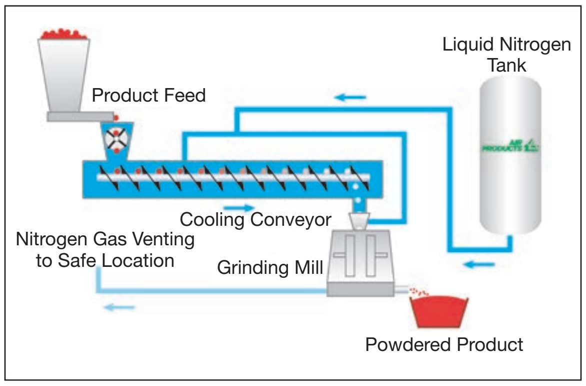

Figure 1

- Product feed system to supply feedstock (unpulverized material) to the system at a controlled rate
- Product cooling system. In this simplified diagram, the cooling system is a modified screw auger.[4] This cooling system could also be a large cooling “tunnel” for high throughput systems or a simple insulated container of liquid nitrogen for a laboratory system. Liquid nitrogen is sprayed onto the feedstock as the material is conveyed along the length of the screw auger. The liquid nitrogen will cool the warm feedstock to low temperatures. In turn, the liquid nitrogen will evaporate, creating very cold nitrogen gas. This gas will flow out of the conveyor, through the mill, and out of the system. The cold gas will cool the mill as it flows through it.
- Since liquid nitrogen is added continuously to the size reduction system, a constant stream of nitrogen gas will be generated. This nitrogen gas must be discharged to a safe location outside of any building containing the size reduction system to prevent the formation of an oxygen deficient atmosphere. Oxygen deficient atmospheres can be very dangerous to people if the hazards are not managed safely.[5] The nitrogen gas may contain some dust from the feedstock as the feedstock is pulverized. This dust must be removed from the nitrogen gas before the gas is discharged.
- Pulverizer or grinding mill. With the proper care, many conventional pulverizing machines can be adapted for use in low-temperature pulverization. Turbomills work well in low-temperature applications. Hammermills and pin mills have also worked well in low-temperature applications.
- Control system to regulate both the mechanical equipment of the pulverizing system and the flow of liquid nitrogen to the system
- Wall-mounted ambient air oxygen sensor(s) to detect an inadvertent oxygen deficient atmosphere
- Safety interlock system. The safety interlock system can be incorporated into the control system. A safety interlock system is a key part of any low temperature pulverizing system. Some important safety interlocks include:

1. Any piece of rotating equipment must be closed before the equipment can be started to prevent personal injury. All guards must be in place to prevent contact with rotating or moving equipment.
2. All equipment must be closed before the liquid nitrogen can be started to make sure the nitrogen is contained in the system.
3. The exhaust system and the fresh air make-up system must be operating before the liquid nitrogen can be started.
4. The oxygen level in the room air must be above 19.5% for the liquid nitrogen to continue to flow.
5. The temperature of the equipment must be above any equipment-specific limitations for the liquid nitrogen to continue to flow.

This may not be a comprehensive list of safety interlocks required for a particular system. Conducting a hazard review of each system is recommended before the system is placed into production.

Systems using liquid nitrogen for refrigeration must be designed to operate at low temperatures, approximately -100˚F or colder. The systems, especially the liquid nitrogen supply piping and manifolds, must be well insulated. Insulation is important to minimize the loss of liquid nitrogen refrigerant power to the surrounding environment. Insulation is also required to prevent the equipment operators from coming into contact with the very cold surfaces of the equipment. The low temperatures can cause physical injuries similar to thermal burns. In addition, proper insulation will prevent the formation of liquefied air, a potential fire hazard. For more detailed information on the safe handling of liquid nitrogen, see Air Products Safetygram #16: Safe Handling of Cryogenic Liquids and Safetygram #17: Liquid Nitrogen.[6,7]

As the cryogenic grinding system cools down from ambient temperature during startup, the system components will shrink. For example, a 10-ft length of stainless steel pipe will shrink by more than 0.125 in. as it cools from ambient to -100˚F. This will generate a significant amount of stress on the stainless steel pipe, enough to potentially distort the pipe or its support structure if the pipe is rigidly anchored. A low temperature grinding system must be designed to accommodate this thermal contraction and the significant stresses it will generate.

