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Effect of drying methods on the functional properties of soy hull pectin

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Abstract

Soy hull pectin preparations produced by freeze drying, spray drying, and vacuum oven drying were evaluated for their surface chemical structure, degree of esterification, appearance, solubility, and flow behavior. FTIR spectral analysis showed no major structural differences in soy pectin samples produced by various drying treatments and their surface structures were comparable to that of analytical and food grade commercial pectin samples. Yields, galacturonic acid contents, and the degrees of esterification for oven dried, freeze dried, and spray dried soy pectin samples were 16–21, 67–69, and 18–20%, respectively. Pectin produced by oven drying had the lowest Hunter values for brightness, redness, and yellowness among the pectin samples produced by various drying methods. Drying methods did not have any significant detrimental effect on the solubility and flow behavior of the soy hull pectin samples.

Keywords: Freeze drying; Spray drying; Vacuum oven drying; Soy hull pectin; Pectin

1. Introduction

The composition and structural entities of pectin depend on their source and extraction method. Pectin is commercially extracted from citrus peels and apple pomace with hot acidified water. Most pectin samples used in the food industry are prepared from citrus peel (Fernadez, Sun, Tosca, & McNamara, 1994). Citrus peel and apple pomace contain about 25 and 12% pectin respectively, and the commercial extraction yield is about 25% (Walter, 1991). During extraction, the pH and the temperature are maintained to obtain pectin with desired levels of esterification. The extract is then centrifuged, filtered, precipitated with alcohol, and washed with alcohol water. The pure pectin obtained from the precipitation process is pressed and gently dried (Herbstreith and Fox, Corporate Group, 2005). The maximum level of alcohol allowed in the dried pectin is 1.0% or less. Most industrial pectin samples are vacuum oven dried to recover the alcohol and to keep the residual alcohol level to its minimum level of 1.0% or less.

Soy hulls are major by-products of the soybean processing industry and their insoluble carbohydrate fraction contains 30% pectin, 50% hemicellulose, and 20% cellulose (Snyder & Kown, 1987). Soy hull is potentially an inexpensive commercial source of pectin. Citrus peel and apple pomace need to be dried before storing and transportation, while soy hull can be stored and transported without further processing. Gnanasambandam & Proctor (1999) extracted pectin from soy hull by adapting the acid extraction and alcohol precipitation method used for citrus pectin production. Kalapathy & Proctor (2000) subsequently optimized the acid extraction and alcohol precipitation conditions on the yield and purity of soy hull pectin. In both cases, freeze-drying was employed to dry the alcohol precipitated pectin. Monsoor & Proctor (2001) described a spray drying method to prepare pectin from soy hull. They also compared the functional properties of spray dried soy hull pectin with commercial food grade and Sigma pectin samples (Monsoor and Proctor, 2001). However, there are no reports available to show if there is an effect of drying methods on the functional properties of soy hull pectin. The objective of this study was to evaluate and compare the surface structure and functional properties of vacuum oven-dried, freeze-dried, and spray-dried soy hull pectin.

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2. Materials and methods

2.1. Pectin samples

Soy hull was obtained from Riceland Foods (Stuttgart, AR). Analytical grade citrus pectin was purchased from The Sigma Chemical Co (St. Louis, MO). Commercial food grade pectin was obtained from Danisco Ingredients Inc. (New Century, KS, USA). The degree of esterification (DE) value for commercial food grade pectin was 32. The DE value for analytical grade citrus pectin was not provided.

2.2. Extraction of soy hull pectin

The soy hulls were ground to a particle size of 80 mesh with a centrifugal grinding mill (Model ZM-1; Retsch/Brinkman, Westbury, NY, USA). Pectin was extracted from ground soy hull (400 g) using 4.0 L of 0. 05 M HCl at 90 °C for 60 min with constant stirring (Monsoor and Proctor, 2001). The extracts were cooled to room temperature in a water bath, and centrifuged (CRU 5000, IEC, Needham Heights, MA, USA) at 2700×g for 15 min. The supernatants were collected, and dispersed in equal volume of 2-propanol. Pectin was precipitated by adjusting the pH of the dispersion medium to 3.5 (Kalapathy and Proctor, 2000) and the suspension was allowed to stand for 6 h. The precipitate was collected by centrifugation, dispersed in 2-propanol (1.0 L), stirred for one hour, and centrifuged again at 2700×g for 15 min. These steps (dispersing and centrifuging) were repeated twice. The pellet was washed with 70% 2-propanol (1.0 L) followed by a centrifugation step to collect the precipitate. Three batches of soy hull pectin were prepared for each drying treatment.

