

Effect of Humidity on in-Process Crystallization of Lactose during Spray Drying

Amirali Ebrahimi, T. A. G. Langrish

Abstract—The effect of various humidities on process yields and degrees of crystallinity for spray-dried powders from spray drying of lactose with humid air in a straight-through system have been studied. It has been suggested by Williams–Landel–Ferry kinetics (WLF) that a higher particle temperature and lower glass-transition temperature would increase the crystallization rate of the particles during the spray-drying process. Freshly humidified air produced by a Buchi-B290 spray dryer as a humidifier attached to the main spray dryer decreased the particle glass-transition temperature (T_g), while allowing the particle temperature (T_p) to reach higher values by using an insulated drying chamber. Differential scanning calorimetry (DSC) and moisture sorption analysis were used to measure the degree of crystallinity for the spray-dried lactose powders. The results showed that higher T_p-T_g , as a result of applying humid air, improved the process yield from 21 ± 4 to $26 \pm 2\%$ and crystallinity of the particles by decreasing the latent heat of crystallization from 43 ± 1 to 30 ± 11 J/g and the sorption peak height from $7.3 \pm 0.7\%$ to $6 \pm 0.7\%$.

Keywords—Lactose, crystallization, spray drying, humid air.

I. INTRODUCTION

SPRAY drying is a well-known process for producing amorphous materials [1]. The main reason for the amorphousness of the spray-dried products is that the drying and solidification (transforming from a liquid to a solid form) of the materials in spray dryers are very fast and there is not enough time for atoms or molecules in the spray-dried substance to arrange themselves in an orderly crystal lattice [2]. Amorphous materials are extremely hygroscopic, cohesive and difficult to flow and disperse [3], [4] causing wall deposition with the associated problems of material loss and browning, affecting the quality of the spray-dried product [5]. Moreover, amorphous materials are very unstable and tend to crystallize during storage as either temperature or moisture content are increased [3], [6], [7]. The adsorbed water acts as a plasticizer and decreases the viscosity and glass-transition temperature (T_g) in which the change from the glassy state (amorphous solid) to the rubbery state (amorphous liquid) occurs. The viscosity of the product in the rubbery state is low enough to allow molecular movement required for crystallization to occur [3]. Roos and Karel [7] studied the crystallization of lactose at constant relative humidities above glass-transition temperature (T_g) during storage. They found

that at constant relative humidity (constant T_g), the time to complete crystallization is related to the temperature according to Williams-Landel-Ferry (WLF) equation. The WLF equation states that the rate of crystallization is a function of the difference between the glass-transition temperature (T_g) of the material and the particle temperature (T_p) [7]–[9]. The magnitude of T_p-T_g , has been widely accepted as a best indicator to avoid stickiness and has been used to obtain partial or complete crystallization of the sticky components through in-process crystallization during spray drying [10], [11]–[13] and post processing units like fluidized-beds [14]–[16]. It has been stated that the problem of stickiness may be avoided by undertaking spray-drying operations at not more than 20°C above the glass-transition temperature or in the range of 30 – 50°C or higher above T_g , which increases the degree of crystallinity of the materials [10], [17], [18]. Thus, applying different operating parameters in spray dryers to achieve a large T_p-T_g within the process is a good way to increase the crystallization rate and reduce stickiness in materials and the problems associated with this phenomenon [10]–[13]. Chiou, D., Langrish, T. A. G., and Braham, R. [12], [13] and Islam and Langrish [19] studied the combined drying and crystallization process of lactose, suggesting that drying at temperatures high enough above the glass-transition temperature enhanced the subsequent transition from a sticky amorphous material to a less sticky crystalline one. Chiou, D., Langrish, T. A. G., and Braham, R. [12] found that the degree of crystallinity could be changed by about 10% for changes in the inlet gas temperatures from 134°C to 210°C . The explanation is that the temperature difference (T_p-T_g) in this high-temperature region is sufficiently high for crystallization to occur, as suggested by WLF equation [8]. Materials with high glass-transition temperature tend to lower the temperature difference (T_p-T_g), which in turn decreases the crystallization rate. Hence, applying higher process temperature in order to maintain the higher temperature difference (T_p-T_g) is necessary. The higher glass-transition temperature for lactose (101°C ; [20]) compared with the lower one for sucrose (62°C ; [20]) resulted in lower degrees of crystallinity for spray-dried lactose when similar processing conditions (inlet gas temperature ranges from 45°C to 220°C) were used [21]. The limitation on the inlet temperature of a Buchi-B290 spray dryer is 220°C , which makes it very difficult to reach an outlet temperature over 130°C in order to achieve higher T_p-T_g for lactose. An alternative way to reach higher T_p-T_g is to increase the humidity of the inlet air to decrease the glass-transition temperature of the lactose particles. According to Gordon–

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Taylor equation [22], increasing the moisture contents of the particles decreases their glass transition temperatures.

