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Effects of Spray-Drying Inlet Temperature on the Production of High-Quality Native Rice Starch

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Abstract: Rice starch is a common functional ingredient used in various food applications. The drying regime to obtain dry starch powder is an important processing step, which affects the functional properties of the starch. The application of extreme thermal treatment during the conventional drying process tends to elicit irreversible changes to the rice starch, resulting in the loss of desired functionalities. In a previous study, we reported the development of a novel low temperature spray-drying based process which efficiently dries waxy rice starch, while preserving its physicochemical properties and functionalities. This study, a follow-up to the previous report, evaluated the effect of different spray-drying inlet temperatures on the production yield, physicochemical properties, and functionalities of waxy rice starch. Increasing the inlet temperature from 40 °C to 100 °C resulted in an increase in the process yield from 74.83% to 88.66%, respectively. All spray dried waxy rice starches possessed a low moisture content of less than 15%, and a consistent particle size (median ~6.00 µm). Regardless of the inlet temperatures, the physicochemical functionalities, including the pasting characteristics and flowability, were similar to that of the native waxy rice starch. The molecular and A-type crystalline structure of the waxy rice starches were also conserved. An inlet temperature of 60 °C represented the optimum temperature for the spray-drying process, with a good yield (84.55 ± 1.77%) and a low moisture content (10.74 ± 1.08%), while retaining its native physicochemical functionalities and maximizing energy efficacy.

Keywords: waxy rice starch; spray drying; physicochemical properties; pasting behavior; particle size; crystalline structure

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1. Introduction

Rice starch is a common food ingredient with beneficial functionalities, including thickening, stabilizing, and gelling capabilities [1]. Rice starch is used in a wide range of food applications, including poultry products, confectionery, baked goods, soups, and sauces [2].

Preparation of rice starch begins with milling of the rice into fine rice flour. The milled flour then undergoes an alkaline steeping treatment to remove the majority of the proteins (<1.5%), deriving the rice starch [3]. The rice starch finally undergoes drying in order to obtain the final starch powder [1]. The choice of drying methodology is crucial in determining the yield and functionalities of the final rich starch product.

Commonly-employed drying processes include drum drying [4], oven drying [5] and flash drying [6]. However, due to exposure to prolonged and high thermal conditions of these drying processes, the physicochemical properties of the resultant rice starches may be modified, resulting in a loss of functionalities of the native rice starch [6–8]. Spray drying represents a possible alternative drying strategy to process rice starch, while retaining its native physicochemical properties and functionalities [9]. Spray drying is different from most drying methods in which the starch is first dried to form a dried starch cake before pulverizing it to powder format. Instead, spray drying first atomizes the starch suspension into small droplets before drying. Using a dual fluid nozzle, the sample and air are pushed through a small orifice at high pressure, breaking up the starch suspension into fine droplets. These droplets then fall through the drying chamber, together with hot air flowing in a co-current fashion, thoroughly drying the droplets in the process. The dried starch powder is separated in the subsequent cyclone and retrieved in the collection chamber [10]. Due to its mechanism, the spray drying process offers various advantages, including continuous processing, uniform particle quality and lower exposure to thermal conditions. In a previous study, we demonstrated the feasibility of using a low-temperature spray-drying process to effectively dry rice starch [11]. Following our previous report, this study examined the effect of the spray-drying inlet temperature on the resultant waxy rice starch. This study aimed to provide meaningful insights into the impact of the spray-drying inlet temperature on the physicochemical properties of the starch, as well as assessing the optimum inlet temperature for spray drying waxy rice starch. These findings substantiate the data from our previous study and show the benefits of using the spray dryer as an effective drying methodology to produce waxy rice starch powder.

2. Materials and Methods

2.1. Materials

The waxy rice flour (Erawan, Cho Heng Rice Vermicelli Factory Co. Ltd., Nakhon Pathom, Thailand) used for the experiments was procured from a local supermarket (Fairprice, Singapore). Chemicals and reagents were purchased from Sigma-Aldrich (Singapore), unless otherwise stated.

2.2. Protein Extraction

Protein extraction of the milled waxy rice flour was carried out using an established alkaline steeping method [1]. The waxy rice flour was incubated in 0.1% (*w*/*v*) sodium hydroxide (NaOH) with continuous stirring at 500 rpm for 18 h, under atmospheric conditions (25 °C). The rice flour to NaOH ratio was maintained at 1:2 (*v*/*v*). The resulting suspension was centrifuged (5430R, Eppendorf, Hamburg, Germany) at 2000× g for 5 min (20 °C) and the separated protein layer was removed by manual scraping. Subsequently, the starch was resuspended in deionized water. The pH of the waxy rice starch suspension was adjusted to pH 6.50, using 1.0 M hydrochloric acid (HCl). The resulting starch suspension was washed thrice with a copious amount of deionized water in order to remove any remnant salt. Finally, the starch solution was kept at 4 °C overnight (18 h) in preparation for the subsequent drying processes. The starch solution before drying is assumed to be the native waxy rice starch and is denoted as "Before Drying" in the rest of the study.

2.3. Spray Drying

The waxy rice starch dispersion (20% *w*/*w* solid content) was spray dried using a lab-scale spray dryer (B-290, Buchi, Flawil, Switzerland), attached with a dehumidifier (IDFA3E, SMC Pneumatics, Tokyo, Japan). The inlet temperature varied from 40 °C to 100 °C, with other process parameters, such as the aspiration rate (100%), feed flowrate (4 mL/min) and air flow rate (601 L/h, pressure drop of 0.75 bar), maintained constant. In the subsequent sections, the waxy rice starches that are spray dried at an inlet temperature at 40 °C, 50 °C, 60 °C, 70 °C, 80 °C and 100 °C are denoted as "SP 40", "SP 50", "SP 60", "SP 70", "SP 80" and "SP 100" respectively.

2.4. Physicochemical Properties of Waxy Rice Starch

All spray dried waxy rice starch powders were subjected to various characterization techniques. The techniques used are detailed in the following sections.

2.4.1. Moisture Content Analysis

The moisture contents of the respective starch samples were determined using a halogen lamp moisture analyzer (Hal. Moisture Analyzer HE53, Mettler Toledo, Columbus, OH, USA). An amount of 1.50 g of starch powder was weighed on a disposable aluminum pan and dried at 140 °C using the rapid setting. The moisture content was presented in terms of the percentage of moisture content.

2.4.2. Kjeldahl Method

The protein contents of the respective waxy rice starches were determined using Kjeldahl method (VAP450, Gerhardt Analytical Systems, Königswinter, Germany). An amount of 1.0 g of starch powder, along with 12 mL of concentrated sulfuric acid and 2 Kjeltabs, were added into Kjeldahl digestion tubes. The mixture was subsequently subjected to digestion at 230 °C for 15 min, before being cooled to room temperature (~25 °C) in a fume hood. The reaction mixture was subsequently distilled and auto-titrated with 0.1 M hydrochloric acid (HCl) and 2% boric acid solution. The ammonia content was evaluated by determining the corresponding amount HCl utilized for the neutralization process. Based on the ammonia content, a conversion factor of 5.95 was used to calculate the protein content in the resultant waxy rice starch.