2.3. Soy hull pectin drying

Three different drying methods (spray drying, vacuum-oven drying, and freeze drying) were employed to dry the pectin precipitates. For spray drying, the precipitates were dispersed in de-ionized water and spray dried in a lab S1 spray drier (APV Anhydro Inc., Copenhagen, Denmark). The inlet temperature of the spray drier was maintained between 200 and 220 °C and outlet temperature was 70–80 °C. For vacuum-oven drying, the precipitates were dried at 37 °C under vacuum in an Isotemp Vacuum Oven (Fisher Scientific, Hampton, NH, USA). A Genesis freeze dryer (The Virtis Company, Gardiner, NY, USA) was used to freeze dry the pectin precipitates. The precipitates were dispersed in deionized water prior to freeze drying. The dried pectin samples were subjected to the following analysis.

2.4. Pectin yield

Pectin yields (w/w) were calculated as the percentage of the total pectin present in dried soy hull. The pectin present in soy hull as percent of galacturonic acid was determined by a colorimetry using m-hydroxydiphenyl (Kinter & Van Buren, 1982).

2.5. Pectin content

Pectin content, as percentage of polygalacturonic acid, was determined by FTIR (Monsoor, Kalapathy, & Proctor, 2001a). A set of 10 calibration pectin standards were prepared by blending polygalacturonic acid (98% polygalacturonic acid, Sigma Chemical Co. St. Louise, MO) with potassium bromide (KBr) to obtain pectin standard with polygalacturonic acid content of 10 to 98%. The polygalacturonic acid contents of the samples were calculated from the linear fit equation of the calibration standards.

2.6. Degree of esterification

A diffuse reflectance Fourier transform infrared spectroscopic method (Monsoor, Kalapathy, & Proctor, 2001b) was used to determine the degree of esterification (DE) of the soy hull pectin samples. A wide range of pectin samples with known DE values were used as standards for developing a linear regression model for a calibration curve. The DE values of dried soy hull pectin samples were determined from the calibration model developed.

2.7. Color values of soy pectin

Hunter color values of soy pectin produced by various drying methods were measured by a Minolta Model DP 301 colorimeter (Minolta, Japan). Before each measurement the colorimeter was standardized with the reference white plates provided with the equipment.

2.8. Surface structure analysis

Diffuse Reflectance Fourier Transform Infrared Spectra (DRIFTS) of soy hull pectin samples were collected using an Impact 410 Nicolet Instrument (Nicolet Analytical Instruments, Madison, WI) (Gnanasambandam & Proctor, 2000). DRIFTS spectra were obtained by co-adding 100 scans at a resolution of 8.0 cm^{-1}. FTIR spectra were analyzed for surface chemical functional groups by a software package (OMNIC FTIR Software, v4.1, Nicolet Analytical Instruments, Madison, WI) and compared with the commercial citrus analytical grade and food grade pectin samples.

2.9. Pectin solubility

The water solubility of dried soy hull pectin sample at pH 2, 4, 6, 8, and10 was determined gravimetrically (Monsoor and Proctor, 2001). Pectin samples (5.0 g) were dispersed in 100 mL of deionized water and either 0.1 M HCl or 0.1 M

NaOH was used to maintain pH in the range of 2 to 10. The insoluble pectin portions were determined after centrifugation (2700×g, 15 min, CRU 5000, IEC, Needham Heights, MA) and used to determine pectin solubility.

2.10. Rheology of pectin solution

The rheology of 3% pectin solution in de-ionized water (w/v) (pH 7.0) was determined with a Haake VT 550 Rheometer (Haake MessTechnik Gmbh Co., Karlsruhe, Germany) with a SV-DIN sensor (Monsoor and Proctor, 2001). All rheological experiments were carried out at a constant temperature (23 °C) immediately after the pectin solutions were prepared. The shear rate was increased from 0 to 400 S^{-1} by the software control, and strain measurement was recorded. Each sample was tested three times. Shear stress was plotted against shear rate.

