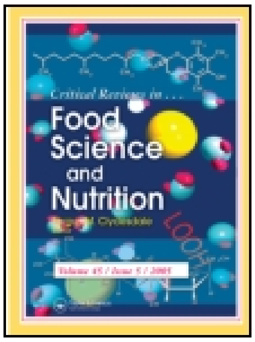

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# Cryogenics and its Application with Reference to Spice Grinding: A Review

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*Cryogenics is the study of very low temperature and its application on different materials including biological products. Cryogenics has numerous applications in space science, electronics, automobiles, the manufacturing industry, sports and musical instruments, biological science and agriculture, etc. Cryogenic freezing finds pivotal application in food, that is, spices and condiments. Although there is a wide range of cryogens to produce the desired low temperature, generally liquid nitrogen ($LN_2$) is used in food grinding. The application of low temperature shows a promising pathway to produce higher quality end product with higher flavor and volatile oil retention. Cryogenic grinders generally consist of precoolers and grinder with the cryogen distribution system. In such grinding systems, cryogens subject the raw material up to or lower than glass transition temperature before it is ground, thus eliminating much of the material and quality hassles of traditional grinding. At present, the capital investment including cryogen and handling costs escalate the final cost of the product. Thus, for large-scale production, a proper design to optimize and make it feasible is the need of the hour and understanding the behavior of different food materials at these low temperature conditions. This article reviews the scenario and application of cryogenics in different sectors, especially to spice grinding.*

**Keywords** Cryogenics, cryobiology, superconductivity, freezing, cryogenic grinding, design considerations, spices, and volatiles

## INTRODUCTION

A Dutch physicist (1894) produced a gas having low boiling temperature, named as cryogen. Cryogens, viz. liquid forms of hydrogen ($LH_2$), helium (LHe), nitrogen ($LN_2$), oxygen ($LO_2$), methane ($LCH_4$), carbon dioxide ($LCO_2$), etc., boil at cryogenic temperatures at atmosphere pressure. $LH_2$ and $LO_2$ are used in rocket propellant and $LN_2$ and $LCO_2$ in liquid or solid form are the major cryogens used for food applications. After World War II, the probable first use of cryogenics was to increase the life of weapons and their operational efficiency. Cryogenics has many applications in industry, defense, and space programs and in the new field of cryogenic engineering. Though $LN_2$ has been used for many decades as a refrigerant, in recent years its widespread applications in almost every branch of science, viz. electronics, space technology, biology, medicine, superconductivity, vacuum technology, sports and musical instruments, and food and agriculture are remarkable.

Cryogenic freezing offers unique benefits including higher cooling rates, throughput, and flexibility in terms of acceptability to different products and better quality with lower capital cost and dehydration loss. Cryogenic technology has found application for production of high value frozen products like fruits and vegetables, meat, and marine products, etc. Cryogenics has limited applications in peeling of fruits and vegetables where these are subjected to immerse in $LN_2$ for a few seconds followed by thawing. Packaging and homogenization of biological tissues have also limited applications of cryogenic technology. Another important application of cryogenic technology is food grinding at low temperature yielding superior quality, maintaining the desired appearance, medicinal, and aromatic properties in spices, herbs, and other food commodities with less specific power consumption, than that of traditional grinding systems. The faster reduction and creation of a low temperature (chilling) environment by $LN_2$ evaporation produces desired raw material characteristics, that is, up to or below glass transition temperature (brittle and crisp).

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Although few studies highlight the importance of cryogenics in spices grinding, the physical and thermal properties of difficult spices, optimization of cryogen consumption, process modeling, feasibility, and validation are still to be established, examined, and explored. This article reviews the chronological development and application of cryogenics in different sectors with special reference to the grinding of spices.

## *CHRONOLOGICAL DEVELOPMENT*

Cryogenics is the branch of physics and engineering that involves the study of very low temperatures, how to produce these conditions, and the behavior of materials at those temperatures (http://www.onecryo.com). According to the International Institute of Refrigeration (1975), cryogenics deals with scientific and technological disciplines involving cryogenic temperatures, that is, below −153°C. The word "cryogenics" originated from the Greek words "*Kryos*" (frost) and "*Genic*" (produce). Probably the research in cryogenic field started with gas liquefaction. In 1845, Michael Faraday succeeded in liquefying most of the gases by immersion in a bath of ether and dry ice and pressurizing the gas until it was liquefied. About six gases, namely, $O_2$, $H_2$, $N_2$, $CO_2$, $CH_4$, $N_2O$ showed resistance for every attempt of liquefication and were called permanent gases. Among them, the primary constituents of air (i.e., $O_2$, $N_2$) received most attention. In 1877, Louis Cailletet from France and Raoul Pictet from Switzerland succeeded in producing the first liquid air droplets and Von Wroblewski in 1883 produced a measurable quantity of $LO_2$. $O_2$ and $N_2$ were found to liquefy at −183°C, and −196°C, respectively. James Dewar succeeded in liquefying $H_2$, thus reaching the lowest temperature of −259°C. In the series of such inventions, argon was discovered in 1894, and as an impurity in $LN_2$, krypton and xenon were discovered (1898) in the fractional distillation of liquid argon, and LHe was discovered in 1908 (http://www.cryogenicsociety.org). Table 1 presents the mile stones in cryogenics.

**Table 1** Milestones in cryogenics

| Year | Event |
|---|---|
| 1877 | Cailletet and Pictet liquefied $O_2$. Cryogenics emerged as a separate area from refrigeration |
| 1884 | Wroblewski (Kracow University, Poland) first liquefied $H_2$, as a mist |
| 1892 | Sir James Dewar (England) developed the vacuum-insulated vessel for cryogenic fluids storage |
| 1895 | H.K. Onnes (Holland) established the Leiden Cryogenic Laboratory. Karl von Linde (Germany) obtained a basic patent for air liquefaction |
| 1898 | James Dewar produced LH2 in bulk at the Royal Institute of London |
| 1902 | Georges Claude developed the first air-liquefaction system using an expansion engine |
| 1908 | H.K. Onnes first liquefied He (earlier considered as permanent gas) |
| 1911 | H.K. Onnes discovered superconductivity |
| 1916 | First commercial American-made air liquefaction plant was established |
| 1922 | First commercial production of Ne was established in United States |
| 1926 | Robert Goddard conducted the world's first successful flight of $LO_2$ powered rocket and non-cryogenic gasoline propellant |
| 1933 | Magnetic cooling used to reach temperatures below −272°C |
| 1934 | Peter Kapitza built the first expansion engine for a He liquefier |
| 1939 | First vacuum-insulated railway tank car built for transport of $LO_2$ |
| 1945 | Successful development of $H_2$ propulsion technology to fuel the upper stages of Saturn V rocket of NASA was made |
| 1947 | Collins cryostat for He liquefaction was developed |
| 1952 | National Bureau of Standards established the cryogenic engineering laboratory in Boulder, Colorado |
| 1957 | Atlas ICBM powered by LOX/RP-1 was test fired. Fundamental theory (Bardeen-Cooper-Schrieffer or BCS theory) of superconductivity presented |
| 1958 | Multilayer insulation (MLI) was developed |
| 1961 | $LO_2$ and $LH_2$ powered saturn launch vehicle was test-fired |
| 1966 | He3/He4 dilution refrigerator was developed |
| 1969 | 3250 hp DC superconducting motor constructed for ship drive application |
| 1986 | Georg Bednorz and Alex Muller discover high-transition-temperature ceramic superconductor with a Tc of about −243°C. |

Source: http://www.cryonicssociety.org and Foerg, 2002.