2.4.3. Process Yield

The process yield from the spray-drying process is calculated, based on the following formula:

$$\text{processyield} = \frac{\text{weightofspraydriedstarch (g)}\frac{(100-\text{moisture content ofspray dried starch})}{100}}{\text{weightofstarchsuspension (g)}\frac{(100-\text{moisture content starch suspension})}{100}} \times 100\% \quad (1)$$

2.4.4. Particle Size Analysis

The particle size of the waxy rice starches was measured using a particle size analyzer (Mastersizer 3000, Malvern Panalytical, Malvern, UK). A starch suspension with a solid content of 5.0% (w/w) was prepared at room temperature (~25 °C) and pipetted into the laser diffraction particle size analyzer dispersion tank until a final obscuration within the range of 5–7% was attained. A sonication protocol (30%, 120 s) was implemented in order to break up loose starchz agglomerates before subjecting the starch dispersion to particle size analysis. The particle size distribution, surface-weighted diameter (D[3,2]) and particle size distribution were obtained. All parameters were defined based on Mie Theory with refractive index set as 1.53.

2.4.5. Density and Flowability Analyses

Bulk densities of the spray-dried waxy rice starches were measured by adding 5.0 g of the respective starch into a graduated measuring cylinder before the initial volume was recorded. The tapped density was determined by subjecting the starch in the measuring cylinder to mechanical tapping for 500 repetitions (Autotap, Quantachrome Instruments, Gras, Austria). The bulk and tapped densities were derived based on the volume of the starch before and after tapping. The bulk density and tapped densities were calculated using the following equations:

$$\text{Bulk density}\left(\frac{\text{g}}{\text{cm}^3}\right) = \frac{\text{Weight of starch (g)}}{\text{Initial volume (cm}^3)} \quad (2)$$

$$\text{Tapped density}\left(\frac{\text{g}}{\text{cm}^3}\right) = \frac{\text{Weight of starch (g)}}{\text{Tapped volume (cm}^3\text{)}} \tag{3}$$

The Hausner Ratio (HR) and Carr's Index were subsequently determined as an empirical number to indicate the flowability of the starches. HR and Carr's Index were determined using the following equations:

$$\text{Hausner Ratio (HR)} = \frac{\text{Tapped density}}{\text{Bulk density}} \tag{4}$$

$$\text{Carr's Index (\%)} = \left(1 - \frac{\text{Bulk density}}{\text{Tapped density}}\right) \times 100\% \tag{5}$$

2.5. Pasting Profiles

Pasting properties of the waxy rice starches were analyzed using a rheometer (MCR 102, Anton Paar GmbH, Gras, Austria), installed with a starch cell (C-ETD160/ST, Anton Paar GmbH, Gras, Austria) and spindle geometry (ST-24-2D/2V/2V-30, Anton Paar GmbH, Gras, Austria). An appropriate amount of the respective spray-dried waxy rice starch was weighed and hydrated in deionized water in order to form a final starch suspension with a solid content of 5.0% (*w*/*w*). The starch solution was pre-stirred at 500 rpm for 30 min at atmospheric conditions (~25 °C) using a benchtop stirring plate (Hei-Connect, Heidolph, Schwabach, Germany). The starch suspension was subjected to pasting analysis. The starch was then preheated from 20 °C to 50 °C at an accelerated heating rate of 4 °C/min. Subsequently, a second controlled heating phase was applied during which the temperature of the suspension was raised gradually, from 50 °C to 95 °C at 2 °C/min, followed by holding the temperature at 95 °C for 5 min. The starch suspension was then cooled to 50 °C at a rate of 6 °C/min. Throughout the entire pasting analysis, a constant shearing of 160 rpm was applied to ensure the homogeneity of the suspension. The viscosity of the starch suspension was recorded throughout the entire pasting process.

2.6. Raman Spectroscopy

A few grams of the sample were placed onto a glass slide before being focused under the objective lens of a Raman microscope (Alpha 300S, Witec, Ulm, Germany). A 100× objective lens with NA of 0.90 was utilized for all measurements. A 532 nm Nd: YAG laser with a power of 7 mW was used as the excitation source. A total of five spectrum measurements were collected for each sample and these were collated to derive the final spectrum. Each point spectrum was taken with an integration time of 5 s and accumulated five times to achieve a better signal-to-noise ratio. Cosmic ray removal on spectra was done using Witec Project software.

2.7. Starch Crystallinity Analysis

The crystallinity of the waxy rice starches was evaluated qualitatively and quantitatively, using Polarized Light Microscopy, Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD).

2.7.1. Polarized Light Microscopy

A drop of 5.0% (*w*/*w*) starch suspension was observed under a polarized light microscope (Eclipse Ci DS-Ri2, Nikon, Tokyo, Japan) with an objective lens magnification set to 40×. Images of the granules with a birefringence cross were taken for the respective samples.

2.7.2. Differential Scanning Calorimetry (DSC)

The thermal properties of the waxy rice starch granules were measured using a differential scanning calorimeter (214 Polyma, Netzsch, Selb, Germany), installed with Proteus-70 analysis software. The waxy rice starches were rehydrated in deionized water at a ratio of 1:4 (*w*/*v*). The starch suspensions were left to stir at 500 rpm for 30 min, before 20 μL was pipetted into the differential scanning calorimeter pan. The pan was hermetically sealed with an inverted unpierced lid. It was left to stand for 12 h at an atmospheric condition of 25 °C in order to equilibrate before being subjected to DSC analysis. For all DSC analysis, a sealed empty aluminum pan was used as a reference. The pans were heated from 20 °C to 110 °C at a heating rate of 10 °C/min, with enthalpy (△H, J/g) being measured throughout the entire heating cycle. The spectrum was further analyzed to determine the properties of the starches, including onset (T_O), conclusion (T_c) and peak gelatinization (T_P) temperatures, as well as the derived parameters, such as degree to crystallization.

2.7.3. X-ray Diffraction (XRD) Analysis

All of the waxy rice starches were left to equilibrate under atmospheric condition for seven days before the XRD measurements. The respective starch powders were pressed manually and mounted onto the sample holder. XRD measurements were conducted with a diffractometer (GADDS, Bruker, Billerica, MA, USA) which was equipped with nickel filtered Cu-K a radiation (wavelength 1.540598Å) radiation. The samples were scanned under fixed conditions of 40 kV and 30 mA. The scan range varied between the 3° to 85° (2θ) with 100 s per frame and three frames per scan. The XRD data were processed and analyzed using Bruker Eva software.

