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Storage Characteristics of the Spray Dried Talisay (*Terminalia catappa*) Leaves as Source of Natural Dye

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Abstract

Recent resurgence on natural dye production and application is observed due to increasing popularity of more natural lifestyle based on naturally sustainable goods. Natural dyes from flora and fauna are viable alternatives to synthetic dyes. Studies shows that Talisay (*Terminalia catappa*) leaves are good sources of natural colorant producing green, yellow and black pigments, depending on the freshness of the leaves. To compete with the synthetic dyes, availability and storage stability of the natural colorants are desired. Spray drying technique is used to address such problem; wherein the liquid extract is converted to its powder form. Storage stability of the powdered dye depends on the spray drying condition used during operation. Hence, to optimize spray drying process, understanding the storage characteristic of the powdered natural dye is desired. In this study, the storage characteristic of powdered Talisay leaves, such moisture content and glass transition temperature, were determined using Thermogravimetric Analysis and Differential Scanning Calorimetry (DSC), respectively. Effects of varying relative humidity on the EMC were also investigated. Results shows that the moisture content of the powder decreases gradually after 173°C indicating that degradation begins at this temperature. Degradation of the sample was confirm through the identified glass transition temperature of 155°C; which is very close to the degradation temperature. In addition, it was also identified that EMC increases as the relative humidity increases. However, results also signify that spray dried Talisay leaves are stable at room temperature even at varying relative humidity.

Keywords: Equilibrium moisture content; Glass transition temperature; Natural dye; Spray drying; Terminalia catappa

Introduction

The environmental and subsequent health effects of synthetic dyes are becoming subject to scientific scrutiny. With these, interest on the development and improvement of natural dyes has been revitalize. Natural dyes are usually derived from plants, animals, fruits, insects, minerals and other natural resources [1]. Philippines are rich in resources that can be used as source of natural colorants. One example of this is the Talisay (*Terminalia catappa*) leaves [2]. The leaves were observed to have a darker green colour on the top surface and paler green on the bottom. Usually, dye are extracted from Talisay leaves using water solvent to produce a yellow, green and black colorant which can be applied in textile materials [3].

One advantage of synthetic dye over natural dye is its availability in the market. Since the natural colorants are extracted using water, the crude extract is prone to contamination which causes early degradation of the sample. Therefore, to ensure successful commercialization of natural dye, it should be able to withstand longer storage period. Spray drying is a technique used to address the said problem with natural dyes; wherein it transform the liquid sample into powdered form. Although powdered colorants are advantageous than the crude extract, identification of the optimize parameter during spray drying is essential in order to produce good quality powder and to increase the production yield. Optimization of spray drying parameters mainly depends on the storage characteristic of the powdered dye [4]. But due to lack in information of the said characteristic, process optimization becomes difficult. Hence, it is vital to understand the storage characteristic of the certain dye powder.

Presence of moisture influences the stability of the powdered dye [5]. Excess amount of moisture may cause stickiness and crystallization of the product, which in effect may lead to the early degradation of the powder. Thus, to increase the shelf-life of the powder it is important to identify the moisture content present in the powdered sample. This information will also serve as basis for drying operation.

Glass transition temperature *(Tg)* is another useful parameter in understanding the shelf-life of the powdered colorant. Several physiochemical changes of the powders are related to glass transition [6]. In general, molecular mobility in the glassy state is limited to molecular rotations and vibration while above the glass transition, translational mobility appears. Therefore many amorphous powders are stable, but long term stability is lost above the glass transition temperature.

In this study, the author analysed the storage characteristic of the spray dried powdered Talisay leaves by identifying the moisture content and the glass transition temperature using the Thermo-Gravimetric Analysis (TGA) and the Differential Scanning Calorimetry (DSC), respectively. The effect of varying relative humidity on the product's Equilibrium Moisture Content was also determined. These studies will serve as baseline in parameter optimization for spray drying process as well as the design of the spray drying machine.

Natural Dye

There is a worldwide and growing interest in natural colorants, as they are considered suitable for various applications in foods, cosmetics, pharmaceuticals and textile materials [1]. Natural dyes/

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colorants derived from flora and fauna are believed to be an eco-friendly, safe and viable substitutes to synthetic colorants because of their non-toxic, non-carcinogenic, and biodegradable nature. These colorants represent potential alternative to synthetic dyes having higher values and comparable quality [7]. The most important class of colorants from the plant resources is basically flavonoids, quinonoids, indigoids, tannins, etc., which are responsible for dyeing textiles.