## *CRYOGENS*

Liquid $N_2$, $O_2$, He, Kr, $CH_4$, $CO_2$ are termed as cryogens. These fluids are used in different fields as per their properties, requirement, and system feasibility. $LO_2$ and $LN_2$ in chemical and metallurgical processes, $LH_2$ and $LO_2$ as cryogenic liquid propellants for rocket engines, and $LH_2$ as a clean energy vector in transportation are few examples. $LN_2$ represents one of the largest and fast-growing industrial domains of application of cryogenics together with air gases liquefaction and separation. The densification (condensation) and separation (distillation) of gases is the main driving force for cryogenics. In cryogenics, low temperatures are achieved by immersing a substance in a bath of cryogen to utilize its latent heat of vaporization (i.e., between triple point and critical point to the saturation temperature at atmospheric pressure). Some physico-thermal properties of $LN_2$ and $LCO_2$ are presented in Tables 2 and 3 (Lebrun, 2007). Louis Clouet and Gaspard Monge (1780) liquefied $SO_2$ by compression and cooling. Martinus van Marum and Adriaan Paets van Troostwijk (1787) succeeded in liquefying ammonia. The chlorine and other gases were liquefied under pressure by Northmere in 1805 and 1806. Subsequently, $SO_2$, $H_2S$, $CO_2$, $N_2O$, $C_2H_2$, $NH_3$, and HCl were also liquefied by Michael Faraday (1845). Recently, almost all permanent gases are successfully compressed and liquefied for low temperature production. Haynes et al. (1987) reported the viscosity and thermal conductivity data in correlations with pure fluids and fluid mixtures encountered in cryogenic process technology.

**Table 2** Characteristic temperatures of cryogens

| | Temperature (°C) | | |
|---|---|---|---|
| Cryogen | Triple point | Normal boiling point | Critical point |
| Argon | −189.4 | −185.9 | −122.3 |
| Helium | −271.0 | −269.0 | −268.0 |
| Hydrogen | −259.4 | −252.8 | −240.0 |
| Methane | −182.5 | −161.6 | −82.7 |
| Oxygen | −218.8 | −183.0 | −118.6 |
| Neon | −248.6 | −246.1 | −228.8 |
| Nitrogen | −210.1 | −195.9 | −147.0 |

## *APPLICATIONS OF CRYOGENICS*

Cryogenics has many established applications in space science, automobile, metallurgical, industrial, and pharmaceutical sectors. Other applications of cryogenics include fast freezing of foods and preservation of biological materials such as livestock semen, human blood, tissue and embryos, and grinding of foods, etc. Scurlock (1990), Morrell (2004), and Ventura and Risegari (2008) reviewed briefly the applications in physics, chemistry, biology, medicine, engineering, and space vehicle, etc.

### *Space Science*

Cryogenics plays a vital role in space science and has given new dimensions not only for facilitating space science missions but also for supporting space transportation infrastructure. Astronomy missions often use cryogenic telescopes to reduce thermal emissions of the telescope, permitting very faint objects to be seen. $LH_2$ and $LO_2$ are used in main engines of space shuttles because they offer a very high specific impulse.

For space shuttles, propellant is a chemical mixture, that is, liquid, solid, or hybrid (fuel and an oxidizer) burned to produce thrust in rockets. Liquids are desirable because of their high mass ratio. Figure 1 depicts the principal components of a liquid rocket engine. Li (1995) has discussed the general aspects of cryogenics and its applications in the space program on rocket vehicles with $LH_2/LO_2$ engines. Birmingham (1965) discussed the LHe and its potential for future applications in aeronautics and space administration of dense low temperature as a refrigerant to precool the $H_2$-$O_2$ engines for the upper stage of a space launch vehicle. Collaudin and Rando (2000) reviewed the non-military space missions using cryogenic instrumentation and envisaged the applications of cryogenics and its impact on main technical solutions the spacecraft system design. Sehwan et al. (2003) described a novel concept of the LHe pressurization system utilizing a heater in a liquid propellant rocket and indicated that the pressurization method satisfied the requirement of the pressurization system. Duband et al. (1991) developed a $^3$He refrigerator suitable to use in zero-gravity during flight. Cho et al. (2004) presented the experimental investigation on vapor generation, mass fraction, and boiling characteristics of $LO_2$ flow in rocket engine manifold and injector.

**Table 3** Properties of nitrogen, helium and water

| Property | Nitrogen | Helium | Water |
|---|---|---|---|
| Normal boiling point, °C | −196.2 | −269.0 | 99.8 |
| Critical temperature, °C | −147.2 | −268.0 | 373.8 |
| Critical pressure, kg/cm$^2$ | 34.7 | 2.4 | 225.0 |
| Liquid density*, kg/m$^3$ | 808.0 | 125.0 | 960.0 |
| Liquid/vapor density ratio * | 175.0 | 7.4 | 1600.0 |
| Heat of vaporization*, kJ/kg | 199.0 | 20.4 | 2260.0 |
| Liquid viscosity*, $\mu$P | 152.0 | 3.3 | 278.0 |

*at normal boiling point

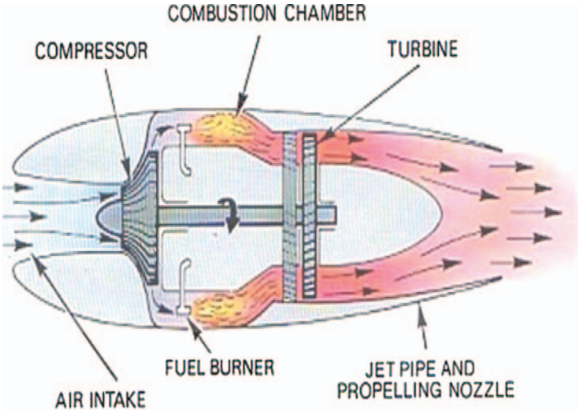


**Figure 1** Liquid Rocket Engine (Courtesy: http://temasekpoly.files.wordpress.com) (color figure available online.)

### *Cryo-Electronics*

It is the study of superconductivity at low temperatures and its applications. Superconductivity is an almost total lack of electrical resistance in certain materials near absolute zero temperature. Superconductivity was discovered (Onnes, 1911) while studying the resistance of solid mercury −269°C using LHe. The superconductivity of lead and niobium nitride was observed at −266°C and −257°C, respectively. Superconducting materials allows low power dissipation, high-speed operation, high sensitivity, and the ability to prevent external magnetic fields (Gallop, 1991). Meissner and Ochsenfeld (1933) postulated the Meissner effect, that is, superconductors expelling the applied magnetic fields. London and London (1935) envisaged this effect as a consequence of the minimization of electromagnetic free energy carried by superconducting current. Superconducting magnets are used in magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) machines, mass spectrometers, and the beam-steering magnets used in particle accelerators and magnetic separation in pigment industries (http://en.wikipedia.org).