2.8. Statistical Analysis

All of the experiments were conducted in triplicate (unless otherwise stated), with the mean and standard deviation computed for all measurements. ANOVA was used to analyze the differences at a 95% confidence interval. The statistical analysis was performed using Graphpad Prism (Version 8, Graphpad Software, San Diego, CA, USA).

3. Results and Discussion

3.1. Physical Properties of Spray-Dried Waxy Rice Starch

The various physicochemical properties of the respective spray-dried waxy rice starches were examined.

Table 1 features the process yield and crucial product quality of the spray-dried waxy rice starches. Changes in the inlet temperature had no significant effect on the protein content of the resultant waxy rice starch. The protein contents (dry basis) of all of the spray-dried waxy rice starches were found to be less than 1%, comparable to commercial rice starches [1]. Similar results were observed in our previous studies, where changes in drying strategies had no significant impact on the protein content [11]. The results and published literature showed that the protein content is reliant on the efficacy of the prior alkaline steeping process that is intended to remove protein, rather than the subsequent drying process.

Table 1. Product specifications and process yield of spray-dried waxy rice starches. Values denoted with different alphabets in the same column are significantly different ($p < 0.05$).

	Protein Content (%)	Moisture Content (%)	Process Yield (%)
SP 40	0.64 ± 0.22^{a}	13.92 ± 0.32^{a}	74.83 ± 4.34^{a}
SP 50	0.79 ± 0.24^{a}	12.42 ± 1.67^{ab}	82.42 ± 5.73^{a}
SP 60	0.66 ± 0.19^{a}	10.74 ± 1.08^{bcd}	84.55 ± 1.77^{a}
SP 70	0.73 ± 0.14^{a}	9.67 ± 0.53^{cef}	85.16 ± 0.82^{a}
SP 80	0.66 ± 0.15^{a}	9.26 ± 0.40^{deg}	88.66 ± 6.19^{b}
SP 100	0.66 ± 0.13^{a}	7.99 ± 0.30^{fg}	85.66 ± 1.18^{a}

Moisture content is another key indicator influencing the quality of spray-dried waxy rice starch [12]. For the food industry, a low moisture content of less than 15% is often necessary for dried products in order to deter undesirable microbial growth and ensure product stability [13,14]. During the spray-drying process, the atomized starch dispersion and hot air flows in the same direction. This co-current spray-drying configuration implies that when the atomized starch particles come into contact with the heated drying air, this results in rapid moisture evaporation from the particles [15]. Interestingly, our data showed effective moisture evaporation from the waxy rice starch, with a final moisture content of 13.92 ± 0.32%, even at a low inlet temperature of 40 °C. As the inlet temperature was increased, from 40 °C to 100 °C, the moisture content of the resultant starch decreased proportionately from 13.92 ± 0.32% to 7.99 ± 0.30%, respectively. Similar findings were reported in a study by Shi, Li, Wang, Zhou, & Adhikari, where the authors observed a decrease in starch moisture content, from 9.78% to 8.31%, when the spray-drying inlet air temperature was increased from 75 °C to 175 °C [16]. Such phenomenon can be attributed to a steeper heat gradient associated with a higher inlet temperature, which results in a higher transfer rate of thermal energy into the starch granules. The higher thermal energy provides an increased impetus for an enhanced rate of moisture evaporation from the starch granules, resulting in a lower moisture content of the waxy rice starch powder.

Process yield is a key parameter when considering the feasibility of the spray-drying process as a drying methodology for the large scale manufacture of dried starch products. An increase in inlet temperature, from 40 °C to 80 °C, resulted in a general increase in the process yield. The increase in the process yield can be attributed to the lowered moisture content of waxy rice starch that is spray dried at a higher inlet temperature, which translated to reduced adhesion on the wall of the drying chamber. A lower moisture content generally reduces the tendency for the deposition of starch particles on the walls of the drying chamber, lowering process losses and improving the yield. However, a further increase in the inlet temperature to 100 °C resulted in a drop in the process yield. The use of too high an air inlet temperature may have resulted in gelatinization of the starch particles which are stuck on the drying chamber wall. This can lead to a higher tendency for the subsequent spray-dried rice starch particles to stick to the wall, due to the formation of a sticky gelatinized starch layer on the drying chamber surfaces.

Rice starch is widely known to have the smallest granule size of commercially available starches, with reported granule sizes ranging from 2 μm to 7 μm [17]. This small granule size is essential for certain functionalities of rice starch in some food applications. Some of such applications include sugar coating in confectionery products and replacing fat in low-fat cream [17]. In order to retain its functionality, it is crucial that the particle size of the rice starch powder be kept as small as possible; ideally similar to that of the granule size. In addition, the particle size distribution of the product should also be uniform (less polydispersed) in order to ensure good consistency. The atomization mechanism of the spray dryer allows the user to maintain good control over the particle size [18]. Spray-drying parameters, such as the air inlet temperature, pump rate and air flow rate, bear great significance in terms of controlling the resultant particle size of spray-dried products. Manipulation of the inlet temperature does not affect the particle size of the spray-dried waxy rice starch, with all spray-dried products having very similar particle sizes (between 5.61 ± 0.57 μm to 6.12 ± 0.11 μm) (Figure 1). The average particle size of these spray-dried waxy rice starches is also similar to that of the native rice starch (5.80 ± 0.01 μm). Furthermore, all spray-dried products show a good particle size distribution, with a unimodal distribution curve (Figure 1b). Such results exemplify the importance of the atomizing process in controlling the particle size of the rice starch and the respective size distributions. Since inlet temperature shows no direct impact on the atomizing process, changes to the inlet temperature do not affect the particle size and size distribution of the waxy rice starch.

(a)

	Dx 50 (µm)	Dx 90 (µm)	D [3,2] (µm)	D [4,3] (µm)
Native	5.80 ± 0.01ᵃ	9.31 ± 0.04ᵃ	5.28 ± 0.02ᵃ	6.09 ± 0.00ᵃ
SP 40	6.04 ± 0.90ᵃ	9.92 ± 1.70ᵃ	5.55 ± 3.36ᵃ	6.74 ± 1.52ᵃ
SP 50	5.61 ± 0.57ᵃ	10.04 ± 1.43ᵃ	5.01 ± 0.59ᵃ	6.84 ± 1.71ᵃ
SP 60	5.99 ± 0.07ᵃ	10.08 ± 0.29ᵃ	5.38 ± 0.04ᵃ	6.40 ± 0.10ᵃ
SP 70	5.96 ± 0.14ᵃ	9.86 ± 0.23ᵃ	5.38 ± 0.15ᵃ	6.33 ± 0.15ᵃ
SP 80	6.12 ± 0.11ᵃ	11.00 ± 0.71ᵃ	5.54 ± 0.13ᵃ	7.72 ± 0.97ᵃ
SP 100	6.04 ± 0.06ᵃ	10.57 ± 0.43ᵃ	5.43 ± 0.11ᵃ	7.25 ± 1.03ᵃ