2.11. Statistical analysis

Results of three replicates were used and Student's 't' test was used to analyze data. Least significance difference (LSD) values were used to differentiate mean values, and significance as defined at $P<0.05$ (SAS, Institute Inc. 1994).

3. Results and discussion

3.1. Pectin yield, pectin content and degree of esterification

The pectin yield, galacturonic acid content, and the degree of esterification of soy hull pectin produced by various drying methods are presented in Table 1. The yields, galacturonic acid contents, and the degree of esterifications for oven dried, freeze dried, and spray dried soy pectin samples ranged between 16–21, 67–69, and 18–20, respectively. There was no difference in yield for oven dried and freeze dried soy hull pectin. The yield for spray dried soy hull pectin was significantly lower than oven dried and freeze dried soy hull pectin. The low yield in spray drying is attributed to the high loss on drying due to small sample size in this study. This kind of loss during spray drying is expected to reduce significantly as the sample size would increase in industrial or large scale operation. The pectin yield for commercial citrus pectin is typically 20 to 26% (Kravtchenko, Voragen, & Pilnik, 1992). The soy pectin yield reported in an earlier study was 7–16% (Monsoor and Proctor, 2001). Drying seemed to have no detrimental effect on the galacturonic acid content and the degree of esterification of the soy hull pectin samples. The galacturonic acid contents in the pectin samples produced by various drying methods were similar to that of commercial citrus pectin, which contains 70% galacturonic acid (Kravtchenko et al., 1992). The low degree of esterification values for soy hull pectin produced by various drying methods may be due to the source of the pectin (soy hull) or due to the ester hydrolysis during acid extraction process.

Table 1
Pectin yield, galacturonic acid content, and degree of esterification of oven dried, freeze dried, and spray dried soy hull pectin

Soy pectin	Yield (%)	Galacturonic acid (%)	Degree of esterification (%)
Oven dried	21.87±2.24a	67.43±1.15a	19.35±0.68a
Freeze dried	21.00±0.28a	69.11±2.95a	18.84±0.39a
Spray dried	16.31±2.74b	68.11±1.10a	20.23±1.43a

Values with different letters in each column are significantly ($P<0.05$) different.

3.2. Color values of soy pectin

Hunter color values and their standard deviation values of oven dried, freeze dried, spray dried and analytical and food grade pectin samples are presented in Table 2. The Hunter 'L', 'a', and 'b' values for oven dried, freeze dried, and spray dried soy pectin samples ranged between 2.7–5.7, 0.15–0.55, and 1.5–2.7, respectively. There were significant differences between the Hunter color values of the soy hull pectin samples produced by various drying methods and the analytical and food grade pectin samples. The food grade pectin had the highest Hunter values for brightness, redness, and yellowness among the pectin samples tested in this study. There was no significant difference between the brightness of freeze dried and spray dried soy pectin and the brightness of spray dried soy pectin was similar to that of Sigma pectin. Pectin produced by oven drying had the lowest Hunter values for brightness, redness, and yellowness among the pectin samples produced by various drying methods. The hunter color values suggested that the vacuum oven drying method had the most negative effect on appearance among the drying treatments tested in this study. Depending on the food application, a drying method may be chosen to obtain pectin with desired appearance.

3.3. Surface structure analysis

The diffuse reflectance FTIR spectra (400–4000 cm^{-1}) of soy hull pectin produced by vacuum oven drying, spray

Table 2
Hunter color values for oven dried, freeze dried, spray dried soy hull pectin, analytical grade (Sigma, St. Louise, MO) and commercial food grade pectin

Pectin samples	L	a	b
Oven dried	2.75±0.13d	0.15±0.01c	1.53±0.07d
Freeze dried	5.13±0.20c	0.19±0.02c	2.07±0.05c
Spray dried	5.72±0.35bc	0.55±0.04b	2.67±0.08b
Analytical pectin	6.28±0.14b	0.51±0.03b	2.37±0.05bc
Food grade pectin	50.62±0.69a	4.45±0.17a	20.84±0.51a

Values with different letters in each column are significantly ($P<0.05$) different.