Continuous exploration for viable sources of natural dyes is currently conducted to provide sustainable coloration of synthetic and natural textile materials. *Terminalia catappa*, commonly known as Talisay and Country-Almond, is a large tropical tree in the lead-wood tree family that grows mainly in tropical regions of Asia, like Philippines. The tree grows from 10 to 25 m high and has horizontal whorls of branches with single and unequal leaves. The leaves are upside down and oval, 20-30 cm long and 10-13 cm broad. Dry and fresh leaves can be collected to produce yellow, green and black dye [2]. Increasing attention is directed to the use of Talisay leaves as a source of natural dyes with good colour fastness. The leaves of the plant revealed the presence of pigments, viz. lutein, zeaxanthin, tannins and flavone glycosides [2], which are responsible for the colours produced by the Talisay leaves.

Glass Transition Temperature (T_g)

Several physiochemical changes of powdered products are directly or indirectly related to the glass transition temperature. It can be defined as the temperature at which an amorphous system changes from the glassy to rubbery state. In some areas it has been used as indicator of the powder stability and predict the behaviour of the dried sample. It is also an important parameter in deter mining the optimum processing conditions of dried products. Therefore, it is used in designing drying equipment to meet the purpose [6]. Furthermore, stickiness and caking of powder may be controlled by the glass temperature.

Studies have shown that the stickiness of dehydrated powders occurs as a result of particle surface plasticisation and concurrent decrease in viscosity allowing the formation of the liquid bridges between powder particles [8]. Further plasticisation is often followed by collapse of structure as a result of increasing flow and crystallization, which may occur instantly at a high level of thermal and water plasticisation. It may be assumed that similar mechanism control particle properties in spray drying process. However, the process involves removal of the solvent and the plasticiser, which has to occur with a rate competing with particle velocity and formation of a dry surface to allow free flow of individual particles throughout the dehydration process.

The glass transition event is one of the most important characteristic properties of a material. As mentioned, it represents the lower end use temperature since a material cannot be processed or worked with once its temperature drops below (T_g). Probably the most traditional and common way of deter mining the glass transition temperature is through Differential Scanning Calorimetry (DSC). In the DSC testing, T_g is manifested by a change in the baseline, indicating a change in the heat capacity of the powdered sample. The baselines before and after the transition are extrapolated to the temperature where the change in the heat capacity is fifty (50%) percent complete. The change in heat capacity is measured at the 50% point. Then T_g is often reported as the temperature at the intersection of the baseline and the line extrapolated from the linear portion during the phase transition. First order phase transitions have an enthalpy and heat capacity change. Meanwhile second order transitions are manifested by a change in heat capacity, but with no accompanying change in the enthalpy. No enthalphy change is associated with the glass transition, indicating that the temperature follows the second order [8].

Moisture Content

Moisture content is a critical component of material quality and essentially a function of quality control in most production and laboratory facilities [9]. Moisture content control greatly influences the physical properties and product quality of nearly all substances and materials at all stages of processing and final product existence [4]. Scientifically speaking, moisture is just water diffused in relatively small amount. Almost all of the materials contain miniscule amount of moisture as a component of the molecular makeup. Moisture in the materials, generally, increases or decreases due to hygroscopic nature and action of the sample. Hygroscopic action is the amount of moisture a material will absorb relative to ambient temperature and humidity conditions. Since temperature and humidity can be controlled during drying process [9], understanding and identifying the amount of moisture present in the final powder can be used as basis in the optimization of the spray drying parameter.

Generally, moisture content is difficult to measure because of the complex inter molecular bonding properties within the substance matrix [9]. Similarly, the identification and efficient operation of reliable moisture analysis equipment is an essential component of any production or laboratory environment. The thermogravimetic analysis (TGA) is an efficient, reliable and cost- effective method for determining moisture content, and can be utilized in any environment.