(b)

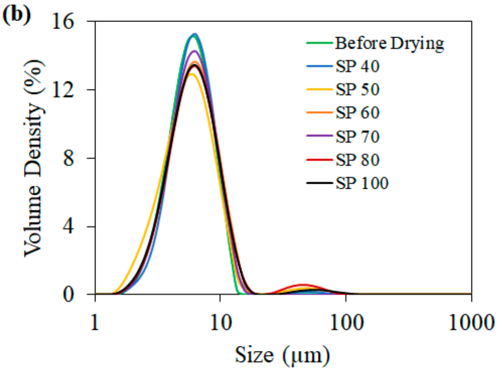

Figure 1. Particle size (**a**) characteristics and (**b**) distribution of native and spray dried waxy rice starches. Values denoted with different alphabets in the same column are significantly different ($p < 0.05$).

The bulk and tapped densities of the spray-dried starches were also examined (Table 2). The Hausner Ratio and Carr's Index, which provided an indication of the flowability of the respective spray-dried waxy rice starch powder, were derived from these parameters. While there exist minute differences in the bulk and tapped density of the respective spray-dried waxy rice starch powders, there are no significant differences when analyzed using the Hausner Ratio and Carr's Index. Generally, all spray-dried waxy rice starches possessed poor flowability, as reflected in the high Hausner Ratio (HR) and Carr's Index [19]. Similar results were reported for waxy rice starch dried using other methodologies, such as oven drying and freeze drying [11]. Rather than being due to the effect of drying methods, the poor flow properties could mainly be attributed to the inherently small particle sizes (5.61 µm to 6.12 µm) of waxy rice starches. Such a small particle size meant that these particles have a larger surface area to volume ratio and a higher tendency for contact between particles, resulting in increased interparticle adhesion forces [20]. Such cohesive forces eventually led to greater resistance in the flowability of the particles [21]. Similar findings were also commonly reported for various starch powders and were not limiting to waxy rice starches. A study by Arollado, Pellazar, Manalo, Siocson, & Ramirez exhibited high HR of 1.39 to 1.44 for fruit starches. The starches had irregular shapes and small particle sizes, which led to the interlocking of particles and limited flowability [22]. A separate study by Odeniyi, Adepoju, & Jaiyeoba revealed a high HR of 1.65 for acha starch. The enhanced cohesive forces between the starch particles was believed to be the main cause for the increased resistance to powder flowability [23]. Therefore, to improve the flowability of the starch powders, formulation additives, such as flow activators (e.g., colloidal silicon dioxide), can be utilized. These flow activators, which are also known as glidants, act by reducing the bulk density which, in turn, decreases the cohesion and adhesion of the particles [24]. Similar strategies can be applied to spray-dried waxy rice starch in order to enhance its flowability.

Table 2. Flow characteristics of spray dried waxy rice starches. Values denoted with different alphabets in the same column are significantly different ($p < 0.05$).

	Bulk Density (g/cm^3)	Tapped Density (g/cm^3)	Hausner Ratio (HR)	Carr's Index (%)
SP 40	0.33 ± 0.01 ʰ	0.47 ± 0.02 ᵃ	1.41 ± 0.02 ᵃ	28.96 ± 1.00 ᵃ
SP 50	0.36 ± 0.01 ᵃᵇᶜ	0.51 ± 0.02 ᵃᵇᶜᵈ	1.40 ± 0.04 ᵃ	28.31 ± 2.06 ᵃ
SP 60	0.37 ± 0.00 ᵃᵈᵉ	0.51 ± 0.00 ᵇᵉᶠ	1.39 ± 0.00 ᵃ	28.00 ± 0.00 ᵃ
SP 70	0.37 ± 0.01 ᵇᵈᶠ	0.52 ± 0.02 ᶜᵉᵍ	1.40 ± 0.02 ᵃ	28.69 ± 1.15 ᵃ
SP 80	0.38 ± 0.00 ᶜᵉᶠᵍ	0.53 ± 0.01 ᵈᶠᵍ	1.38 ± 0.02 ᵃ	27.35 ± 1.15 ᵃ
SP 100	0.40 ± 0.00 ᵍ	0.57 ± 0.01 ʰ	1.42 ± 0.02 ᵃ	29.34 ± 1.15 ᵃ

3.2. Pasting Behaviour

Having a good understanding of the pasting behavior of waxy rice starches is important, as this is an indicator of the functionalities of starch granules when subjected to heating in excess water. This is especially the case for dried starches, as they had been exposed to prior thermal treatment, which could significantly affect the physicochemical properties and functionalities of the starches. As reported in our previous study, oven-dried waxy rice starch demonstrated a significantly different pasting profile as compared to the native rice starches. There were significant increases in the peak, breakdown and final viscosities as compared to the native rice starch. These differences could be attributed to minute changes in the starch, which include leaching of amylopectin and the formation of minute fissure cracks on the granule surface during the process of oven drying [11]. The findings further supplement the hypothesis that the drying process can have a significant effect on the resultant starch properties and functionalities. Figure 2 illustrates the pasting curves of waxy rice starch which were spray dried at different inlet temperatures. Regardless of the inlet temperatures, the pasting profiles for all spray-dried waxy rice starches are similar. The pasting profiles are also identical to that of the native waxy rice starch (Before Drying). In contrast to other thermal-based drying methods, the results from our study highlight that the inlet temperature of the spray dryer had no significant effect on the functionalities of the waxy rice starch obtained. Interestingly, even at an inlet temperature of 100 °C, which is beyond the gelatinization temperature of rice starch (~64 °C), there is no adverse effect on the general pasting behavior of the produced starch. This may be due to the very short time during which the starch granules were exposed to the high inlet temperature; a timeframe which did not provide sufficient thermal energy to elicit any changes to the pasting properties of the starch granules. Table S1 lists the pasting properties of the respective spray-dried way rice starches. In comparing these against the native waxy rice starch (Before Drying), there is no significant difference in the respective pasting parameters. Similar to the pasting curve, even at the highest inlet temperature of 100 °C, the respective pasting parameters remained consistent with that of the native waxy rice starch and reported results [25]. The results from this study highlight that the choice of spray-drying inlet temperature does not significantly affect the pasting behavior of the product. This can be attributed to the rapid drying mechanism of the spray-drying process, during which exposure to thermal conditions removes only the surface water without affecting the properties of the starch granules. The residence time of the particles in the drying chamber typically ranges from 12 to 30 s [26]. This means that exposure to the thermal conditions is greatly reduced, compared with other drying methods which have a longer drying time (e.g., oven drying, ~12 h). Moreover, the spray dryer utilizes co-current product-air flow configuration, which means that the hottest gases are in contact with the wettest materials and the temperature of the solids decrease as they moves through the dryer, preventing the potential for overheating [27]. In addition, it is known that waxy rice starch possesses a semi-crystalline structure, due to the presence of high amylopectin content (>98%) [28]. It is plausible that due to the extensive branching amylopectin chains, they are likely to be less mobile within the granules due to steric hindrances as compared to the amylose. Thus, amylopectin molecules are less likely to re-arrange and form new associations with one another [25] during the brief spike in temperature. This possibly explains why, even at a high air inlet temperature of 100 °C, gelatinization of the waxy rice starch (with high amylopectin content) is not observed. This multitude of different factors work in tandem to avoid undesirable thermal degradation of the spray-dried starches, even at a high inlet temperature of 100 °C.

