Biochemical, antioxidant and thermal properties of cryogenic and ambient ground turmeric powder

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Biochemical, antioxidant and thermal properties of cryogenic and ambient ground turmeric powder

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Abstract: In present study, effect of grinding conditions, namely ambient and cryogenic, on the quality traits such as colour parameters, volatile oil, curcumin content, oleoresin content, total phenols and antioxidant activity in DPPH assay, specific heat, thermal conductivity, thermal diffusivity, glass transition temperature of turmeric powder were investigated at a moisture content of 11.5% (d.b.). Volatile oil, oleoresin, curcumin, total phenols content, antioxidant activity and b colour value varied significantly with the grinding conditions. Cryo-ground turmeric powder retained 15%-25% more volatile oil, oleoresin, curcumin, phenol content and antioxidant activity as compared to ambient grinding. Specific heat increased from 10.36 to 15.57 kJ kg^{-1} $°C^{-1}$ with increasing temperature (-100ºC to +100ºC) at both grinding conditions. Thermal conductivity and thermal diffusivity increased from 0.049 to 0.061 W m^{-1} $°C^{-1}$ and 9.509×10^{-8} to 11.4×10^{-8} m^2/s, respectively in a temperature range of -40°C to 55°C. A higher value of glass transition temperature was found at ambient grinding conditions. Specific heat and thermal diffusivity displayed second order polynomial relationships whereas thermal conductivity was found to be varied linearly with temperature. Such biochemical and thermal property evolution data are useful in academia as well as applicable in designing and fabrications of ambient and cryogenic grinding system for turmeric and other similar commodities.
Keywords: Turmeric, ambient grinding, cryogenic grinding, curcumin, oleoresin, specific heat

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1 Introduction

Turmeric (curcuma longa linn), plant of family zingberaceae, is native to India and Southeast Asia. India is a leading producer and exporter of turmeric in the world. Andhra Pradesh, Tamil Nadu, Orissa, Karnataka, West Bengal, Gujarat, Meghalaya, Maharashtra, Assam are some of the important states cultivates turmeric. It is valued principally for its yellow-orange colouring compound. It possesses an appreciable aroma and flavour due to the volatile oil present in the rhizome which necessitates classifying it as a spice. It is directly used as a spice or colouring agent in the ground form and also for the preparation of solvent-extracted oleoresin. It is used to colour liquor, fruit drinks and cakes. It is one of the principal ingredients of curry powder also.

Turmeric contains natural antioxidants, and is reported to possess numerous medicinal properties including antioxidant and anti-protozoal activities (Tuba and Ilhami, 2008). The major biologically active components of turmeric are curcuminoids which include

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curcumin, demethoxycurcumin and bis-demethoxy curcumin. Curcumin which makes up 2% to 5% of the spice is a yellow coloured phenolic pigment and is an effective antioxidant that can scavenges superoxide radicals, hydrogen peroxide and nitric oxide from activated macrophages. Much work has been carried out on the antioxidant and related anticancer activities of compounds (especially curcuminoids) derived from turmeric rhizomes. In *ayurvedic* medicinal system, turmeric has been extensively used in both fresh and dried forms internally as a stomachic, tonic and blood purifier and externally in the prevention and treatment of skin diseases (The Wealth of India, 2001). The main activities of curcuma rhizome have been found to be anti-inflammatory, hepatoprotective, anti-microbial, antifungal, antiviral, wound healing, anticancer, antitumor, anti-inflammatory and antivenom agents (Jayaprakasha, 2005; Negi et al., 1999; Raina et al., 2002).

Thermal properties such as thermal conductivity, thermal diffusivity, and specific heat of spices and their powders are necessary for efficient design of processes involving heat transfer. In agricultural materials, temperature and moisture content greatly influence the specific heat, thermal conductivity and thermal diffusivity owing to the relatively high specific heat, thermal conductivity and heat of sorption of water (Mohsenin, 1980). The glass transition is the temperature where the material goes from a hard, glass-like state to a rubber-like state. DSC defines the glass transition as a change in the heat capacity as the solidified oil goes from the glass state to the rubber-like viscous state. This is a second order endothermic transition (requires heat to go through the transition) (Goula et al., 2008).