Islam, Langrish, and Chiou [11] produced fully crystalline lactose powders with the yields of 20% by spray drying in humid condition. They applied the humidity concept by using humid air produced by a humidification column in a closed loop system combined with an insulated drying chamber to achieve higher particle temperatures, in order to increase the crystallization rate as a result of higher $T_p - T_g$, according to the WLF theory.

Using the humid air in a closed loop may causes problems regarding fungi growth and associated health concerns. The overall objective of this work was to investigate the effect of different inlet humidities on process yields and the degrees of crystallinity for spray-dried lactose powders in a combined crystallization and spray drying process with freshly-humidified air in a straight-through system rather than in the closed Humid Loop [11].

II. MATERIALS AND METHODS

A. Sample Preparation

A 10 % (w/v) lactose solution was prepared by dissolving pure lactose monohydrate ($C_{12}H_{22}O_{11} \cdot H_2O$) (analytical-grade reagent from Ajax Finechem Pvt. Ltd., Australia) in tap water with a magnetic stirrer.

B. Experimental Setup for the Spray Dryer

The solution was spray dried using a Buchi-B290 mini spray dryer with inlet air temperatures ranging from 130 to 220°C, an aspirator rate of 100% ($\sim 38 \text{ m}^3/\text{h}$) for the main air flow through the dryer, a rotameter setting of 50 mm (601 l/h) for the atomizing air flow, and a pump rate for liquid of 5 % (1.5 ml/min). The main drying chamber was insulated using a layer of glass wool (25 mm) to minimize the heat loss. The dryer was allowed to reach steady state by operating it for at least 30 minutes with water spray before the lactose sample solution was sprayed. Humid air with different relative and absolute humidities was produced by water spraying in another Buchi-B290 spray dryer as a humidifier section shown in Fig. 1. A set of temperature measurement probes (to measure dry-bulb and wet-bulb temperatures) was used to estimate the relative and absolute humidity of the humid air before entering the spray drying section.

III. INSTRUMENTAL ANALYSIS

A. Moisture Sorption Measurements

Crystallization behaviour was initially studied with the moisture sorption method. A mass of $\sim 0.5 \text{ g}$ (measured by Mettler Toledo balance, model AB204-S, Switzerland) of the product obtained just after spray drying the sample solution was placed on a Petri dish, and the mass change as a function of storage time (at $\sim 25^\circ\text{C}$ and $\sim 70\%$ relative humidity) was recorded (by computer using the Mettler Toledo Balance Link v3.01 program) once per minute over a period of 1–2 days. Afterwards, a moisture content measurement was done by oven drying the samples for $24 \pm 3 \text{ h}$ at 100°C . This

gravimetric moisture sorption method gives reasonably good results for measuring the amorphicity of spray-dried lactose as compared with other conventional analytical methods [11], [23]. The moisture sorption test has been used in parallel with differential scanning calorimetry (DSC) to investigate the degree of crystallinity for the spray-dried lactose powders in this study.

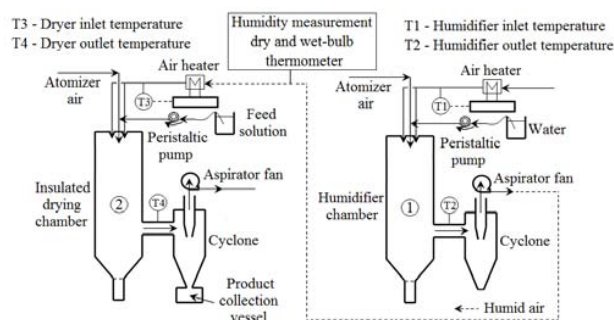


Fig. 1 The humidifying system (1), attached to the main spray dryer (2) for gas humidity control

B. Differential Scanning Calorimetry (DSC)

The degrees of crystallinity of the powders were also determined by differential scanning calorimetry (DSC). DSC samples were prepared according to standard procedures using aluminum hermetically sealed pans. Three samples of each material were analyzed. An empty pan was used as a reference. The samples were heated from 0 to 250°C with a ramp rate of $5^\circ\text{C}/\text{min}$ using a differential scanning calorimeter (TA Instruments Q1000, DE, USA). The scans were normalized by the system according to the sample mass. The integrated peak energies were used to compare the differing degrees of crystallinity (according to the latent heat of crystallization) between different spray-dried products.