### *Automobiles*

Cryogenics applies in all engine parts, namely pistons, rings, push rods, connecting rods, valves, crank and camshaft, and even block, etc. Cryogenics increases the molecular density of treated materials and improves the distribution of energy through the object. Even parts like brake rotors, drums, and brake pads can benefit from cryogenic treatment. Peschka and Carpetis (1980) designed and tested a semi-automatic $LH_2$ refueling station for automobiles. The first public filling station for $LH_2$ was started at Munich airport during the year 1999 (Pehr et al., 2001). Ahluwalia and Peng (2008) characterized $LH_2$ storage in an insulated pressure vessel with flexibility to hold compressed $H_2$ at 10.13 kg/cm$^2$ for automotive application in a dynamic model.

### *Industrial Application*

Cryogenic treatments are used in manufacturing of workshop production tools such as reamers (carbide or HSS), tool bits, drills, cutters, millers, form tools, dies, etc., resulting in stronger and more wear resistant metals. Paul and Bandyopadhyay (1993) studied the effect of cryogenic grinding of steel and Paul (1996) validated a hypothesis on the mechanics of cryogenic grinding of steel and reported its substantial reduction with different grinding forces under cryogenic conditions. Paul and Chattopadhyay (1996) stated the effect of cryogenic cooling on grinding zone temperature for five commonly used steels and depicted the effectiveness of cryogenic cooling throughout the experimental domain. Venkatesh et al. (2010) reported that the use of cryogenics in steel grinding increased the life of steel with less wear and tear. Torrance (1991), Munehiko et al. (1997), and Munehiko and Yokogawa (1998) also discussed the importance of cryogenics in industrial use. Bradley (1987), Lavine (1990), Campbell (1993), Tso (1995), Inada (1996), Mahidi (1997), and Klocke (2000) have discussed the various aspects of cryogenic grinding, namely, metal ductility, thermal aspects of grinding, cryogen film boiling limitations, fluid cooling in shallow grinding, high efficiency deep grinding, ultra high speed grinding, chip types in grinding, and applied mechanics in grinding for various industrial applications, respectively.

### *Sports and Musical Instruments*

Cryogenics is used to treat many types of sports including instruments used in golf and cricket, etc. It has been reported that cryogenically treated bats reduce residual stress, improve durability and resistance to denting; solid sound upon impact with ball yielding reduced internal bat vibration and increased hitting distance by 2 to 4% (http://www.cryoeng.com). In musical instruments a crisper and clearer sound can be achieved through cryogenically treated sections of instruments. When the musical instruments are treated at sub-zero temperatures, inherent and residual stresses within the brass structure are released, which provide increased tonal quality, volume, and a purer and cleaner sound by enhancement in playability (Kim, 2005; Chen et al., 2006).

### *Cryobiology*

Cryobiology deals with the application of low temperature in biology or environments with reference to the study of living plants and animals. It causes extreme cold conditions for living tissue to destroy in seconds or to preserve for centuries with no detectable biochemical activity. Reasonable findings about the causes of cell death during freezing supported the discovery of methods for practical applications in long-term storage (cryopreservation) and selective destruction of living cells or tissues (cryosurgery). Further, cryogenics has a wide spectrum of utilities in the medicine industry for the manufacturing and preservation of sensitive drugs. Katkov (2006) discussed the use of modern cryopreservation and related techniques for conservation of genetic resources of plants, endangered species, and economically important breeds of wild and domesticated animals. Several researchers have used cryogenics in the field of biology, viz., artificial insemination (Ostashko, 1963), freezing of biological systems (Peter, 1970), embryos preservation (Steponkus et al. 1990), grinding of soft tissues (Chen et al. 1996), teeth grinding for DNA extraction (Sweet and Hildebrand, 1998), and electron cryptomography (Cristina et al. 2006). Kamogawa et al. (2001) pulverized a hair sample using cryo-milling to determine heavy metals. Jorge et al. (2006) studied a unified thermal expansion analysis throughout the entire cryogenic temperature range and analyzed the glass transition temperature, based on thermal strain data. A review on current cryopreservation procedures for stallion semen, cryobiological determinants of sperm function, and mechanisms of cryoinjury and cryoprotectant action have been reported by Sieme et al. (2009). Jeunghwan Choi et al. (2010) reviewed the biomaterial thermal properties in the cryogenics regime for the application of cryobiology.

### *Food Sector*

Applications of cryogenics revolutionized the food industry providing low temperature applications for food preservation, quick freezing, and food grinding, etc. Industrial gases (not only cryogens) are used to promote seed germination, plant and flower growth, and to enrich the greenhouse environment. Oxygen is added to water in aquaculture to enhance yields. Special gas mixtures are used for preharvest insect control and fruit ripening. Gases are used to stun red meat animals and poultry during slaughter and fish prior to freezing. The injection of $CO_2$ or $N_2$ vapor into a natural seam of meat carcass yields a ballooning effect of meat. This helps to separate the membranes between muscle groups and bone without damaging meat, resulting in increased boning efficiency and reduced labor, etc. (http://www.cryogenicsociety.org). In the bakery industry, $LN_2$ vapor is used to cool baked products. Cryogenic freezing is defined as freezing at $-59°C$ or below. Cryogen temperatures can reach to $-160°C$ having an overall internal freezer temperature of $-65.5°C$. $LN_2$ ($-196°C$) is one of the coldest substances and is completely inert, colorless, tasteless, and odorless with no adverse environmental effects. Davidge (1981) discussed the application of cryogenics in food industry, that is, technical and control systems methods to distribute $LN_2$ for economic feasibility of the processes.

Miller and Roberts (2001), and Ramakrishnan et al. (2004) have presented the potential applications of cryogenic freezing as an upcoming food processing technology augmenting its low setup costs, high flexibility and described benefits in food industry. Cryogenic freezing of food products for better quality, longer shelf life, and higher production capacity have been reported by various authors (Cowley et al., 1962; Schoef, 1970; Hoeft et al., 1973; Streeter and Spencer, 1973, Arafa and Chen, 1978; Sebranek, 1982; Sacs, 1985; Acharya et al. 1989; Goswami, 2010). Awonorin (1997) compared the heat transfer and operating characteristics of tunnel and spiral belt freezer using $LN_2$ sprays under typical commercial freezing conditions and determined the average heat transfer coefficients (28 and 35 $Wm^{-2}K^{-1}$) in the precooling section of tunnel and spiral belt freezers. Kock et al. (1995) ascertained the effect of freezing rate on the quality of cellular and non-cellular convenience in food products. Foods frozen under cryogenic conditions rapidly freeze the cellular starch resulting in a better quality product than slow freezing. Sheikh and Prabhu (2007) developed a composite model combining the freezer and food freezing dynamics using a two-step finite difference methods to optimize the operating costs of tunnel freezers. Sheikh and Prabhu (2007) proposed and tested a design of a model predictive control algorithm with a zero absolute error minimize. Tassou et al. (2010) reviewed the current state-of-the-art technologies and emerging refrigeration technologies having the potential to reduce the environmental impacts of refrigeration in food industry.