Grinding is one of the most common operations used to prepare turmeric powder for consumption and resale. However in ambient grinding of spices temperature rises to the extent of 42-93°C as grinding is the most power-consuming operation because only 1% of the energy imparted into the material is utilized loosening the bond between particles, whereas almost 99% of input energy is dissipated as heat, rising the temperature of the ground product, etc. The rise in temperature causes the loss of volatile oil and flavouring constituents; for high oil bearing material, oil comes out from oil bearing material during grinding, which makes ground product gummy, sticky and results in chocking of sieves through which the product passes (Singh and Goswami, 1999).

The loss of volatile oil, moisture, and colour can be significantly reduced by a cryogenic grinding technique. Liquid nitrogen at -195.6°C provides the refrigeration needed to pre-cool the spices and maintain the desired low temperature by absorbing the heat generated during the grinding operation.

The knowledge of thermal properties constitutes an important and essential engineering data for the processing of turmeric, design of processing equipment, e.g., cryogenic system for grinding of turmeric/spices, pre-cooler of cryogenic grinder, etc., and in evaluating and retaining the quality of the final product. This information is necessary for simulation and modeling of heat transfer phenomenon in the grinder. It would also be useful for researchers, engineers, processors and other scientists who may exploit these properties and find new uses. In addition, knowledge of the thermal properties leads to optimize processing and leads in knowledge-based development of all processes and equipment that deal with heat transfer in turmeric processing.

Despite an extensive literature search no published information was found on quality attributes of ambient and cryogenic ground turmeric powder. Therefore, this study was performed with the objective to compare some of the major quality characteristics such as volatile oil, curcumin content, oleoresins, total phenols, colour parameters, antioxidant activity and thermal properties, namely, bulk thermal conductivity, specific heat and bulk thermal diffusivity of turmeric powder ground at different conditions.

2 Materials and methods

Samples of turmeric rhizome were procured from Indian Institute of Spices (IISR), Kozhikode, Kerala, India. The turmeric samples were cleaned manually to remove undesirable materials and broken into smaller pieces and passed through BSS 10 (2.034 mm opening) and 20 sieve number (0.894 mm opening). The broken rhizomes retained on BSS 20 sieve was considered for the experiment. The moisture content of the broken turmeric rhizome was determined with the help of vacuum oven drying method and was 11.5% (d.b.). The broken rhizomes were divided into two equal lots. One lot was ground in cryogenic grinder (Model: 100 UPZ, Hosokava Alpine, Germany) using liquid nitrogen (LN2) at grinder speed of 12000 r/min and 1 kg/h feed rate and the other lot in the same grinder at ambient conditions. The temperature during cryogenic and ambient grinding varied from -30°C to -70°C and 30°C to 56°C, respectively. The ambient and cryogenic ground turmeric rhizome samples were packed in sealed, moisture free and water proof flexible polythene bags for further analysis of quality characteristics.

2.1 Volatile oil

The volatile oil from turmeric powder ground at ambient and cryogenic conditions was extracted by hydro-distillation using Clevenger apparatus (Saxena et al., 2012) until all the oil is collected (8 h). Each of the samples was subjected to distillation thrice and the results were expressed as mean ± standard deviation.

2.2 Curcumin content

Curcumin content of turmeric powder ground at different conditions were determined as described by Sogi et al. (2010). Turmeric powder with measured amount of absolute alcohol was transferred to double jacketed flasks (which were simultaneously stirred and heated using water bath (Brookfield Inc. USA) at a selected temperature for a predetermined time. Absorbance of sample was taken at 425 nm using UV-spectrophotometer (1601-Shimadzu Co. Ltd., Japan) and the amount of curcumin was calculated from standard curve using Equation (1):

$$Curcumin\ yield\ (\%) = \left(\frac{Curcumin\ extracted\ (g)}{Turmeric\ used\ (g)} \right) \times 100 \quad (1)$$

2.3 Preparation of standard curve

A stock solution was prepared by dissolving 10 mg of curcumin in absolute alcohol to get concentration of 1 mg/mL. Different concentrations were made by diluting the stock solution with absolute alcohol. The absorbance was read at 425 nm and plotted against concentration.

2.4 Oleoresin content

Oleoresin content of turmeric powder ground at ambient and cryogenic conditions was extracted using Accelerated Solvent Extraction System (Dionex India Ltd.) with hexane as a solvent (Saxena et al., 2012).