The measure of moisture content during TGA defines moisture as the loss mass of a substance when heated, by the process of water vaporisation. The substance difference is continually calculated and recorded by a precision balance. Sample substance mass is measured before and after the drying process for final moisture determination on percentage basis. To fully understand the drying process of moisture vaporisation, users should be aware of the auxiliary fundamentals associated with the process for optimum result. In addition to water vaporisation, thermogravimetric drying methods do not distinguish weight loss of arbitrary compounds during the test cycle. Also, if the drying temperature is set to high, sample decomposition may result.

TGA method is also used to identify the degradation temperature of the sample. This temperature may be used as the optimum limit for the heating rate during the Differential Scanning Calorimetry (DSC) testing.

Equilibrium Moisture Content

At any given moment, there is a dynamic exchange of moisture occurring between an object's core, its perimeter, and the air of the environment. The moisture is transferred in the form of water vapour by the process of diffusion. The moisture diffuses from the material into the air, then it diffuses back to the material and then back to the air. Roughly speaking, this diffusion is driven by the differences in moisture content. So, when an area with more moisture comes in contact with an area of less moisture, it is transferred from the area of higher concentration to the area of lower concentration. Because this exchange of moisture is continuous, eventually enough moisture is diffused form the air into the material that it neither gains nor loses moisture in the exchange. At this point, the object has reached moisture equilibrium with the environment. This dynamic, continuous exchange is why hygroscopic materials equilibrate with the relative humidity of the environment.

When hygroscopic materials are moved from one humidity condition to another or when they are exposed to humidity fluctuations, the moisture content of the materials is no longer in equilibrium with the relative humidity of the air [10]. Confronted with this difference in moisture content, the materials will absorb or release moisture until its moisture content reaches equilibrium with the new environ mental condition. In other words, if the moisture content of the air increases, the materials reacts so that its moisture content will also increase. During absorption, the moisture travels from the outside of the object inward, affecting the edges and the top of the object before reaching the object's core. Similarly, if the relative humidity of the environment decreases, the material will release moisture in the environment. The materials thus respond to the changes in the moisture content of the air [4]. But, just as the temperature equilibration, the new moisture equilibrium is not attained instantly. It takes time for the material to respond to the new conditions, to absorb or desorb the appropriate amount of moisture. Only if the new humidity conditions persist long enough will the entire object from its perimeter to its core reach moisture equilibrium with the relative humidity of the environment.

Because hygroscopic materials equilibrate with the relative humidity of the environment, the relative humidity is the primary determinant of a material's moisture content [9]. The amount of moisture a material contains when it has reached equilibrium with its environment is described as the equilibrium moisture content (EMC). Expressed as a percentage, the EMC describes how much of the material's mass is made of water. The relationship between EMC and relative humidity can be seen in the representation of moisture equilibrium curves, which graph the EMC of a material at a given RH and constant temperature [11].

Materials and Methods

Natural dye from the crude extract of Talisay (*Terminalia catappa*) leaves was converted into its powdered form to increase the shelf-life. Storage characteristics of the dried colorant, such as moisture content and glass transition temperature are then analyse using Thermogravi metric Analysis (TGA) and Differential Scanning Calorimetry (DSC), respectively.

Powdered dye preparation

Fresh Talisay leaves (green in colour) were gathered and extracted with water. The dye bath from this solution was boiled to produce a dark green liquid colorant. Then the crude extract is placed inside the feed tank of the spray dryer and were heated and atomized to produce powdered Talisay leaves.

After collection, the powder is then immediately subjected to different testing procedures to identify the moisture content, glass transition temperature and equilibrium moisture content.

Moisture analysis

Thermogravimetric Analysis (TGA) is used to identify the moisture content and the initial, moisture content of the dried powdered Talisay leaves. For both moisture analysis, five (5) to ten (10) milligrams of powdered sample were placed inside a platinum cell of TGA Q-50 and were heated at the rate of 10°C min^{-1} up to 110°C min^{-1} and 10°C min^{-1} up to 800°C min^{-1} for the initial moisture and moisture content analysis, respectively.

The heating rate of 10°C min^{-1} up to 800°C min^{-1} were set as basis to identify the degradation temperature of the powdered sample. This temperature will provide the heating rate limit during the DSC operation. Meanwhile, the identified initial moisture content is used to calculate the equilibrium moisture content of the powdered Talisay Leaves.