Many materials typically used in size reduction equipment, such as carbon steel, lose their ductility at low temperatures. This means equipment fabricated from typical materials can fail in an unpredictable brittle fashion during low-temperature operation -- a very hazardous situation. Low-temperature grinding systems must be designed with materials that do not lose their ductility at low temperatures.

Process Optimization

Size reduction is traditionally a highly empirical technology. A longstanding challenge in low-temperature size reduction is predicting the operating conditions -- essentially the operating temperature -- required to achieve brittle fracture of the substrate being processed. Developing the operating conditions can be straightforward with a low molecular weight organic material, such as a wax, or extremely complicated for a biological product, polymers, and materials fabricated from polymers. Using the Glass Transition Temperature (Tg) of the substrate as a target temperature has proven to be inadequate because many polymers are ductile well below their Tg. Traditional tests, such as an ASTM D746, Brittleness Temperature Test, or Izod Impact Test, following ASTM D256 can provide some insight into the fracture response of some but not all of the materials ground at low temperatures. The results of these tests also tend to be qualitative rather than quantitative and are difficult to use to predict operating conditions. Performance testing in a pilot system is highly recommended to develop the low temperature operating conditions.

A typical performance test involves grinding a known amount of material under rigidly controlled conditions in a pilot low-temperature size reduction system. The feed rate, operating temperature, and grinding mill operating parameters should be fixed for each grinding trial. A trial will generate data about the effect of these parameters on the particle size of the powder, the power consumption of the mill, and the amount of liquid nitrogen required to process one kilogram of material.

Ideally, enough material should be provided for the trial to ensure the size reduction system achieves steady-state operation at system loadings that are consistent with the loadings that are expected on a production scale. Pulverizing 100 g of material in a bench-top system would not be expected to generate the quality of data required to design a production system for pulverizing thousands of kilograms per hour. Therefore, the performance test should be conducted on a scale large enough to provide accurate scale-up data to design a production-scale system.

A series of performance tests were conducted on an EPDM (ethylene propylene diene-monomer) rubber to examine the effect of temperature on the particle size of the resulting EPDM powder. The tests were conducted in a low-temperature size reduction demonstration laboratory that is equipped with a production-scale turbo mill system and a pilot-scale hammermill system designed for low-temperature operation. In these tests, the EPDM was pulverized in a PolarFit UFGM Model 200 mill.[8] This mill is equipped with a 20-kw motor and can pulverize materials at production-scale rates on a continuous basis. These tests were conducted at a constant mill operating speed, but varying operating temperatures. The amount of material finer than 212 microns (70 mesh) was used as a metric for the particle

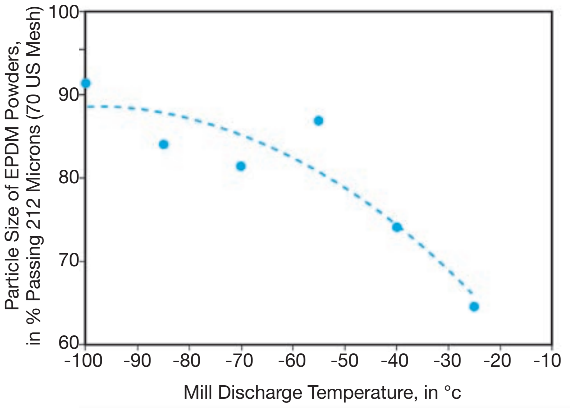

Figure 2

size of the powder. That is, the more material finer than 212 microns, the smaller the powder particle size. Figure 2 presents the results of the EPDM performance tests. The amount of material passing 212 microns increased as the operating temperature decreased. This relationship displayed an asymptotic functionality with the operating temperature. This asymptotic relationship is commonly observed in low temperature pulverization.

Materials will respond differently to low-temperature size reduction. Figure 3 illustrates the results of a series of performance tests studying the effect of the rotational speed of the PolarFit UFGM Model 200 mill on the particle size of three different thermoplastic resins: a plasticized poly(vinyl chloride) resin (PVC), a low-density polyethylene resin, and an ethylene copolymer resin. The PVC tested is an amorphous polymer that was plasticized for improved flexibility. The low-density polyethylene and the ethylene copolymer are partially crystalline polymers. The crystals in these polymers act as cross-links and reinforce these polymers. These performance tests were conducted using the PolarFit UFGM Model 200 mill. The trials were conducted at -100˚F with identical mill set-up arrangements. The amount of material passing 212 microns was used as a metric for the particle size. The PVC was ground finer than both the low-density polyethylene and the ethylene copolymer at any given mill speed. This is consistent with the concept that the crystalline nature of the ethylene polymers toughens these polymers and makes them harder to pulverize than PVC.