### *Grinding of Food Material*

Grinding is the process of size reduction of any substances subjecting to mechanical forces. The practical fracture occurs with the failure of internal molecular binding forces with respect to external forces. The energy requirement increases with the reducing particle size and this can be attributed to the lesser number of defects in the already fragmented particles. Broadly speaking, material can be classified as hard (rocks, ore, etc.) and soft (plastics and food stuff, etc.). Hard materials are easy to disintegrate and operating temperature is not an issue. Plastics and elastomers respond to stress by uncoiling their long chain of molecules and by sliding of the molecules one over the other, thus making grinding difficult. Cryogenic grinding technology has vast potential application in the grinding of steel, thermoplastics, thermo sets, adhesives and waxes, explosives, and food material. The cooling of material results in contraction leading to propagation of cracks from defects or flaws in the molecular bonds. Cryogenic grinding lowers the temperature of the product to −195.6°C. In practice, temperatures are regulated between −195.6°C to a few degrees below ambient temperature. Usually a grinding zone is well below −73°C. The embrittlement of the sample makes even elastic and soft samples grindable. Fineness below 5 $\mu$m can be achieved through cryogenic grinding. This overcomes the heat generation during the established process of normal grinding of food material and provides higher flavor retention and quality. Grinding of food stuff is difficult because of its moisture, fat, and fibrous structure.

## *CRYOGENIC GRINDING OF SPICES*

The quality of spices is assessed by its intrinsic (chemical quality, viz., the retention of volatile oil, alkaloids and oleoresins, etc.) and extrinsic (physical quality, viz., appearance, texture, shape, impurities, color, etc.) characters. In addition, certain export quality standard envisaged some health requirements including pesticide residue, aflatoxin, heavy metals, sulphur dioxide, solvent residues, and microbiological quality. The physico-chemical characteristics vary widely on variety, agro-climatic conditions existing in the production area, harvest, and post-harvest operations. However, the physicochemical quality remains the ultimate attribute for export requirement of spices as these properties delineate its grade in the market. Thus, the prevailing stringent regulations and quality preferences demand on superior technology for production, processing, packaging and transportation. Thus, cryogenic grinding of spices shows promising features for the promotion of export or for the domestic market.

### *Indian Scenario in Spices Production*

India is known as “the home of spices.” In general, an Indian meal is not complete without the tangy and delectable flavor of spices and different spices are used to prepare a variety of different cuisines to produce different taste. Indian spices are famous all over the world for their gastronic and medicinal values. India is the world’s largest spice producer contributing 44% share in output and 36% in global spice trade, that is, 500,000 tons of production which is equal to US$ 1.5-2 billion. Out of the 109 spices listed by ISO, India produces about 75 from its different agro climatic regions. India produced 4.66 million tons of spices during 2007-2008 and increased its export by 24.05% during 2007-2008 compared to the previous year. (http://www.indianspices.com).

### *Advantages of Cryogenic Grinding over Traditional Grinding*

The fat content of spices generally poses the problem, whereas other considerations are product particle size, yield, uniformity, freedom form contamination, economy, and dust from operation. The flavor strength per unit mass of resultant cryogenically ground product is twice than that of the conventionally ground spice product. Pruthi and Mishra (1963) reported the rise in product temperature (42–95°C) during normal

**Table 4** Comparison between traditional and cryogenic grinding

| Parameter | Cryogenic grinding | Traditional Grinding |
|---|---|---|
| Energy Consumption$^{+}$ | Low | High |
| Throughput$^{+}$ | High | Low |
| Mill Clogging$^{+}$ | No Clogging | Frequent |
| Volatile Losses$^{+}$ | Minimum | Higher |
| Motor Capacity$^{+}$ | Low | High |
| Control on particle size$^{+}$ | Effective | No control |
| Grinding of soft material$^{+}$ | Possible | Very difficult |
| Fire Risk$^{++}$ | No | High |
| Air Pollution$^{+++}$ | No | Yes |
| Microbial Load$^{+++}$ | Does not exist | Possible |

$^{+}$Singh and Goswami (1999; 2000), Goswami and Singh (2003), Murthy and Bhattacharya (2008)
$^{++}$Goswami and Singh (2003)
$^{+++}$http://spectracryogenic.tradeindia.com

grinding with significant loss of their volatile oil or flavoring components. The use of circulating air, cooling water, etc., reduces the amount of heat generation to some extent in standard grinding mills. Losses of volatile oil reported for different spices, namely, nutmeg, mace, cinnamon, oregano, and caraway seed are 37%, 14%, 17%, 17%, and 32%, respectively (Andres, 1976; Wolf and Pahl, 1990). Jacob et al. (2000) reported that the cryogenically ground black pepper retained 2.61% of volatile oils compared to 1.15% of the traditionally ground samples. Bera et al. (2001) reported that the product temperature rose to 95°C during conventional grinding of cumin seeds and there was considerable loss in volatile oil and its constituents. The production of the finest powders from viscoelastic and plastic materials is high energy consuming and cost-intensive or even not possible at ambient temperatures. In general, cryogenic grinding referred to as freezer milling, freezer grinding or cryo-milling, that is, grinding material near to glass transition temperature or embrittlement temperature of the material. Cryogenic grinding permits the heat sensitive, thermoplastic, and elastic materials to be economically ground to make very small particle sizes. The potential differences between traditional and cryogenic grinding of spices are given in Table 4. Recently, adaptation of cryogens viz., $LN_2$ or $LCO_2$ in the grinding process has given impetus to milling industries in order to retain food quality.

## *Some Developments in Spice Grindings: A Glance*

### *In Abroad*

Pesek and Wilson (1986) investigated the effect of cryogenic and ambient milling on the color of spice to ascertain cryogenics influence on ground spice quality. They reported that the cryogenically ground spices had better color retention, because of grinding at very low temperature, compared to those spices ground in traditional mill at ambient conditions. Landwehr and Pahl (1986) reported the spray of $LCO_2$ directly into the turbo mill for pepper grinding and found that almost all experiments without chilling (without spray of $LCO_2$) caused choking of sieve and ultimately breakdown of the mill (a major constraint of ambient milling). Wilczek et al. (2004) discussed the effect of low temperatures on many materials to become brittle to facilitate and improve the efficacy of grinding. A low-temperature fine-grinding plant in technical scale was erected for research and $LN_2$ consumption was optimized and dramatically reduced with this technology. A comparison of this new development to those established techniques have also been discussed. Gouveia et al. (2002) used the cryogenic grinding method for homogenization of breakfast cereals. The grinding resulted to be more efficient than the earlier one. Cryogenic grinding proved to be effective process for fast sample particle size reduction.

### *In India*

Murthy et al. (1996) found that cryogenic grinding of black pepper in the laboratory scale grinding system resulted in better product characteristics. Singh and Goswami (1999; 2000) studied the effect of cryogenic temperatures on volatile oil content of cumin seed and clove and reported the significance of cryogenic grinding and the quality of ground samples. Manohar and Sridhar (2001) reported the effect of cryogenic grinding on particle size distribution of turmeric and confirmed the usefulness of cryo grinding process for heat-sensitiveness. Jacob et al. (2001) developed a bench top pilot plant (pin mill) model having 120 kg/h throughput capacity and 0.5 kg consumption of $LN_2$/kg of pepper. Singh and Goswami (1999) had developed a cryogenic grinding system for spices (cumin and clove) consisting of a screw conveyor assembly, a compressor, a liquid nitrogen dewar, power transmission, and a grinder. The precooler consists of a screw assembly enclosed in a properly insulated barrel with a system for $LN_2$ circulation. The design considerations, calculations, and development of the precooler have been discussed in detail.