Determination of glass transition temperature *(T_g)*

Differential Scanning Calorimetry (DSC) technique was used to deter mine the glass temperature of the powdered Talisay leaves. Eleven (11) milligrams of the sample was placed inside a T-zero aluminium pan and crimped with a T-zero aluminium lid. An empty aluminium pan covered with aluminium lid was also provided to serve as reference cell. These two pans are placed inside the DSC Q-200TA and were heated at the rate of 5-190°C min^{-1}. Note that the heating rate was based on the degradation temperature of the Talisay leaves identified during the TGA testing.

Calculation of equilibrium moisture content (EMC)

To determine the EMC of the powdered colorant, one (1) gram (± 0.01 g) of the powder were placed inside the weighing bottle and transferred inside the desiccators that contains sulphuric acid solutions with concentrations of 50%,70% & 90% (by weight) to maintain the relative humidity of the system. Temperature in this part was held constant; using room temperature as the basis. To prevent the formation of moulds in the sample, cottons containing 2-3 drops of formic acid were placed at the top of each weighing bottles. Samples are taken out of the desiccators every 48 hours to measure the change in their weight. This is done until the reading reached a constant weight (equilibrium). Then EMC is calculated using the equation below:

$$EMC = \frac{\left(w_f - w_i\right) + \left(M_i.W_i\right)}{W_i\left(1 - M_i\right)} \tag{1}$$

Where *wi* is the initial weight of the samples,

wf is the final weight of the sample after equilibrium

Mi is the initial moisture content fraction that was determined in TGA Q-50.

The effect of the varying relative humidity is then analysed by graphing the calculated EMC against the said parameter.

Results and Discussion

Moisture content plays significant role in the stability of the dried powder. Excessive or deficient moisture content of a substance can adversely impact the physical properties of the materials. Presented in Figure 1 is the TGA thermograph for the moisture analysis of the Talisay Leaves. It can be noted from this that the initial weight of the sample decreases as the temperature increases; indicating that moisture is evaporated during the test.

For powdered Talisay leaves, as represented in Figure 1, the initial decomposition temperature (IDT) begins at 172.87°C losing 10.73% moisture. This temperature only signifies that the powder starts to disintegrate and should not be operated nor stored at the said temperature. In addition, this parameter also served as basis for the limitation of the DSC heating rate to avoid full decomposition of the sample. Meanwhile, the maximum rate of decomposition temperature (MRDT) for powdered Talisay leaves is observed to be at 279.03°C, losing 54.11% moisture content; and the material eventually degrade as the temperature increases. This rate is displayed by the diagonal slope that can be observed after the radius of curvature in Figure 1. Lastly, based on the same figure, the final moisture loss at 800°C is 80.47%, this value denotes that at this condition, the powder had shrink or clump

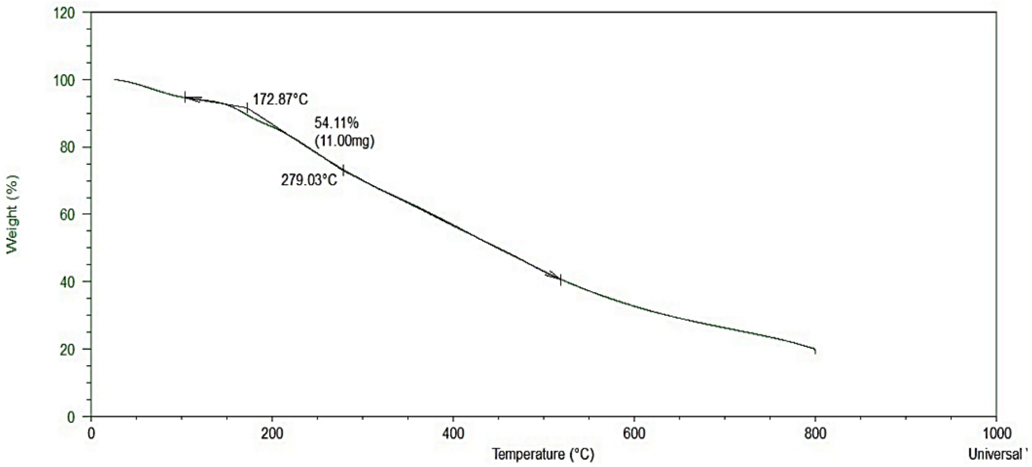

Figure 1: Powdered Talisay Leaves TGA Thermograph.