IV. RESULTS AND DISCUSSION

A. The Effect of Different Humidities on the Process Yield

Fig. 2 shows the process yields obtained at different humidities as a function of outlet temperatures. As can be seen from the curves, increasing the humidity of the air from normal condition to medium humidity condition increases the process yield from 21 ± 4 to $26 \pm 2\%$. This behaviour can be explained by the decrease in the glass-transition temperature of lactose particles as a result of the rise in their moisture contents. In other words, humidity lowers the glass-transition temperature, thereby increasing the temperature differences ($T_p - T_g$) at the higher outlet temperatures here (above 105°C). Hence, less stickiness and greater process yields due to greater crystallization rates according to WLF theory can be achieved. The low process yields resulting from high-humidity conditions suggest that there is a limitation in applying high-humidity conditions. Using high humidities during spray drying significantly decreases the drying rates, resulting in producing wet particles which is the reason for the particles being very sticky. High moisture contents in the wet particles

can significantly reduce the glass-transition temperature and increase the stickiness too much during the process. High

relative and absolute humidities can also cause the problem of condensation in the cyclone and collection container.

TABLE I
AVERAGE YIELDS OF THE SPRAY-DRIED PRODUCTS AT DIFFERENT INLET GAS TEMPERATURES

Humidity	Inlet Temperature (°C)						
	130	150	170	190	200	210	220
Yield, % (mean \pm standard deviation)							
Normal Condition	71	76	-	78 \pm 1	19 \pm 7	18 \pm 5	21 \pm 4
Medium Humidity	-	68	60	16 \pm 1	20 \pm 1	25 \pm 5	26 \pm 2
High Humidity	-	-	43 \pm 7	18 \pm 2	-	5	0

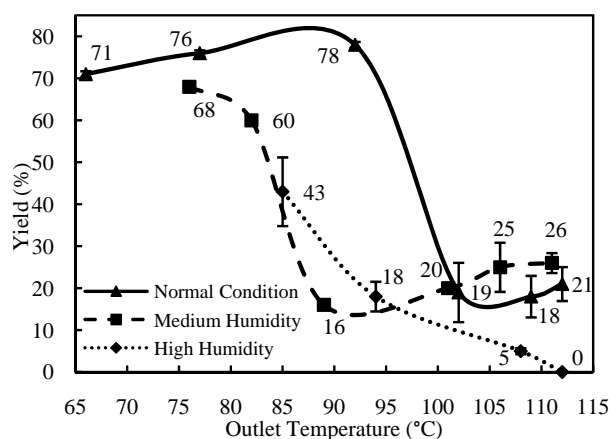


Fig. 2 The effect of different humidities on process yields at different outlet temperatures. Lactose solution: 10%, Pump rate: 1.5 ml/min, Aspirator rate: 38 m³/h, Rotameter: 601 l/h, Medium humidity condition: AH = 58 g/kg D_A, RH = 67 %; High humidity condition: AH = 70 g/kg D_A, RH = 75 %.

It has been stated that the drying performance of small-scale spray dryers, such as Buchi-B290, is limited by the particle drying kinetics [24], [25], so the particle temperature does not approach the outlet temperature of the air so closely at high humidities compared with medium and lower ones. Thus, the $T_p - T_g$ may not be large enough to achieve high crystallization rate and avoid stickiness. Hence, direct deposition of wet particles (whether or not they contain amorphous or crystalline material) is likely to be greater under high-humidity conditions.

B. Assessment of the Degree of Crystallinity of Spray-Dried Powders

Different inlet humidities change the drying and crystallization behaviour of powders and consequently the yields and the degrees of crystallinity for the spray-dried particles. Figs. 3 and 4 show the crystallization heats and sorption peak heights for spray-dried lactose at different humidities and outlet temperatures. The crystallization heat decreases as the temperature increases, indicating an increase in the degree of crystallinity for the particles. This observation agrees with the trend observed for the sorption peak heights obtained from moisture sorption tests.