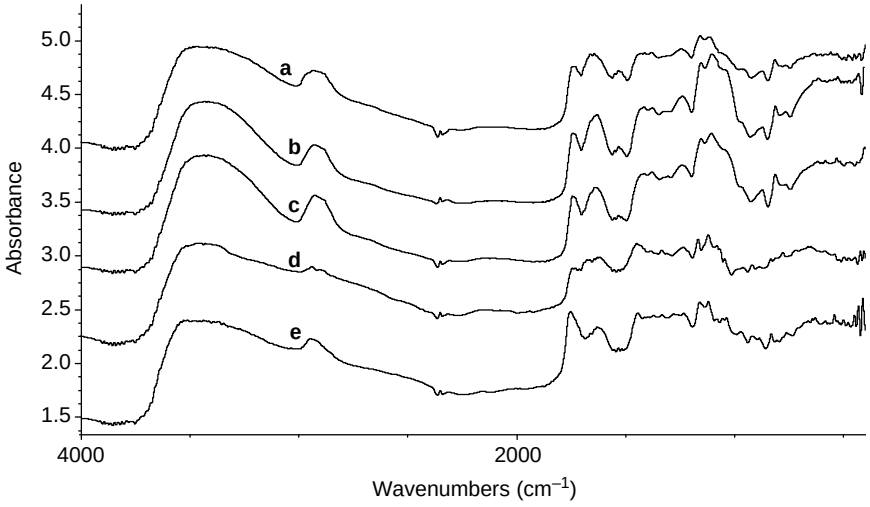

Fig. 1. Diffuse reflectance Fourier transform infrared spectra of the 4000–400 cm^{-1} region of soy pectin produced by (a) vacuum oven drying, (b) freeze drying, and (c) spray drying; (d) food grade, and (e) Sigma pectin.

drying, freeze drying, analytical grade and food grade pectin samples are presented in Fig. 1. FTIR spectra in the region between 1000–2000 cm^{-1} represents the major chemical functional groups in pectin (Filippov & Shamshurina, 1972; Kacurakova, Capek, Sasinkova, Wellner, & Ebringerova, 2000; Pappas, et al., 2004; Synytsya, Copikova, Matejka, & Machovic, 2003; Wellner, Kacurakova, Malovikaova, Wilson & Belton, 1998) and those regions are typically used to identify different types of pectin. FTIR spectra showed no major structural differences in pectin samples produced by various drying treatments and the soy pectin structures were comparable to that of analytical and food grade pectin samples. The region between 1000 and 1140 cm^{-1} corresponds to the stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration. The absorption bands between 1100 and 1200 cm^{-1} were from ether (R–O–R) and cyclic C–C bonds in the ring structure of pectin molecules. The absorption band at 1500 cm^{-1} was due to OH bending vibration. The band around 1540–1560 cm^{-1} corresponds to the protein amide in the pectin molecules. The regions between 1590 to 1600 cm^{-1} are due to the aromatic ring stretching. The region between 1600 and 1800 cm^{-1} is of special interest, since it provides structural information that could be used to compare different types of pectin. This spectral region reveals the existence of two bands at 1630–1650 and 1740–1760 cm^{-1} from free and esterified carboxyl groups, respectively. It was observed that the esterified carboxyl groups showed an increase in their intensities and band areas as the DE values increased. The intensity and band area of esterified and free carboxyl groups were similar for all the soy hull pectin samples produced by various drying methods (a, b, and c). Bands around 2800–3000 cm^{-1} corresponds to the C–H absorption and due to the stretching vibration of methyl (CH_3) group of the methyl ester. The broader band from 2400 to 3600 cm^{-1} was from stretching of the hydroxyl (O–H) groups due to moisture in the pectin samples.

FTIR structure analysis shows that the drying methods had not any detrimental effect on the structure of soy hull pectin, and soy pectin produced by various drying methods were comparable to commercial food and Sigma pectin.

3.4. Pectin solubility

Solubility of soy hull pectin samples produced by vacuum oven drying, spray drying, freeze drying, and food and Sigma pectin samples are presented in Fig. 2. Soy pectin produced by oven drying method had the lowest solubility among the pectin samples tested in contrast to Sigma pectin which had the highest solubility. The low water solubility of soy pectin produced by vacuum oven drying method may be attributed to the temperature used in vacuum oven drying. Like Hunter color values, the water solubility also suggested that the vacuum oven drying method was the most influential drying among the drying