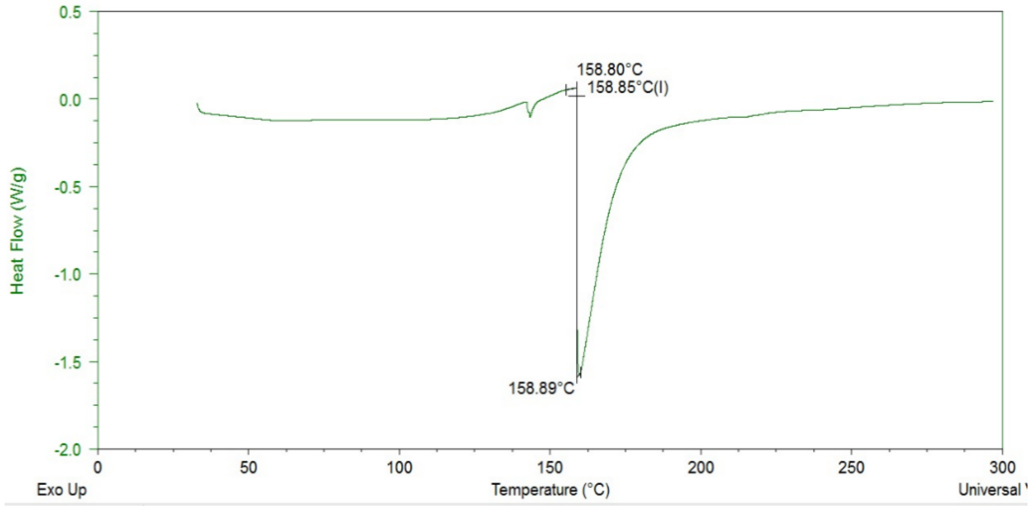

Figure 2: Talisay Leaves DSC Thermograph.

due to loss of water. Therefore, to prevent degradation of the product, it is advisable to operate such materials at the temperature range before IDT, which is represented by the plateau part of the thermograph.

After spray drying process, the moisture distribution within the particles becomes even and the moisture content is reduced to a sufficiently low level to maintain the glassy state at typical storage condition of powdered sample. With this, it is important to identify the glass transition temperature. Figure 2 shows the thermograph for the powdered Talisay leaves which is operated at the heating rate of 5°C/min to 190°C/min. Based from this figure, it can be noted that the glass temperature is very close to the observed endothermic peak. By getting the midpoint temperature between the observed changes in heat flow, the recorded glass temperature for Talisay leaves is 155°C. This temperature is significant because it influences the process ability and storage stability of the powder. Storing dried powder and operating spray dryer above the glass transition temperature may cause stickiness and caking of the product. Meanwhile, the observed endothermic peak shows that the sample will begin to melt at 160°C. This temperature is very close with the previous recorded IDT of 172.87°C. In addition, careful analysis of DSC result is needed, since some of the data from the graph may cause confusion during interpretation. As observed, a small endothermic peak at temperature of 145°C is noted in Figure 2. This peak is caused by impurities present in the sample and should not be mistaken to glass temperature.

Comparison of TGA and DSC thermograph were also presented in Figure 3. This figure was shown to validate the results of the two test. Based from this, it can be noted that initial degradation temperature of the sample is very near the melting temperature. Confirming that the powdered sample will degrade between this temperature range.

As mentioned, the equilibrium moisture content (EMC) of the dried powder plays a vital role in the storage characteristic of the product. When equilibrium condition is reached, the net exchange of moisture between the material and the surrounding air is zero, which results in possible increase in the shelf-life of the powder. Literatures indicate that EMC is a function of the temperature, relative humidity and the nature of the product. In this study the EMC is determined using eqn 1 and were graphed against the varying relative humidties (Figure 4).