2.5 Total phenolic content

Total phenol concentration was determined using a Folin-Ciocalteu assay, as was described by Amin et al. (2006) with slight modification. The crude extracts in methanol, water and petroleum ether were prepared by soaking the cryogenically ground turmeric powder for overnight, extraction was repeated three times and supernatants were pooled for analysis. After collecting the supernatant of all the samples the extracts were diluted to make a stock solution of known concentration. These diluted extracts were used for determination of the total phenolic content. An aliquot of 0.1 mL extract (5 mg/mL in respective solvent) was taken in a test tube and made the volume 1 mL by adding solvent. 3 mL of 10% sodium carbonate was added. Previously 10-fold diluted Folin-Ciocalteu reagent was added to the mixture. The mixture was allowed to stand at room temperature for 90 minutes and then absorbance was measured at 710 nm. Gallic acid was used as the standard phenol. The amount of phenolic content was calculated by using the standard curve of Gallic acid prepared with respective solvent having R^2 value ranged from 0.96-0.99 and was expressed as ppm Gallic acid equivalents (ppm GAE / 1000 ppm) crude seed extract.

2.6 Antioxidant activity

The antioxidant activity of each extract was evaluated on the basis of its activity in scavenging the stable DPPH (1, 1-Diphenyl-2-picrylhydrazin) radical, using a slight modification of the method described by Shimada et al. (1992). Each extract as prepared above was diluted in methanol, water and petroleum ether to give at least five different concentrations. An aliquot (1, 1.5, 2, 2.5 mL) of the extract of each concentration was mixed with 1 mL of 1 mol/L DPPH. The mixture was then homogenized and left to stand for 30 min in the dark. The absorbance was measured at 517 nm against a blank of methanol using a spectrophotometer. DPPH solution plus methanol was used as control and Butyl hydroxyl toluene (BHT) was used as a standard reference synthetic antioxidant with R^2 value ranged from 0.95-0.99. Results were expressed as a mean standard deviation from three replicate measurements. The percent scavenging effect was calculated in Equation (2):

$$\textit{Scavenging effect}\ (\%) = \left(\frac{A_{517}\ \textit{of control} - A_{517}\ \textit{of extract}}{A_{517}\ \textit{of control}}\right)\times 100 \qquad (2)$$

where, A_{517} is absorbance measured at 517 nm using a spectrophotometer.

2.7 Colour

Colour values (namely L, a and b) of turmeric powder, ground at ambient and cryogenic conditions, were determined using Hunter lab colorimeter (D-65 illuminant and 10° observer). L value varies between 0 and 100. A perfectly white body has L=100 and a black body has L = 0. A positive value of 'a' indicates the redness and negative value greenness. A positive value of 'b' indicates yellowness and negative value of b shows blueness.

2.8 Specific heat

The specific heat of ambient and cryogenically ground turmeric powder was determined by using the Differential Scanning Calorimeter (DSC 6000 Perkin Elmer, USA) operated by Pyris software. Before conducting the experiments, the DSC was calibrated using indium at the scanning rate of 10°C/min. For determination of specific heat, the cryogenic ground turmeric rhizome samples were kept in an aluminium crucible (capacity 10 μL) in small quantity (5-5.5 mg). The aluminium crucible was sealed and run in the DSC for the temperature range of -100°C to 100°C. The DSC provided thermogram, in which ordinate shows the heat flow rate mW/mg as a function of time and temperature. Specific heat and glass transition temperature (T_g) were determined from the thermogram according to the procedure given in software. All experiments were performed in triplicate and the mean values were reported.

2.9 Thermal conductivity

The bulk thermal conductivity (k_b) was measured by using portable Thermal Conductivity Meter (Model: KD-2 PRO, Decagon Devices, Inc. USA). The ground turmeric rhizome powder were filled into 100 mL beaker and complete tapped, then the beakers were covered using aluminium foils stored over night in deep freezer (U 410-86, New Brunswick Scientific, England) at -50°C for the conditions of below 0°C. For the higher temperature, i.e., above 0°C the samples were put in recirculation type tray dryer (BTPL, Kolkata, India) at 60°C for 4 h. The thermal conductivity meter was calibrated with glycerine. After calibration, the sample was taken out from the deep freezer and immediately the single needle (KS-1, 1.3 mm diameter × 60 mm long) of thermal conductivity meter was inserted in the sample and reading was taken at interval of 2 min.