Studies conducted by Jacob et al. (2001) clearly indicated that the quality of the end product (cryogenically ground) was superior in terms of increased volatile oil contents and flavor components. The retention of volatiles, $\alpha$-pinine and limonene were 2.61%, 1.4%, and 8.3% for a cryogenically ground sample and 1.15%, 0.29%, and 1.18% for traditionally ground sample of pepper samples. Singh and Goswami (1999) studied the effect of grinding temperature and number of ribs on particle size distribution, volume mean diameter, specific energy consumption, and volatile oil content of the ground powder of cumin seed. They highlighted the increase in particle size and volume mean diameter with the increase of temperature (−160 to −70°C), increase in specific energy consumption (55–98 kJ/kg) with increase in temperature (−160 to −70°C), and decrease in particle size with increase of number of ribs on rotor (8–12), The volatile oil content was found decreased (2.86−2.26 mL/100 g) with increase in grinding temperature (40–85°C). The increase in retention of volatile oils $\alpha$-pinene, $\beta$-pinene, $\chi$-terpinene, p-cymene, and cuminaldehyde were 22%, 20.2%, 7.4%, 40.9%, and 35%, respectively, were reported under cryogenic as compared to ambient grinding conditions.

Singh and Goswami (2000) found blockage of sieve at temperatures more than −50°C and increase in particle size for the same cumulative volume fraction at stipulated grinding temperature range (−110 to −50°C). Higher feed rate (1.5-6 kg/h) and higher rotor speed showed coarser particles of clove. The volume mean diameter increased with increase in feed rate at all grinding temperatures, rotor speeds, and sieve opening sizes. However, it decreased with increase in rotor speed (69-92 m/s). Specific energy consumption increased (62-81 kJ/kg) with increase in temperature (−110 to −50°C); however, it decreased with increase in sieve size. Increase in grinding temperature (−110 to −50°C) had no significant effect on the volatile oil content (13.31−13.16 mL/l00 g). However, the volatile oil decreased (11.0−9.3 mL/l00 g) in ambient grinding. Cryogenic grinding of cloves yielded 129.5% of volatile oil recovery compared to that of ambient grinding of clove.

Goswami and Singh (2003) experimented an attrition mill with different feed temperatures (−100, −40, and 30°C ) and feed rates (12, 18, 24, and 30 kg/h) and reported the temperature rise for cumin at higher feed rates, coarser particles (105.9-158.2 $\mu$m) at higher feed rate (12−30 kg/h), lower specific energy consumption (132.8-99.4 kJ/kg) for higher feed rate (12−24 kg/h), finer particle size (94.63–139.5) with lower temperature (−100°C to −40°C), and higher specific energy and work index with increase in temperature. Murthy and Bhattacharya (2008) studied the effect of variables, viz. the feed rate (7–60 kg/h) and product temperature (−15 to 60°C) on grinding in a pin mill and product characteristics to its optimization for black pepper. The volatile oil yields in cryogenic grinding were higher (1.42−1.91 mL/100 g) than that (0.78-0.98 mL/100 g) in the ambient grinding system. The average monoterpenes content was 0.80 mL and 0.15 mL/100 g for cryogenic and for ambient ground samples, respectively. Thus, an optimum feed rate (47–57 kg/h) and product temperature (−15 to −20°C) were recommended. The studies indicate the judicious control on process parameters to regulate desired responses for optimum utilization of resources without affecting final product quality. Table 5 summarizes different process parameters and their respective responses.

**Table 5** Suggested process parameters and responses for cryogenic grinding

| Particular | Parameter | Process/instrument required | Responses |
|---|---|---|---|
| **Feeding Material** | **Physical Properties** | | |
| | Geometric mean diameter, sphericity, surface area, unit volume, bulk density, true density, angle of repose, coefficient of friction, etc. | Vernier calipers, pycnometer, and standard apparatus and formulae. | Feeder type, screw diameter and length, conveyor selection, residence time, grinder capacity, cooling load, and optimization. |
| | **Thermal Properties** | | |
| | Specific heat, thermal conductivity, thermal diffusivity, latent heat of fusion, freezing point, etc | DSC and thermal conductivity meter | Liquid and gaseous zone length cooling load, residence time, glass transition temperature, insulation material selection and design of cryogenic grinder. |
| | **Chemical profile** | | |
| | Volatiles oils, fat composition, Proximate analysis | Gas Chromatography, and other standard chemical methods | Performance evaluation and efficiency of cryogenic grinder. |
| | **Mechanical Properties** | | |
| | Hardness, rupture force, Deformation and energy absorbed, | Texture analyzer and UTM | Feed rate, rotor speed, energy consumption, deformation pattern, fineness modulus of end product. |
| **Machine** | **Feeding mechanism** | | |
| | Screw or spiral type | Standard calculation and methods | Construction material, slope, throughput, feed controller, flow type, etc |
| | **Precooling unit** | | |
| | Construction material, feed rate, residence time, type of raw material, temperature profile, flow type (concurrent or counter current), type of pump, distribution and control mechanism of cryogen | Wear and tear, load testing studies, feed controller, $LN_2$ flow meters and other standard methods. | |
| | Size reduction ratio, particle size distribution, volume mean diameter, sieves Choking behavior, specific energy consumption, working efficiency coefficient, volatile oil content. | | |
| | **Grinder** | | |
| | Construction material, feed rate, type of grinder, rotor speed, sieve size, residence time, cryogen used and flow, temperature gradient, etc. | Wear and tear, load testing studies, feed controller, cryogen flow meters and other standard methods. | |
| | Size reduction ratio, particle size distribution, volume mean diameter, sieves Choking behavior, specific energy consumption, working efficiency coefficient, volatile oil content, process parameter optimization and modeling. | | |

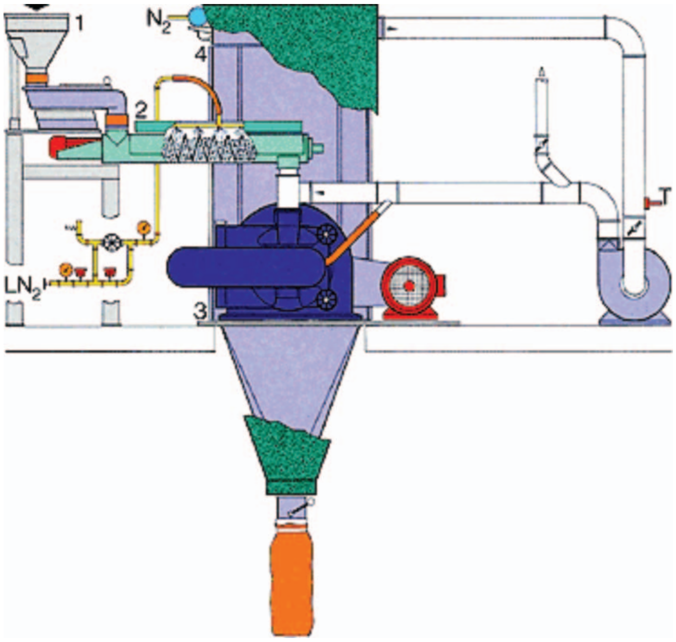


**Figure 2** Schematic diagram of a simple cryogenic grinding setup (Courtesy: www.alpinehosokawa.com). 1. Loading hopper, 2. LN2 distribution device, 3. LN2 feed metering unit, 4. Screw cooler with LN2 supply, 5. Grinder and 6. Temperature sensor). (color figure available online.)