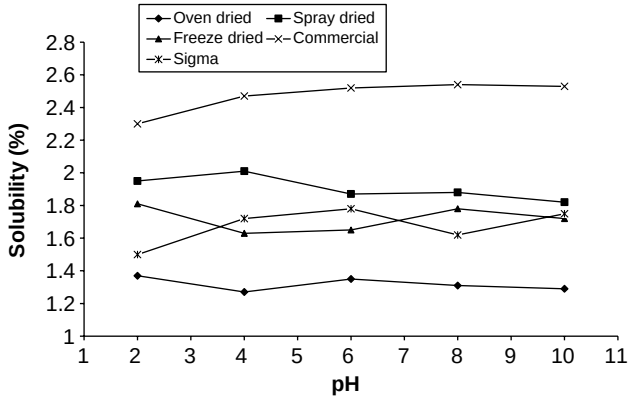

Fig. 2. Water solubility of commercial food and Sigma pectin; soy hull pectin produced by vacuum oven drying, freeze drying, spray drying methods.

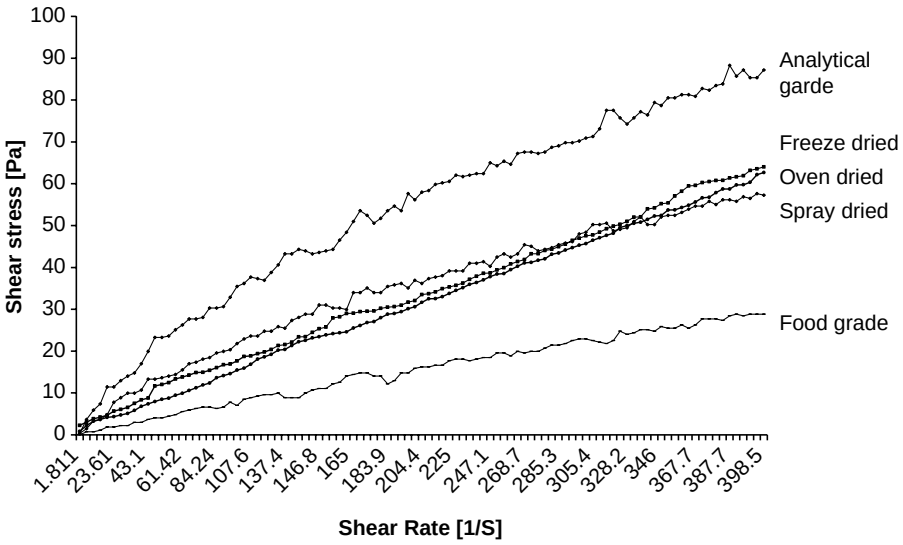

Fig. 3. Changes in shear stress as a function of shear rate of pectin solution: commercial food and Sigma pectin, soy hull pectin produced by vacuum oven drying, freeze drying, and spray drying.

treatments used in this study and affected the solubility of the soy hull pectin. The solubility of soy hull pectin samples produced by freeze drying and spray drying methods were comparable to that of commercial food grade pectin. The pH values (2 to 10) did not have any significant effect on the solubility of the pectin samples.

3.5. Rheology of pectin solution

The shear stress [Pa] as a function of shear rate [1/S] for the soy hull pectin samples produced by vacuum oven drying, spray drying, and freeze drying, and commercial food and Sigma pectin samples are presented in Fig. 3. The flow behavior of the pectin solutions represents a classic example of Newtonian fluid. There was a linear relationship between shear stress and shear rate for all the pectin samples studied. The shear stress changed with shear rate for all the soy hull, analytical and food grade pectin samples. The slope of the straight line model of the curve showed that there was no significant difference in viscosity between the soy hull pectin produced by various drying treatments (The slope value is not presented). The changes in shear stress for soy hull pectin samples produced by various drying methods were greater than the commercial food grade pectin but lower than the Sigma pectin. This indicated that the viscosity of soy pectin produced by various drying methods were greater than the commercial food grade pectin but lower than the Sigma pectin. The shear stress as a function of shear rate also indicated that the drying method did not influence the flow behavior of the soy hull pectin samples.

This study showed that drying method used in this study had no detrimental effect on the structure or composition of the soy hull pectin. Drying also had very little or no effect on the solubility and flow behavior of soy hull pectin samples. Drying had significant effect on the physical appearance of the soy hull pectin. Depending on the food application or end product quality, a drying method may be chosen to obtain pectin with desired functional properties and appearance.

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