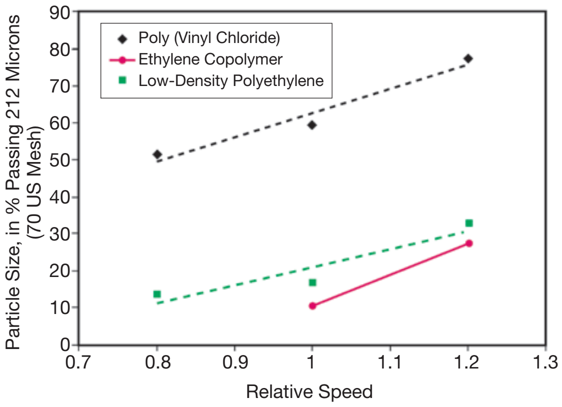

Figure 3

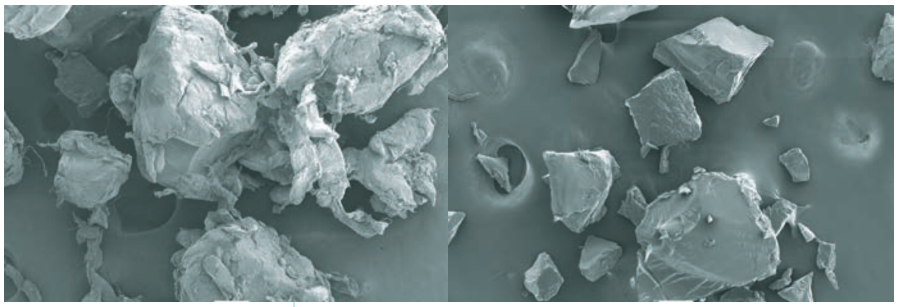

Figure 4 - Micrograph: High-density polyethylene (left) and ethylene copolymer (right)

Figure 3 also illustrates the effect of mill speed on the particle size of the powders. The amount of material finer than 212 microns is directly proportional to the speed of the pulverizer for all of the polymers tested. This result is consistent with results from theoretical studies conducted at ambient temperatures.

Scanning Electron Microscope (SEM) micrographs can provide insight into the low temperature size reduction process. Figure 4 compares micrographs of an ethylene copolymer resin and a high-density polyethylene resin that were pulverized at low temperatures using a PolarFit UFGM Model 200 mill. The high-density polyethylene resin had a higher crystallinity and higher molecular weight than the ethylene copolymer. The high-density polyethylene was much tougher and harder to pulverize than the ethylene copolymer. The micrographs of the powders produced from the two resins were significantly different. The particles of the ethylene copolymer resin were very angular with relatively smooth surfaces. The particles of the high-density polyethylene resin were rounded with rough surfaces that exhibit tearing and the formation of “strings.” The “strings” and surface roughness are indications that the high-density polyethylene fractured in a more ductile fashion than the ethylene copolymer.

Conclusion

Low-temperature pulverization opens up a world of opportunities for manufacturers looking to achieve particle sizes and efficiency rates that would not be possible at ambient temperature. The key to effective scale-up and process optimization is conducting performance tests in a production-scale pilot lab, where process parameters like mill speed and operating temperature can be more accurately determined.

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References

1. Luff, B.A. and M.C. Kazarnowicz, US Patent 4,483,488, “Method and Apparatus for Recovering Thermoplastic From Coated Fabric Scrap”, 1984
2. Singh, K.K. and T.K. Goswami, J. Food Process Engineering, 22, 1999, 175-190
3. Nitrogen can react with some metals at elevated temperatures and can also cause suffocation when present in elevated concentrations as compared with air.
4. PolarFit cryogenic cooling conveyor; Air Products and Chemicals Inc. 2014
5. Air Products and Chemicals Safetygram #17: Dangers of Oxygen-Deficient Atmospheres; Air Products and Chemicals Inc. 2009
6. Air Products and Chemicals Safetygram #16: Safe Handling of Cryogenic Liquids; Air Products and Chemicals Inc. 2010
7. Air Products and Chemicals Safetygram #7: Liquid Nitrogen; Air Products and Chemicals Inc. 2013
8. PolarFit Ultra-Fine-Grinding Mill; Air Products and Chemicals Inc. 2011

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