**Table 6** Major design components and their considerations

| S.No. | Consideration |
|---|---|
| 1 | Refrigeration load determination<br>• Thermal load due to conduction<br>• Thermal load due to convection<br>• Thermal Load due to radiation<br>Refrigeration load curve to determine required system capacity. |
| 2. | Dewar Construction<br>• Mechanical strength of dewar material to withstand 1 atm pressure.<br>• Thickness of end plates<br>• Selection of 'O' rings types, which may be conflate flanges or metal seals<br>• Vacuum grease to lubricate 'O' rings<br>• Selection of valve to evacuate dewar. Usually right angle bellow-sealed stainless steel valves are used to handle very low pressure<br>• S/S-304 steel is widely used for dewar construction, Design of radiation shields<br>• Design of vacuum windows |
| 3. | Distribution System<br>• Distribution lines<br>• Compressor selection<br>• Cryogen introduction system in freezer<br>• Control valves to regulate cryogen supply |
| 4 | Cleaning of dewar, freezer, and compressor. |

## *CRYOGENIC GRINDING SYSTEM*

Efficiency of a cryogenic grinder hinges on its design and raw material properties (physical and thermal) to be ground. Cryogenic grinder design includes proper selection of construction material, pre-cooler, $LN_2$ storage and distribution system, grinder, and data acquisition system. Figure 2 depicts the schematic diagram of cryogenic grinder. The principal parts of the system are feeder, pre-cooler, $LN_2$ distribution device, a grinder, temperature controls, and sensors. Table 6 presents major design components and their considerations specific to spice grinding.

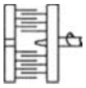
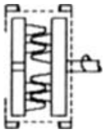
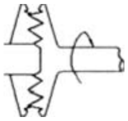
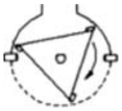
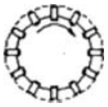
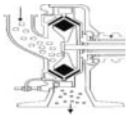
### *Construction Material*

The behavior of material at lower temperature is different from ambient temperature conditions. Oxygen free copper, 6061-T6 aluminum, G-10CR fiberglass epoxy, 718 Inconel, Kevlar 49, niobium titanium (NbTi), beryllium copper polyamide (nylon), polyimide, 304 stainless steel, Teflon, and Ti-6Al-4V titanium alloy are generally chosen as some of the most common materials for cryogenic systems (Marquardt et al., 2000). Material properties, namely, thermal conductivity, specific heat, and thermal expansion are considered mainly for the selection of appropriate construction material in cryogenics. Properties of different materials under cryogenics conditions are available (http://cryogenics.nist.gov). Cryogenically treated carbide tools and copper electrodes serve 400% longer, while treated milling tools, drill bits, and piston rings exhibit 100% to 1200% increase in service life. Treated dies may serve 200-800% than that of non treated ones. Cryo-treated automobile engine components exhibit 50% to 200% increase in service life. Ball and roller bearings show 200%–700% improvements in load and wear characteristics. Cryogenic treatment of cobalt end mills showed 2600% the wear life as against untreated ones.

### *Precoolers*

Different types of precoolers/cryo-freezers, namely spiral freezers, flighted freezers, straight belted freezers (standard $CO_2$ or $LN_2$ tunnels, impingement tunnels, $LN_2$ immersion tunnels), triple pass freezers, rotary drum freezers, and cryo mechanical systems are used. Straight belted and spiral type freezers are generally used as precoolers for the food industry and spice grinding. Spiral type freezers requires less labor, capital, space, technical skills to operate, and dwell time. Chourot et al. (2003) proposed a detailed calculation model to evaluate and compare the technical and economic aspects of different freezing techniques (immersion, air blast, and cryo-mechanical freezing). The precooling unit consists of a screw conveyor covered with an insulated barrel having inlet for $LN_{2.}$ $LN_2$ mixes with the raw material and increases the heat transfer between them.. Some of the engineering considerations for the precooler are retention time of spices in the unit (in liquid as well as gaseous state of $N_2$), $LN_2$ control mechanism for regulation, and screw design to suit the grinding capacity (Wagner, 1972; Singh and Goswami 1999). Modified Plank's equation (Barron, 1972) is used to calculate the resident time of spice seeds in liquid and gaseous state of $N_2$. Venetucci (1980) reported that the cryogenic precoolers should be designed to reduce the temperature below the brittle point of spice seeds and its oil, before it enters the grinder.

**Table 7** Size reduction machinery

| Type | Schematic | Size reduction mechanism | Peripheral speed (ms$^{-1}$) | Typical applications |
|---|---|---|---|---|
| Pin and disc mill |  | Impact | 80–160 | Starch, sugar, caffeine, legumes, yeast, potato flakes, milk powder, spices, urea, pigments, hard waxes |
| Wing beater Mill |  | Impact and Shear | 50–70 | Alginates, pepper, pectin, paprika, dried vegetables |
| Disc Beater Mill |  | Impact and Shear | 70–90 | Milk powder, lactose, cereals, dried whey |
| Vertical toothed mill |  | Shear | 4–8 | Frozen coffee extract, plastic material, coarse grinding of rye, maize, wheat, fennel, pepper, etc. |
| Cutting granulator |  | Impact and Shear | 5–18 | Fish meal, pectin, dry fruits and vegetables |
| Hammer mill |  | Impact | 40–50 | Sugar, tapioca, dry vegetables, extracted bones, dried mills, spices, etc. |
| Ball mill |  | Impact and Shear | – | Food colors |
| Roller mills |  | Compression and shear | 1–8 | Sugar cane, wheat, chocolate refining, etc. |
| Knife mill Granulator |  | Cutting | 5–20 | Cutting and disintegrating tea leaves, cheese, asparagus, leaf, bark, and root-based drugs, resin blocks, rubber bales |
| Turbo Mill |  | Impact, shearing and Cutting | 80–120 | Grinding and pulverizing or fiberizing and disintegrating oil seeds, fat, nuts, milk powder, flax meal, corn, cacao beans, salt, paper, organic and inorganic pigments |

### LN$_2$ Distribution System

It includes cryogenic storage vessel of cryogen, cryogenic delivery system, distributor, and heat exchanger in the form of a conveyor coupled with the distribution lead tubes, etc. The cryogenics delivery system consists of vacuum insulated supply hoses and valves. The system uses a proportional control valve set up with a redundant safety valve. The cryogenic delivery system will have one or more relief valves to distribute cryogen and facilitate pressure drop zone for enthalpic processes. The distributor uses nozzles to maintain homogeneous distribution of cryogen. Generally, the reliquifier reuses the cryogen or exhaust capture unit recycle the gas to an alternate recovery process.

### Grinder

Size reduction machines operate on compression, impact, cutting, shearing, or combinations of these techniques.