2.10 Bulk density

The average bulk density of ambient and cryogenic ground turmeric rhizome was determined by using a container of known volume. The container was weighed and the weight was noted down. Then the container was filled with turmeric powder and total weight was noted down. The subtraction of weight of container from total weight (i.e., turmeric powder and container) will give the mass of sample. Now, by using the following Equation (3) bulk density was calculated:

$$\rho_b = \text{mass (kg) / volume (m}^3\text{)} \qquad (3)$$

2.11 Thermal diffusivity

The bulk thermal diffusivity of ambient and cryo-ground turmeric rhizome powder was calculated from the obtained values of bulk thermal conductivity, specific heat and bulk density using Equation (4):

$$\alpha_b = \frac{k_b}{\rho C_p} \qquad (4)$$

where, α_b is the bulk thermal diffusivity in m^2/s; C_p is the specific heat in kJ kg^{-1} °C^{-1}; k_b is the thermal conductivity in W m^{-1} °C^{-1} and ρ_b is the bulk density in kg/m^3.

2.12 Statistical analysis

Univariate analysis of variance was used to analyze the effect of grinding conditions on quality characteristics of turmeric powder using SPSS 12.0.

3 Results and discussion

3.1 Volatile oil, curcumin and oleoresin content

Volatile oil content in the spice powder is a measure of its aroma and flavour, and hence its quality. Higher the volatile oil content in spice powder, the higher is its market value in financial terms since spices are valued for their aroma and flavour (Gopalkrishnan et al., 1991). The volatile oil content, curcumin content and oleoresin of turmeric powder was found to be varied significantly with the grinding conditions, i.e. ambient and cryogenic. A higher value of volatile oil, curcumin and oleoresin content (Table 1) were observed in cryogenically ground turmeric powder as compared to ambient ground turmeric powder.

Table 1 Effect of grinding conditions on the quality characteristics of turmeric powder

S.No	Parameter	Cryo-ground	Ambient ground
1	Volatile oil content, %	5.18±0.05[a]	4.27±0.11[b]
2	Curcumin content, %	5.17±0.02[a]	4.17±0.02[b]
3	Oleoresin content, %	13.28±0.02[a]	10.12±0.63[b]
4	Total phenols (ppm GAE 1000^{-1} ppm)		
	Alcohol extract	2.11±0.01[a]	1.54±0.06[b]
	Water extract	0.70±0.01[a]	0.57±0.02[b]
	Petroleum ether extract	0.31±0.02[a]	0.24±0.01[b]
5	DPPH Scavenging, %		
	Alcohol extract	84.88±0.03[a]	63.14±0.47[b]
	Water extract	72.38±0.06[a]	54.16±0.04[b]
	Petroleum ether extract	40.28±0.02[a]	31.14±0.18[b]
6	Colour values		
	L	54.76±1.17[a]	52.64±0.78[a]
	a	17.39±0.82[a]	17.70±0.73[a]
	b	36.29±0.44[a]	33.34±0.74[b]
7	Glass transition temperature, ℃	74.15±1.47[a]	82.84±2.83[b]

Note: Mean values with the same superscript letters within the same row do not differ significantly ($p > 0.05$).

The volatile oil, oleoresin and curcumin retention is 80%, 82% and 88% respectively, i.e., 15%-25% greater than ambient processed at cryogenic grinding of turmeric. This may be due to the fact that at higher grinding temperatures, mass transfer increased due to the increase in vapour pressure which resulted in a loss of volatile oil. Similar results have been reported by Gopalkrishnan et al. (1991), Singh and Goswami (2000), Mathew and Sreenarayan (2007) for ambient grinding of cardamom, cumin seed and black pepper, respectively.

3.2 Total phenolic content

The phenol content by Folin-Ciocalteu reagent method and antioxidant activity by DPPH free radical scavenging (%) in different solvents is shown in Table 1. DPPH is a chemical compound which generates free radicals. When any crude extract is incorporated in test solution, this scavenges the free radical generated by DPPH. If percent scavenging is more, the test solution has more anti-oxidant activity. It was ascertained that the maximum values for phenols and percentage free radical scavenging was found in alcohol extract as compared to water and petroleum ether extract. The cryo-ground turmeric powder retained approximately 93% and 85% total phenols and antioxidant activity respectively, i.e., 20%-25% more than ambient grinding. Phenolics are quite heat unstable and reactive compounds (Cheynier, 2005) and during ambient grinding there is temperature rise leading to reduction in phenols which can be appreciatory reduced in cryogenic grinding, i.e., grinding at a very low temperature. The enhanced retention of total phenolic content and antioxidant activity may be due to the fact that in cryogenic grinding the vaporization of liquid nitrogen to the gaseous state creates an inert and dry atmosphere which ultimate reduces the loss of quality parameters of spices (Singh and Goswami, 1999). Higher phenolic content and antioxidant activity was also found in cryo-ground coriander and fenugreek (Saxena et al., 2012).