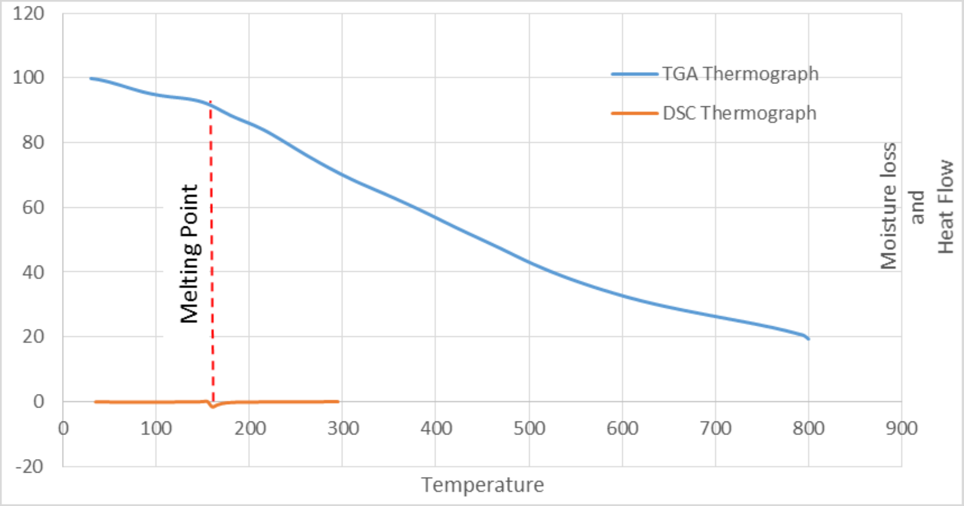

Figure 3: TGA and DSC Thermograph of Powdered Talisay Leaves.

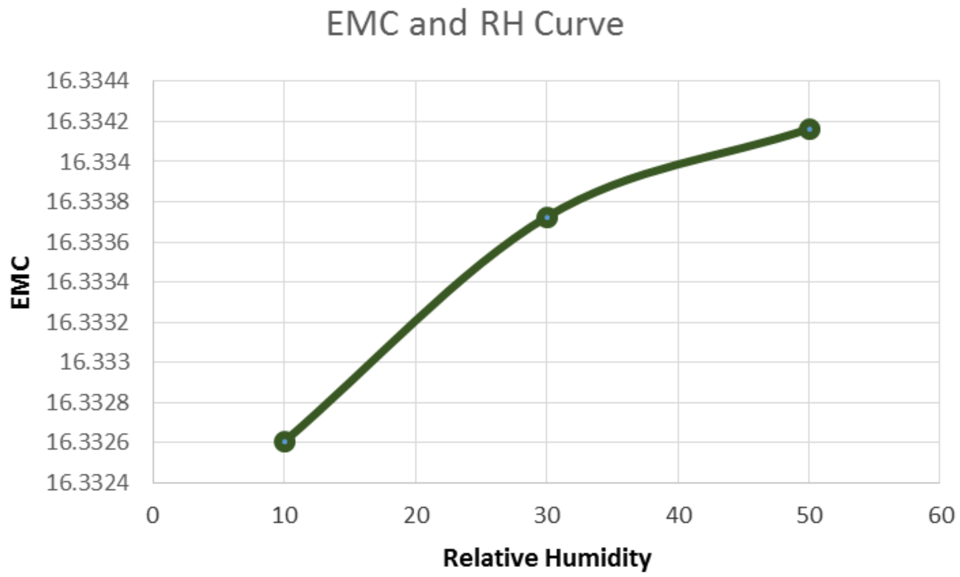

Figure 4: EMC and Relative Humidity Curve.

However, prior to eqn 1, the initial moisture content were identified using TGA Q-50 and based from the result the initial moisture content of the powdered Talisay leaves is 0.05769.

Results show that at higher relative humidity, the spray dried samples absorbs more moisture from the environment. Meaning, the moisture content of air is proportion to the moisture content of the samples. However, the graph also indicates that increased in relative humidity results to a minimal effect on the EMC which indicate that spray dried powders can be stored at room temperature even at high humidity.

Conclusion

Thermogravimetric Analysis (TGA) and Differential Scanning (DSC) are two techniques used to understand and identify the moisture content and the glass transition temperature of the spray dried natural dye. Results show that the optimum drying temperature for Talisay leaves is up to 155°C only. Temperature higher than the given limit may cause the undesirable quality of the powder. Meanwhile, the curve generated during Equilibrium moisture content signifies that varying relative humidity has a mini mal effect on the increase or decrease of the moisture. Indicating that powder produced during spray drying is stable and can be stored in room temperature with varying relative humidity.

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