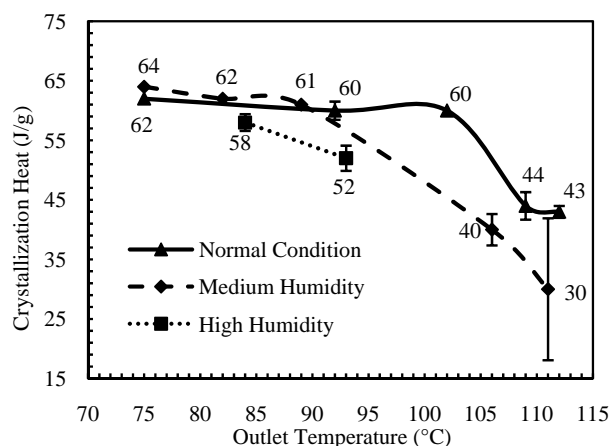


Fig. 3 Crystallization heat (J/g) from DSC at different humidities and outlet temperatures. Lactose solution: 10%, Pump rate: 1.5 ml/min, Aspirator rate: 38 m³/h, Rotameter: 601 l/h, Medium humidity condition: AH = 58 g/kg D_A, RH = 67%; High humidity condition: AH = 70 g/kg D_A, RH = 75 %

The results also show that increasing the humidities improved the degree of crystallinity of the spray-dried powders by decreasing the sorption peak height from $7.3 \pm 0.7\%$ under normal conditions to $6 \pm 0.7\%$ for medium-humidity conditions and the latent heat of crystallization from 43 ± 1 to 30 ± 11 J/g at the same outlet temperature, indicating a greater degree of crystallinity for the spray-dried powders under medium-humidity conditions. Very low yields and degrees of crystallinity observed under high-humidity conditions can be attributed to inadequate drying as a result of the relative and absolute humidities being too high. The evaporation rate is proportional to the difference between the relative humidity at the droplet interface and the relative humidity of the bulk air, so increasing the relative humidity of the bulk air increases the time-to-full drying of droplets [26]. Consequently, because of the very short residence time of particles in the Buchi-B290 spray dryer, there is almost no time left for the crystallization process to occur at high relative humidities.

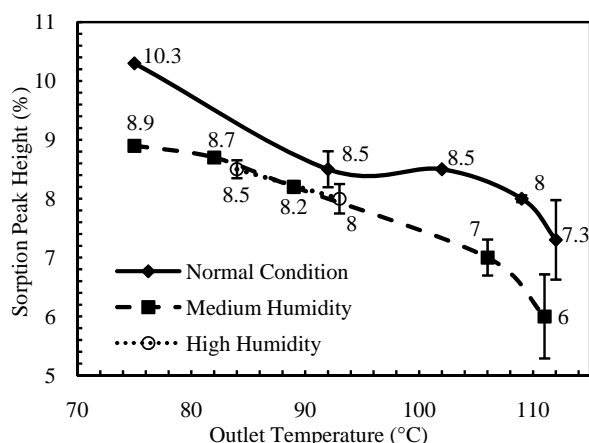


Fig. 4 Sorption peak heights at different humidities and outlet temperatures. Lactose solution: 10%, Pump rate: 1.5 ml/min, Aspirator rate: 38 m³/h, Rotameter: 601 l/h, Medium humidity condition: AH = 58 g/kg DA, RH = 67 %; High humidity condition: AH = 70 g/kg DA, RH = 75 %.

V. CONCLUSION

Applying humid air in a straight-through spray drying system decreased the particle glass-transition temperature, while maintaining the high particle temperature using an insulated drying chamber. This situation effectively increased the T_p - T_g and the lactose crystallization rate according to the WLF theory during the drying process. The samples obtained from this process were analyzed for their degrees of crystallinity using moisture sorption and differential scanning calorimetry. These analyses showed that the samples produced under medium humidity conditions had higher degrees of crystallinity compared with spray-dried lactose particles from normal conditions. Using high humidity conditions resulted in low process yields and degrees of crystallinity due to the poor drying rates and water condensation in the cyclone.

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