3.3 Colour

The colour values (namely *L*, *a* and *b*) of turmeric powder ambient and cryogenically ground are depicted in Table 1. It was depicted that the colour values *L* and *a* were found to be varied non-significantly with grinding conditions, whereas *b* value which is indicator of yellowness varied significantly with grinding conditions. In case of ambient grinding due to rise in temperature powder turns into dark in colour and lost its brightness. On the hand, in cryogenic grinding, a light and vivid powder obtained due to preservation of brightness and natural lust of powder (Meghwal and Goswami, 2010).

3.4 Specific heat

The specific heat of ambient and cryo-ground turmeric powder was found to increase with the increase (Figure 1) in temperature (-100°C to 100°C).

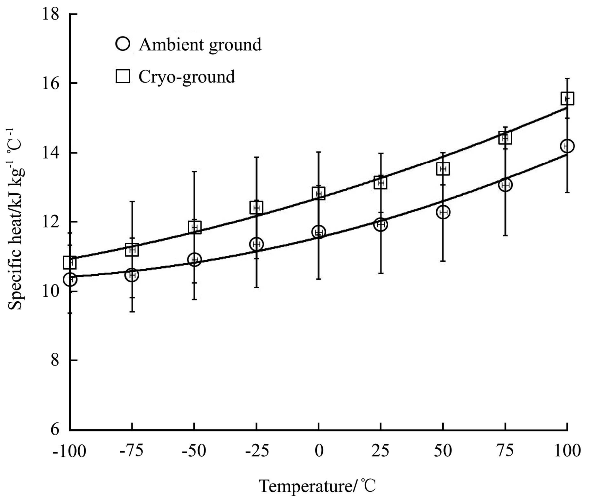

Figure 1 Effect of grinding conditions on specific heat of turmeric powder

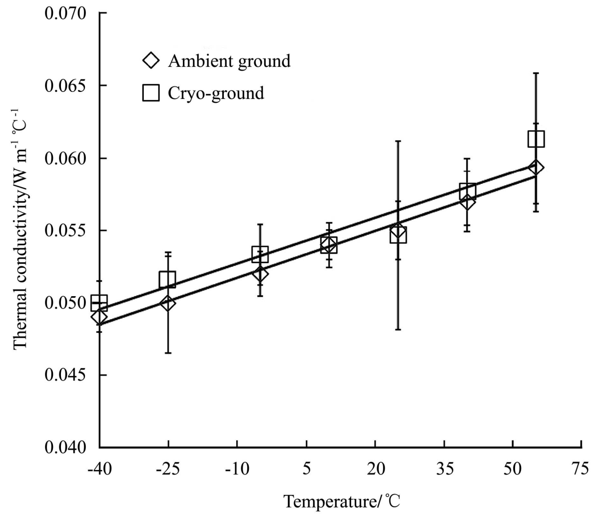

Figure 2 Effect of grinding conditions on thermal conductivity of turmeric powder

The specific heat followed a second order polynomial relationship (R2>0.96) with temperature irrespective of the grinding conditions. The results are in agreement with the findings of Singh and Goswami (2000) who reported specific heat of cumin seed as a non-linear function of temperature. Nevertheless other research workers (Tang et al, 1991; Wang and Brennan, 1993) observed linear relations of specific heat with temperature for other agricultural materials. A higher value of specific heat in the temperature range of -100°C to 100°C was found for cryo-ground turmeric powder as compared to ambient ground turmeric powder. This may again be due to the fact of more retention of volatile oil and moisture due to inert grinding during cryogenic size grinding (Singh and Goswami, 1999). The specific heat of turmeric powder found to be varied significantly with the grinding conditions and temperature at 5% level. The empirical equation showing the relationship of temperature with specific heat at both the grinding conditions is described in Table 2. The values of specific heat increased from10.53 to 16.26 kJ kg^{-1} $°C^{-1}$ in the range of temperature -100°C to 100°C at a moisture content of 11.5% (d.b.).