**Table 8** Different temperature sensors for cryogenic applications

| Sensors | Temperature range (°C) | Performance in magnetic field | Remark |
|---|---|---|---|
| **Diodes** | | | |
| Silicon | −271.74 to 226.86 | Fair above −213.14°C | Silicon Diodes are easy and inexpensive to instrument, and are used in a wide variety of cryogenic applications, such as cryo-coolers, laboratory cryogenics, cryo-gas production, and space satellites. |
| GaAlAs* | −271.74 to 226.86 | Fair over the whole range of temperature | They are useful in moderate magnetic fields, and offer many of the advantages of Silicon diodes |
| **Positive temperature coefficient RTDs** | | | |
| Platinum | −259.14 to 599.86 | Fair above −243.14°C | widely used in cryogenic applications at liquid nitrogen temperatures or greater |
| Rhodium-Iron | −272.49 to 226.86 | Fair above −196.14°C | Used over a wide temperature range, and are resistant to ionizing radiation |
| **Negative temperature coefficient RTDs** | | | |
| Germanium | −273.09 to −173.14 | Not recommended | Highest accuracy, reproducibility, and sensitivity from −273.09 to −243.14°C. |
| Carbon-Glass | −271.74 to 51.86 | Good | Useful in most cryogenic applications requiring high sensitivity in magnetic fields |
| Ruthenium oxide | −273.13 to −233.14 | Good below −272.14°C | Low magneto-resistance sensor and follow a standard curve. Used in MRI. |
| **Others** | | | |
| Thermocouples | −272 to 1270 | Fair | Less accurate at cryogenic temperatures |
| Capacitance | −271.74 to 16.86 | Excellent | Used as temperature control sensor in strong magnetic fields |

*Gallium-aluminum-arsenide (GaAlAs) Diode

Brittle material can be easily reduced by compression and impact, whereas tough material requires combined action of impact, cutting, and shearing. Soft material (with Mohs hardness, 1-4) can be reduced by cutting and shearing and, under certain conditions, by compression and impact. Such material typically behaves like a tough liquid during size reduction, which disperses material, agglomerates, opens the material's inner cell structures, and homogenizes the material. The mechanism (or combination of mechanisms) best suited to reducing material depends on the characteristics of the components and the desired final results. Table 7 shows the different types of grinding machinery as per size reduction mechanism and product nature. The selection of appropriate size reduction machine requires the understanding of the machine's parameters, namely, the grinding tools shape, size, sharpness, clearance, and screen opening size, etc. and material, namely, type, size, shape, hardness, and other characteristics which affect the size reduction mechanisms, handling, etc.

The general considerations of any size reduction machines are

- *Rotor*: One or two rotors rotating parallel or coaxial.
- *Axle direction*: Horizontal, vertical, or angled inside the machine.
- *Material inlet*: Central or periphery of the rotor.
- *Material flow*: Radial direction (outward from the machine centre), axial direction (along the machine axis), or peripheral direction (around the machine perimeter).
- *Grinding tools*: Hammers (fixed or movable), pins, plates, knives, cams, or grinding segments.
- *Fineness control*: Internal or external components for controlling the final particle fineness, including an adjustable grinding gap between the rotor and stator or a grate, screen, or classifier.

Grinders may be a hammer mill (Singh and Goswami, 1999), an attrition mill (Goswami and Singh, 2003), or a Pin mill (Murthy and Bhattacharya 2008). In modern spice milling, usually pin mills are used for better performances. In addition to the cooling effect of $LN_2$, the pin mill produces finer size particles and also has the provisions to change the pins in reference to the physical characteristics of spices and raw material. Design consideration should match grinder capacity with the precooler's to avoid any overfeeding to the grinder causing temperature rise in grinding zone. However, literatures available are very scarce regarding the design parameters of cryogenic grinders for spices. A proper distribution of $LN_2$ both for precooler and grinder with cost reduction are the need of the hour and yet have to be designed. Also, there is a lack of mathematical models and special attention is needed to understand and simulate cryogenic grindings of spices. Since, the thermo-physical properties of raw material are the prime criteria for the cryogenic grinder, separate design procedures and system for optimal utilization of $LN_2$ is required.

### *Sensors*

A variety of temperature sensors working on different principles are available, but resistance temperature detectors (RTD) are most common for reliable measurement because of their good accuracy, and excellent stability and repeatability. RTDs are also relatively immune to electrical noise and thus well suited for temperature measurement in industrial environments, especially around motors, generators, and other high voltage equipment. A normal sensor does not work for cryogenic temperature because at very low temperature probe's resistance become undetectable. Hence, special sensors such as diodes (silicon or GaAIAs), RTDs (ruthenium oxide, carbon-glass, platinum,

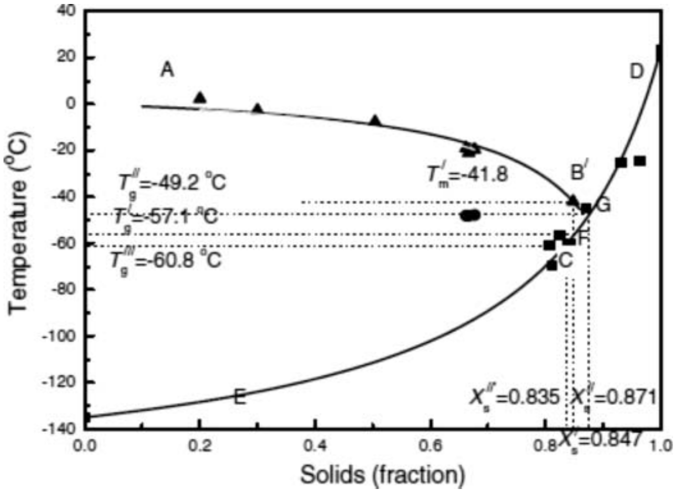


**Figure 3** State diagram of Chinese gooseberry (Wang et al., 2008) (AB′: freezing curve, DE: glass transition line, F: glass transition point of maximally freeze-concentration). where, T′g is maximally freeze-concentration glass transition temperature (°C), T″g is characteristic temperature of intersection of glass transition and freezing lines (°C), T‴g is the characteristic glass transition temperature measured by DSC, T′m is the end point of freezing (°C), X′s is the solid content at the maximally freeze-concentration (g solids/g wet basis) and X″s is the solids mass fraction at T″g (kg solids/kg sample)

rhodium-iron, or germanium), and capacitance sensors are used for cryogenic temperature measurements. However, platinum RTDs are most common in industries. They follow an industry standard curve (−200 to 600°C) with high sensitivity. Such RTDs are inexpensive and require simple instrumentation. Table 8 presents the different type of sensors that can be used to measure cryogenic temperatures. Sensors are placed to measure average temperature and the data are used for accurate control of the cryogen to optimize its use.