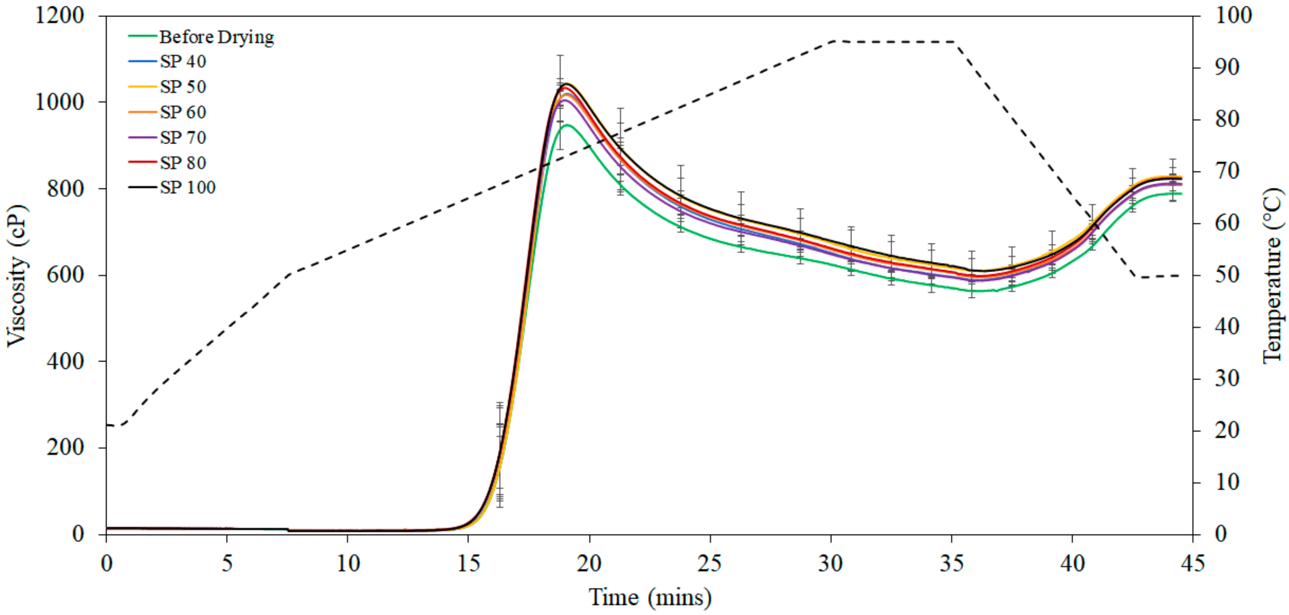

Figure 2. Pasting profile of native and spray dried waxy rice starches.

3.3. Crystalline Structure

Crystallinity of starch has a direct impact on its hydration and paste-forming properties [29]. Starch granules possess semi-crystalline structures, which are comprised of both crystalline and amorphous regions. Rice starches, in particular, are well-known to have densely packed glucose helices, forming a typical A-type crystalline structure [30]. In order to preserve the native functionality of the rice starch, it is important to conserve the extension and type of crystalline structures in the spray-dried starches.

Through the polarized light microscope, it was clearly observed that all spray-dried waxy rice starch granules exhibited the characteristic birefringence with a "Maltese Cross" (Figure 3). Extensive modifications to the crystalline structure of the granule are often accompanied by the loss of its characteristic birefringence. For instance, starch gelatinization would result in loss of birefringence due to absorption of water by amorphous regions, resulting in destabilization of its crystalline structure [31]. The presence of birefringence provides a preliminary indication that the crystalline structures and crystallinity of the starches was not affected by the spray-drying process or the varying inlet temperatures.

While polarized microscopy provides a qualitative estimation of the crystallinity, X-ray Diffraction (XRD) is a high-resolution tool used to determine any modification in the crystalline structure of the respective spray-dried starch granules. Waxy rice starch generally possesses an A-type crystalline structure, formed via the interaction of amylopectin with short branch-chains and closed branching points [32]. As such, a XRD spectroscopic analysis of rice starches would often show the characteristic diffraction patterns as defined by peaks at 15°, 17°, 18°, 23° and 26° [33].