The analysis of variance for specific heat showed that grinding conditions significantly affected the specific heat at 5% level.

3.5 Thermal conductivity and thermal diffusivity

The variation of thermal conductivity with temperature at both the grinding conditions is shown in Figure 2.

It can be observed that the thermal conductivity increased linearly (R2>0.91) with the increase in temperature from -40°C to 55°C irrespective of grinding conditions. Similar findings have been reported for sheanut kernel, cashew apple, maize and cowpea, by Aviara and Haque (2001), Kurozawa et al. (2008) and Bart-Plange et al. (2009), respectively. The values of thermal conductivity varied from 0.049 to 0.077 W m^{-1} $°C^{-1}$ in the range of temperature -40°C to 55°C at a moisture content of 11.5% (d.b.).

The relationship between temperature and thermal diffusivity at both the grinding conditions is shown in Figure 3. It can be observed that the thermal diffusivity increased with the increase in temperature despite of the grinding conditions. The variation of thermal diffusivity with temperature exhibited a second order polynomial relationship (R2>0.92). Singh and Goswami (2000) also reported increase in thermal diffusivity of cumin seed with the increase in temperature and the relationship was non-linear.

Furthermore, the thermal diffusivity was found high for ambient ground turmeric powder. This may be due to the fact that cryo-ground turmeric powder has higher bulk density and specific heat as compared to ambient ground turmeric powder. The analysis of variance for thermal diffusivity showed that temperature and grinding conditions both significantly affected the thermal diffusivity at 5% level. The thermal diffusivity varied from 9.509×10^{-8} to 11.4×10^{-8} m^2/s with increase in temperature from -40°C to 55°C at moisture content of 11.5% dry basis.

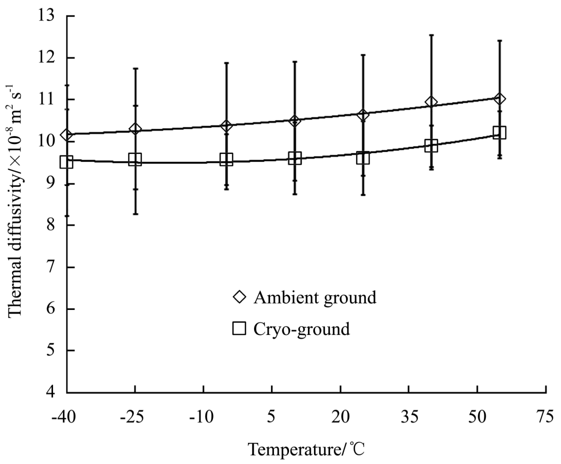

Figure 3 Effect of grinding conditions on thermal diffusivity of turmeric powder

3.6 Glass transition temperature

It can be scrutinized that lower value of T_g was incurred for cryo-ground turmeric powder as compared to ambient ground turmeric powder which may be due to plasticizing effect of water (Table 1). As in cryogenic grinding, pre-cooling of raw spice and the continuous low temperature maintained within the mill reduces the loss of volatile oils and moisture (Singh and Goswami, 2000) whereas in ambient grinding increase in temperature leads to loss of moisture and volatile oil.

4 Conclusions

From present study, following conclusions may be drawn:

Cryo-ground turmeric powder retained 15%-25% more volatile oil, oleoresin, curcumin, phenol content and antioxidant activity as compared to ambient grinding.

Volatile oil, oleoresin, curcumin, total phenols content, antioxidant activity and *b* colour value varied significantly with the grinding conditions.

Specific heat and thermal diffusivity displayed second order polynomial relationships whereas thermal conductivity was found to be varied linearly with temperature.

Specific heat increased from 10.36 to 15.57 kJ kg^{-1} °C^{-1} with increasing temperature (-100ºC to +100ºC) at both the grinding conditions.

Thermal conductivity and thermal diffusivity increased from 0.049 to 0.061 W m^{-1} °C^{-1} and 9.509 × 10^{-8} to 11.4×10^{-8} m^2/s, respectively in a temperature range of -40°C to 55°C.

A higher value of glass transition temperature was found at ambient grinding conditions in comparison to cryogenic grinding conditions.

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