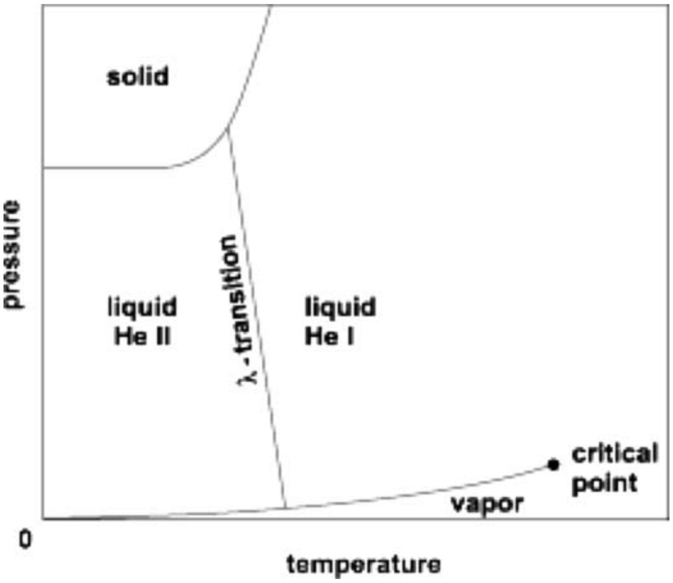


**Figure 4** Phase diagram for $^4$He (Critical point at $T_c = 5.20$ K, and $P_c = 229$ kPa).

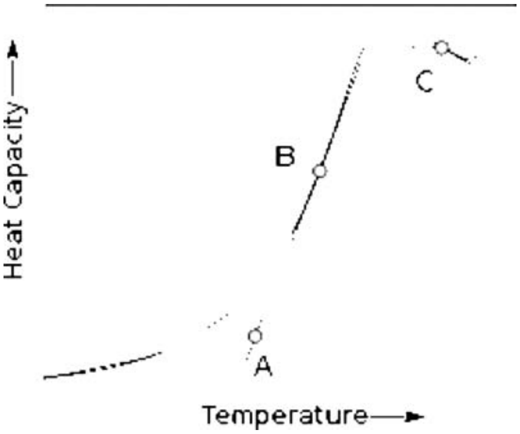


**Figure 5** Determination of glass transition temperature ($T_g$) using differential scanning calorimeter (DSC).

## *IMPORTANT CONSIDERATIONS IN DESIGN AND SAFETY*

$LN_2$ consumption in cryogenic grinding is the major cost factor, which influence the overall cost of ground spices. Optimization of the cryogen consumption is very necessary to popularize cryogenically ground spices. Accurate measurement of glass transition temperature and state diagram of produce to be ground are quintessential for preventing unnecessary consumption of the cryogen. Human safety while working with cryogens is another necessary consideration and safety measures must be ensured before working with such low temperature liquids.

### *Glass Transition Temperature and State Diagram*

Glass transition is the transformation of a glass-forming liquid into a glass and usually occurs upon rapid cooling. It is a dynamic phenomenon occurring between two distinct states of matter (liquid and glass). At glass transition temperature (Tg), metastable melt transforms into glass during cooling and glass transforms into metastable melt during heating (Mazurin and

**Table 9** Glass transition temperature of selected biological materials

| S.No. | Commodity | $T_g$ (°C) | Reference |
|---|---|---|---|
| 1 | Mushroom | −76.1 ± 0.8 | Haiying et al., 2007 |
| 2 | Cumin | −70.0 | Singh and Goswami, 1999 |
| 3 | Raspberries | −63.1 ± 5.0 | Roopesh et al., 2010 |
| 4 | Chinese gooseberry | −60.8 | Wang et al., 2008 |
| 5 | Navy beans | −57.8 ± 1.0 | Haiying et al., 2007 |
| 6 | Pea Pods | −56.7 ± 1.2 | Haiying et al., 2007 |
| 7 | Surimi without sugar | −55.0 to −65.0 | Ohkuma et al., 2008 |
| 8 | Tuna Meat | −54.2 | Rahman et al., 2004 |
| 9 | Green Cauliflower | −50.3 ± 0.4 | Haiying et al., 2007 |
| 10 | Honey | −42.0 to −51.0 | Kántor et al., 1999 |
| 11 | Sea bass muscle | −20.0 | Tironi et al., 2008 |
| 12 | Chicken meat | −16.8 | Delgado and Sun, 2002 |
| 13 | Beef | −9.0 to −13.0 | Akkose and Aktas, 2008 |

**Table 10** Potential hazards and safety measures for working with cryogens

| Hazard | Cause | Symptoms | Precautions | Rescue measures |
|---|---|---|---|---|
| Oxygen deficiency | Dilution and displacement of air, in turn, reduction in $O_2$ level, poor ventilation | Rapid breathing, shortness of breath, rapid fatigue, nausea, vomiting, inability to move, unusual behavior | Continuous monitoring of $O_2$ levels, avoiding working in confined premises, good ventilation, the area should be marked with sign of *'asphyxiant'* | Adequate first aid facility, isolation of $N_2$ supply if possible, use of life line and '*buddy*' system, artificial respiration facility |
| Intense cold | Direct contact with cryogen or cold surface, prolonged exposure to cold environment, frostbite, vapour cloud and brittle fraction | Skin sticking to cold surface, frozen tissues and localized damage to cell structure, slowed physical and mental responses, speech and vision difficulty, | Use of non absorbent gloves, wear full face mask, safety shoes, and sleeve cuffs, non absorbent apron, warm cloths. Proper handling, transportation storage, use, and exhaust of cryogens. Proper material for cryogens handling. | Adequate first aid facility, isolation of $N_2$ supply if possible, flushing of cold burn area with tepid water, loosening of tight cloths and complete avoidance of drinking and smoking |
| Pressurization | Phase change from liquid to gas | | Bursting of pipe lines | Use of rated and sized pressure relief valves |
| $O_2$ enrichment | Condensation of air (40 % of $O_2$) | | Fire risk | Proper insulation of pipe lines and equipments, regular check for leakages |

Gankin, 2007). $T_g$ is the intersection point between the cooling curve (volume versus temperature) for glassy state and supercooled liquid (Moynihan et al., 1976, Angell, 1995; Stillinger, 1995; Angell and Nagel, 1996) and depends on the cooling rate, molecular weight distribution, and additives in the material. Food materials are in an amorphous or non-crystalline state below $T_g$, that is, they are rigid and brittle. State diagram of Chinese gooseberry (Wang et al., 2008) has been presented in Fig. 3. Figure 4 depicts the phase diagram of LHe to ascertain the heat transfer by different mechanism between cryogen and system. Table 9 presents glass transition temperatures of selected biological materials. Among several methods to measure glass transition temperature differential thermal analysis (DTA) or differential scanning calorimetry (DSC) are commonly used. DSC measures the change in heat capacity between glassy and rubbery states and indicates as baseline change (Fig. 5). Three different points on curve of temperature and heat capacities are used to determine Tg. The intersection of two tangents at the start of the corresponding endotherm (point A) is treated as $T_g$. Point B is midpoint of glass transition and C represents on set of glass transition.

### *Precautionary and Safety Measures in Cryogenics*

Cryogens are extremely cold and require proper precautionary and safety measures during handling and operation. An instantaneous contact between cryogen and exposed skin can produce a painful burn and a splash of cryogenic liquid to eye can cause loss of vision, too. Therefore, proper personal protective equipment, that is, heavy gloves, face shield, safety goggles, and adequate safety mechanism should be installed including warning sensors whenever handling with cryogens. The commonly associated cryogen hazards are presented in Table 10.

## *THE FUTURE*

The phenomenon of cryogenics shows a new perspective to use low temperature in food sector and understand the behavior of raw materials and product under such low temperature regime. The proven application of low temperature in cryo freezing and preservations of biological and food materials requires research and government initiatives to make the technology feasible for mass-scale production of cryogenic grinder for spices to boost up the domestic and the export market. To demonstrate and promote cryogenic grinding in spice pilot plants are to be installed considering economics and eco-friendly features to produce higher quality end-product characteristics with lower price tags. A holistic system approach demands optimized cryo-grinders to promote the adoption rates in the tune of established traditional grinding systems.

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