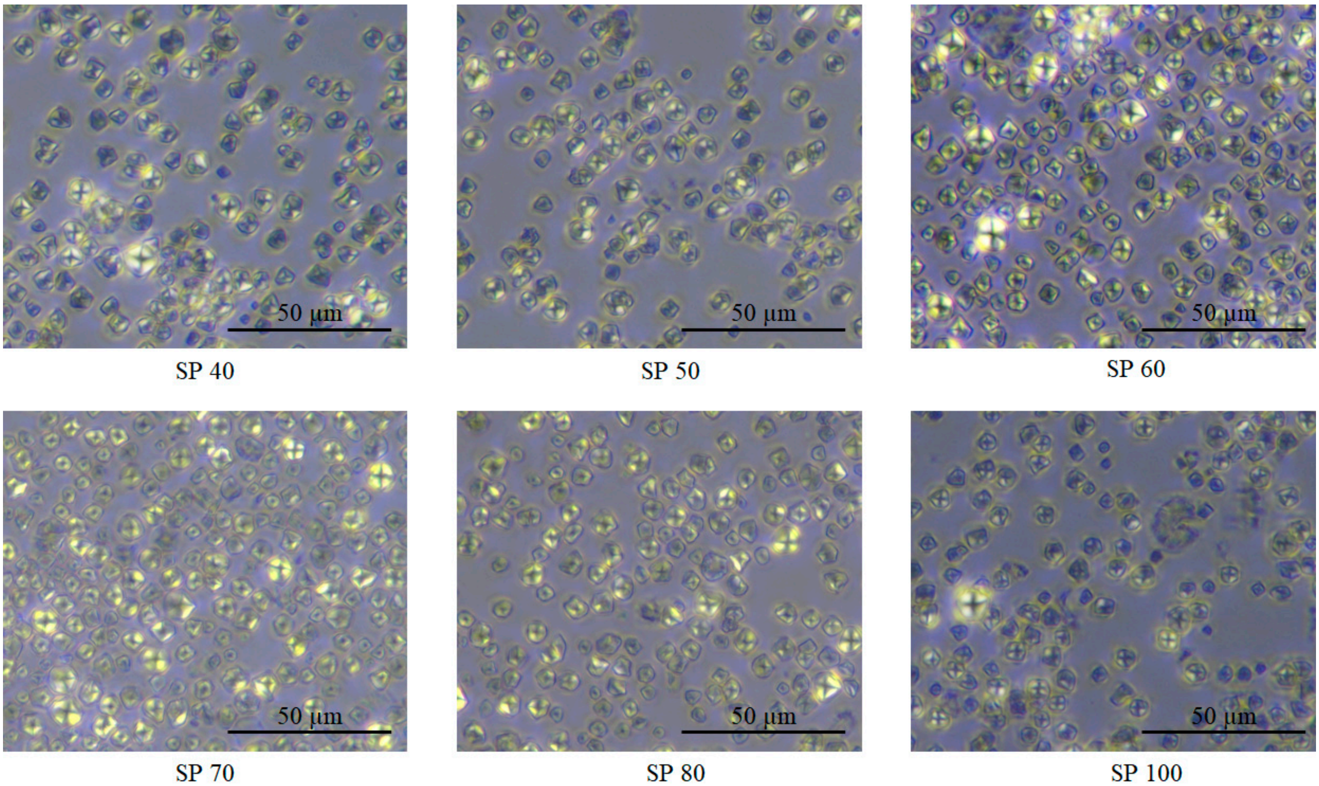

Figure 3. Spray dried waxy rice starches observed under polarized light microscope at 40× magnification.

Upon exposure to the extensive drying process, changes in the crystalline structure of the starch are expected [34]. A report by K. Liu, Hao, Chen, & Gao explored the effects of dry heat treatment on waxy potato starch. Changes in the X-ray pattern (from B to B + A type) were observed after the starch samples were exposed to heat treatment. Furthermore, it was reported that the peaks at 5.5° and 17.1° had weakened [34]. The change in crystalline structure was attributed to the reorientation of the double helices during the thermal treatment, which could have led to crystalline disruption. In contrast to other drying methods, spray drying does not affect the crystalline structure of the rice starch. In comparing the XRD spectroscopic diffraction patterns exhibited by native (Before Drying) to the spray dried waxy rice starches, it is evident that the XRD spectrometric fingerprint are identical. The five characteristic peaks (15°, 17°, 18°, 23° and 26°) can be clearly distinguished in Figure 4. This result further affirms the previous polarized microscopy results. The spray-drying process and, more importantly, the variation in inlet temperature did not induce any change to the crystalline structure of the granules. Even with a higher inlet temperature (100 °C), the A-type crystalline structure of the waxy rice starch was preserved in the resultant spray-dried waxy rice powder.

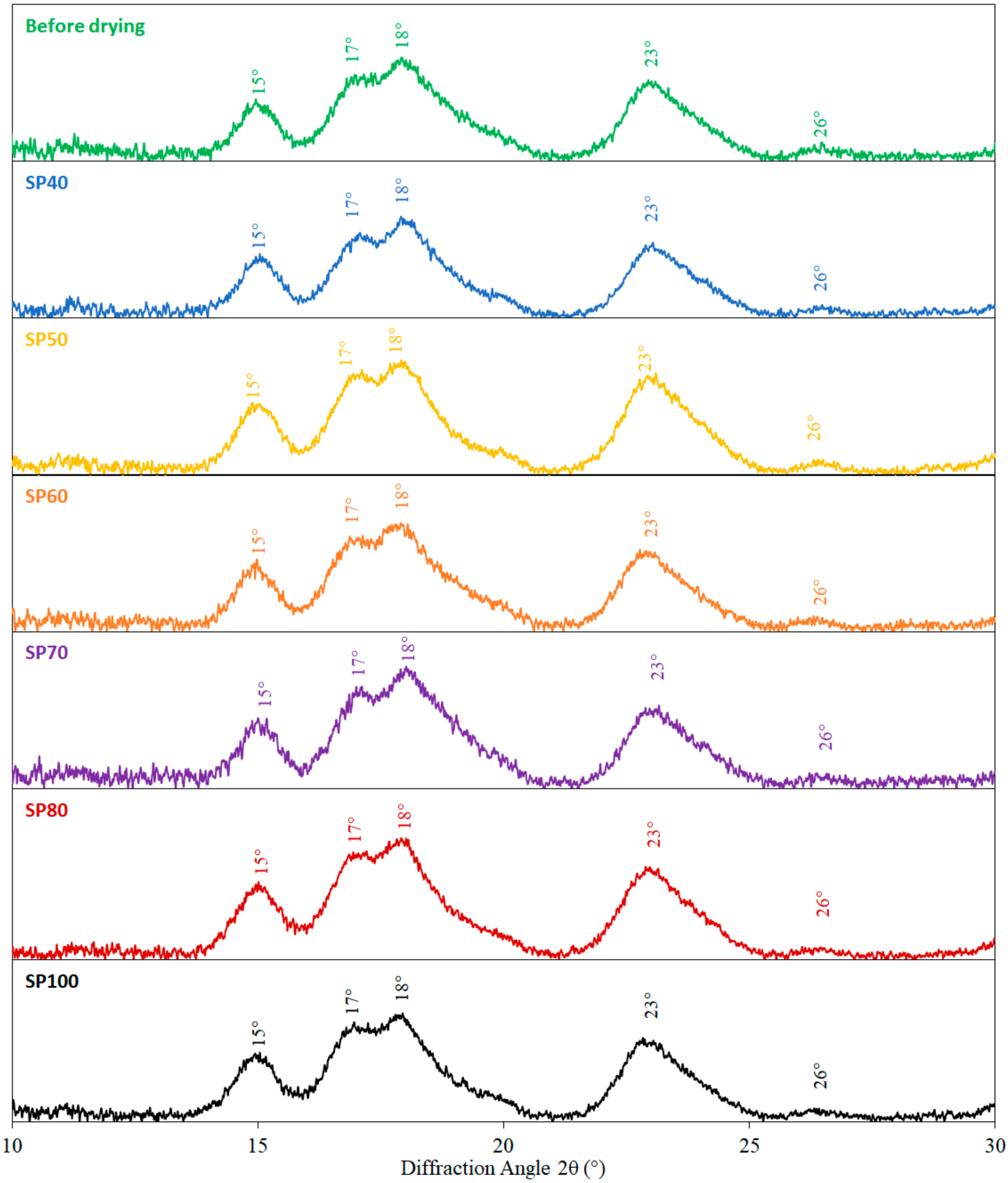

Figure 4. X-ray diffractograms (XRD) of native (Before Drying) and spray dried waxy rice starches.

Both polarized microscopy and XRD represent excellent qualitative tools to determine the retention of crystallinity and the crystalline structure type. Differential Scanning Calorimetry (DSC) is a quantitative tool used to determine the degree of crystallinity and various pasting parameters. Upon prolonged heating, starch generally undergoes gelatinization. This is an endothermic process that corresponds to the loss of starch crystallinity after being exposed to heat and moisture treatment [35]. As starch granules change from a semi-crystalline to amorphous phase, breakage of the crystallites occurs.

This is a molecular disordering transition [17]. However, based on our study (Table 3), there is no significant difference in the gelatinization characteristics (T_O, T_P, T_C, T_C-T_O and $\triangle H$) between the native waxy rice starch and the spray-dried waxy rice starches. These results also correspond to that of native waxy rice starch. In the experimental findings reported by Y. Qin et al., T_O, T_P and T_C of native waxy rice starch were found to be 59.08 °C, 64.21 °C and 72.09 °C, respectively [36]. Despite slight deviances, our results generally agree with that reported in the literature. The slight differences in gelatinization characteristics may be due to variances in the botanical source of the rice starches [37]. More importantly, $T_{C\text{-}O}$ provides an indication of the degree of crystallinity of the respective waxy rice starches. Increases in the inlet temperature do not significantly affect the degree of crystallinity. This, again, is due to the low exposure time to thermal treatment during the spray-drying process. This result corresponds to the XRD result, in which the calculated area under the curve for the spray-dried rice starches dried at different inlet temperatures (data not shown) showed no significant difference. This result is different from that of other drying methods. Li et al., have explored the impacts of oven drying on waxy rice starch. After the rice starch samples were oven dried, there was a significant increase (by 9.11%) in the degree of crystallinity and change in enthalpy. The authors reported that during the thermal exposure of starches, there were changes to the amorphous regions, which led to differences in the degree of crystallinity [8].

Table 3. DSC thermogram of native and spray dried waxy rice starches. T_O, T_P, T_C, T_C-T_O and $\triangle H$ represents onset, peak, conclusion, difference between conclusion and onset temperature and change in enthalpy. Values denoted with different alphabets in the same column are significantly different ($p < 0.05$).

	T_O (°C)	T_P (°C)	T_C (°C)	T_C-T_O (°C)	$\triangle H$ (J/g)
Native	59.00 ± 0.00^a	68.50 ± 0.57^a	76.70 ± 0.57^a	17.70 ± 0.57^a	2.12 ± 0.10^a
SP 40	57.90 ± 2.72^a	66.03 ± 1.42^a	75.97 ± 0.84^a	18.07 ± 3.16^a	1.42 ± 0.69^a
SP 50	57.87 ± 1.27^a	65.33 ± 0.45^a	74.90 ± 0.85^a	17.03 ± 1.88^a	0.99 ± 1.07^a
SP 60	58.23 ± 1.36^a	67.07 ± 2.29^a	75.90 ± 0.78^a	17.67 ± 1.16^a	1.47 ± 0.84^a
SP 70	58.07 ± 1.60^a	66.20 ± 1.23^a	75.10 ± 1.10^a	17.03 ± 2.70^a	1.53 ± 0.53^a
SP 80	58.50 ± 1.32^a	65.97 ± 0.81^a	76.13 ± 0.65^a	17.63 ± 1.88^a	1.80 ± 0.45^a
SP 100	57.97 ± 2.12^a	66.07 ± 1.17^a	75.67 ± 1.04^a	17.70 ± 2.21^a	1.45 ± 0.12^a

All in all, on a macroscopic level, changes in the inlet temperature do not affect the crystallization and pasting functionalities of the spray-dried waxy rice starches. As such, the spray-dried waxy rice starch still retains the properties of its native state, preserving the desired functionalities, including pasting profile, gelatinization characteristics and crystalline structure.

3.4. Molecular Changes

While there are no changes in the macroscopic system, heat treatment may lead to the occurrence of minor molecular changes in the waxy rice starches. Such molecular changes might also lead to deviation of physicochemical properties of the resultant starches.

In a published report by Kamal et al., the authors explored the effect of heat treatment on sago starch [14]. The starch samples were oven dried for a duration between 8 h to 24 h. The results revealed that the crystalline and amorphous index decreased as the duration of heat treatment increased. The authors have suggested that these findings could be due to rearrangements of the molecular order during the heat treatment process [14]. In addition, molecular changes could also be in the form of existing bonds breaking and/or new covalent bonds forming. To detect such microscopic modifications, the Raman spectroscopy is often utilized to evaluate the molecular structure of the granules. The vibrational characteristics of the granules are represented by the Raman peak position, intensity and spectra range [38]. A study by Qin et al., revealed the effects of maleic anhydride on the molecular changes of corn starch. The modification of corn starch resulted in the modification of several discrete Raman peaks in the spectrum. In particular, a new peak was observed at 1839 cm^{-1} due to C=O stretching in the maleic anhydride [39]. Another study by Volant et al., on acetylated waxy maize starch demonstrated a new peak at 1740 cm^{-1}, which was attributed to the deformation of the C=O bond. In addition, there was disappearance of a peak at 480 cm^{-1}. These modifications in the Ramen fingerprint indicate the occurrence of modification on the molecular level after the acetylation process [40].

Figure 5 illustrates the Raman spectrum for spray-dried rice starch processed at different inlet temperatures (Figure 5). The spectroscopic fingerprints of the spray dried waxy rice starches were identical to that of native waxy rice starch (Before Drying), indicating no drastic changes to existing molecular structures and biochemical bonding. An in-depth analysis of the respective Raman peak intensities highlighted that the incremental increase of the spray-drying inlet temperature, from 40 °C to 100 °C, did not significantly impose any changes to the molecular structure (e.g., formation of new bonds) within waxy rice starch granules. Even at the high spray-drying temperature of 100 °C, undesired reactions were not exhibited in the Raman spectra. The previous results from the DSC and pasting profile supplement the Ramen result, as any molecular changes due to spray drying will also present some deviation in the respective parameters. As aforementioned, this could be attributed to the short contact time with the heated air, thus avoiding undesirable thermal degradation to the waxy rice starch granules.

3.5. Optimized Spray Drying Temperature for Production

Based on the results, varying the spray-drying inlet temperature bears no effect on the physicochemical properties of the resultant waxy rice starch. However, an increase in the inlet temperatures has a significant impact on the process yield and product quality. On these fronts, it is ideal for the process to have an optimum moisture content (typically below 15%) and a high process yield. At the same time, the inlet temperature should also be kept low to minimize energy usage. Considering these factors, the inlet temperature for spray drying of waxy rice starch is recommended to be 60 °C. At temperatures below 60 °C (i.e., 40 °C and 50 °C), the moisture of the product is significantly higher (at approximately 13%), which is quite close to the standard set for dried products. This is coupled with a lower process yield. As such, decreasing the temperature further than 60 °C is not ideal, although the energy consumption is lower. At higher inlet temperatures of 70 °C and 80 °C, the drop in moisture content is rather minor. On the contrary, the energy requirements for these temperatures are much higher, especially when we are considering large-scale production. An inlet temperature of 60 °C represents the most optimum inlet temperature. At this temperature, the drying process can potentially achieve a good product yield of 84.55 $\pm$ 1.77%, with low moisture content of 10.74 $\pm$ 1.08%. This process yield of the spray-drying process is also expected to be enhanced with upscaling of the process from lab-scale to industry-scale [16]. A report by Georgia et al. highlighted that upscaling the spray drying from pilot-scale to production-scale saw the process yield increase from 65.0% to 73.15%. At the recommended spray drying condition, the resultant product quality is also good, and the particle size of the resultant waxy rice starch is well-controlled with a median of 5.99 $\pm$ 0.07 μm with unimodal size distribution. Pasting behavior and crystallinity were also well preserved. In addition, spray drying at 60 °C, means that the processing temperature is kept below the gelatinization onset temperature of the waxy rice starch, thus minimizing the possibility of undesired modification to the rice starch [25]. This will help to preserve the functionalities of the native waxy rice starch. On top of that, the energy consumption for the spray drying process at 60 °C is much lower, compared to drying at 100 °C (data not shown), making the drying process more economical and environmentally sustainable.

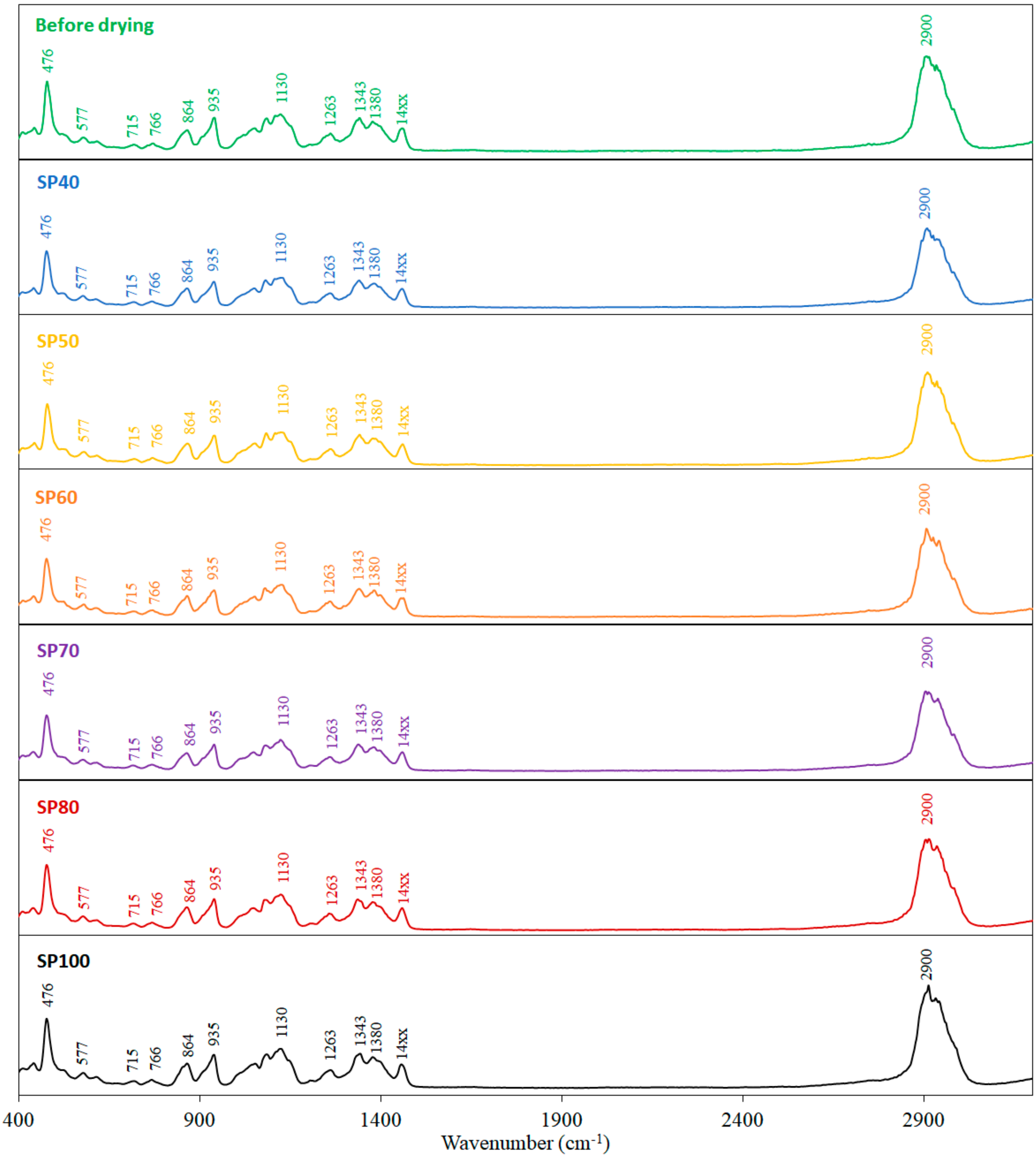

Figure 5. Raman spectra of native (Before Drying) and spray dried waxy rice starches.

4. Conclusions

Low temperature spray drying was proposed as an alternative method for drying rice starch in a previous study [11]. This study evaluated the effect of different spray-drying inlet temperatures (40 °C to 100 °C) on various aspects, such as the physicochemical properties and functionalities of waxy rice starch. While bearing a significant effect on process parameters, varying the air inlet temperatures has no significant impact on the physicochemical properties and functionalities of the resultant spray-dried waxy rice starch. An air inlet temperature of 60 °C is shown to be optimal, producing homogeneous native waxy rice starch with low moisture content (10.74 ± 1.08%) and good process yield (84.55 ± 1.77%), while retaining the native physicochemical functionalities (e.g., pasting characteristics) of rice starch. The current study bears importance to potential manufacturers who are considering the use of spray drying for starch manufacturing. Compared to current drying strategies for starch, which generally operate at temperatures at 130 °C and above, the proposed optimized spray-drying process offers various advantages in terms of better energy savings, improved thermal efficiency, lower costs and higher productivity. Beyond the production capabilities and costs, operating at lower temperatures also will translate to enhanced safety for the production process and workers.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9091557/s1, Table S1: Pasting characteristics of native and spray dried waxy rice starches.

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