Effect of Pomace Drying on Apple Pectin

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The effect of temperature used for drying apple pomace on apple pectin characteristics, including chemical composition, color and gelpoint temperature (T_g) was determined. Pomace was obtained from commercial Granny Smith apples and dried in a rotary drier at different air temperatures (T_{dr} = 60, 70, 80 and 105 °C). Pectin was extracted from dried pomace in nitric acid solution (pH = 2.5) at 80 °C. Major minerals in apple pectin were Ca > Na > Mg. Galacturonic acid content (% AGA = 60.6 ± 1.8) was practically unaffected by drying temperature. Conversely, T_{dr} affected both the degree of methoxylation (DM) and the molecular weight (M_w) of extracted pectin. M_w was estimated by applying the Mark Houwink – Sakurada equation, through determination of intrinsic viscosity of pectin solutions. M_w reduced with T_{dr} from approximately 122,000 (60 °C) to 57,000 (105 °C). Pectin color, as Hunter ΔE, was also affected by T_{dr}. A lighter color was obtained at 80 °C. The higher gelpoint value (T_g = 80 °C) was obtained with pectin from pomace dried at 80 °C. Gelpoint was shown to be more sensitive to T_{dr} than other quality parameters: while DM had the same value both at 80 and 105 °C, minimum T_g occurred at the higher temperature. T_g was also very sensitive to pH.

Introduction

Pectin has been used as a gelling agent for the past two centuries (Oakenfull and Scott, 1984). Pectins consist of a backbone, in which 'smooth' α-D-(1-4)-galacturonan regions are interrupted by ramified rhamnogalacturonan regions, highly substituted by neutral sugar-rich side chains (Schols *et al.*, 1996). An important feature of galacturonans is the esterification of the galacturonic acid residues with methanol. The degree of methoxylation (DM) is defined as the number of moles of methanol per 100 mol of galacturonic acid.

The process of extracting apple pectin includes the drying of apple pomace to prevent enzymatic destruction. It is known (Bhalla *et al.*, 1993) that dried apple pomace contains 100–180 mg/g pectin. Papers on the quality of pectin extracted from commercially dried citrus pomace are available (Crandall *et al.*, 1978; Rouse and Crandall, 1978). However, work showing the loss of pectin quality from apple pomace as influenced by drying conditions are scarce (Dryden *et al.*, 1952; Crandall *et al.*, 1978). It is known that both DM and the anhydrogalacturonic acid (AGA) content of pectin are affected by the processing conditions, especially during drying of pomace. DM controls the setting properties of pectin.

The gelation of high methoxyl pectin (HMP) with sugar was described as quite a complex process (Oakenfull, 1991). HMP with DM > 50% forms a gel if the pH ≤ 3.6 and if a co-solute like sucrose at concentration > 0.55 g/g is present. Physical properties of a pectin gel are the formation of a 3-D polymer network, created by the combination of hydrogen bonding and hydrophobic effects. When a hot solution of pectin and soluble solids is cooled, a progressive association of galacturonic acid molecules takes place, in which larger and larger clusters are formed until a critical temperature (T_g) is reached where viscosity tends toward an infinite value and the shear modulus G diverges from zero. This gel point may also be defined as the stage at which a liquid begins to exhibit pseudoplastic properties. This stage may conveniently be observed from the inflection point on a viscosity time plot. After some time, a stable gel is reached (Doublier *et al.*, 1992). The rates of gel-structure development and gel strength are affected by type of pectin, pH, solute used and temperature. It is very difficult to predict the modulus (G) and the temperature of gelation (T_g), which must be determined experimentally. A small amplitude oscillatory rheological test (SAOT) has been used for studying the gelling mechanism (Doublier *et al.*, 1992). Characterization of G and T_g can be obtained using a rheometer either with controlled step displacements or with dynamic oscillatory deformations (da Silva and Gonçalves, 1994) and if fracture at the tool surfaces can be prevented, the yield stress can also be determined. The transition from viscoelastic liquid to viscoelastic solid is a gradual one. There is no discontinuity in the rheological behavior. At

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least three conditions must be satisfied by any gelling point determination method: (i) it must be nondestructive; (ii) gels must be deformed within the linear viscoelastic range; and (iii) results should be expressed in fundamental terms.

By using low strain amplitude ($< 1\,^\circ$) and measuring the phase angle, it is possible to study gelation with minimal risk of damage to the gel structure. The elastic modulus (G') and the viscous modulus (G'') as a function of frequency (ω) have been used to define the gelling temperature (T_g) and setting time (t_g) (da Silva and Rao, 1999).

The main objective of this work was to determine the effect of the temperature of drying apple pomace on pectin characteristics, including chemical composition, color and gelpoint temperature.

Materials and Methods

Apple pomace drying

The apple pomace studied was obtained from commercial Granny Smith apples. Apple fruits were washed and crushed in a Model No. 6, Fitz Mill Comminutor (Fitzpatrick Co., Chicago, IL, U.S.A.). Juice was extracted by pressing in a hydraulic rack-and-cloth press (180 kPa for 10 min) and pomace dried in the same continuous, rotary drier used by Pelegrina et al. (1998). Drying conditions were speed of rotation, 17 rpm; air velocity, 1.5 m/s; initial pomace load, 2.3 kg; and four values of air temperature (T_{dr} = 60, 70, 80 and 105 °C) measured at the air outlet. Initial pomace moisture content was approximately 0.80 g/g. A typical experimental run lasted 6–8 h to reach a final to initial water content ratio (X/X_o) < 0.07, where X is the water content, depending on the air temperature (**Fig. 1**).

Pectin isolation

Pectin was extracted from dried apple pomace in a nitric acid solution (pH = 2.5) for 1 h with solid:liquid ratio of 0.04 kg:L, at 80 °C. After extraction, the pectin solution was filtered through a Büchner funnel with a Whatman No. 4 filter paper and diatomaceous earth pre-coat, and concentrated under vacuum (60 °C) in a Büchi Rotovaporator (Büchi Co., Zurich, Switzerland), volume ratio 4:1. Concentrated pectin solution was precipitated with ethanol (0.96 mL/mL) and the resulting product washed twice with 0.70 mL/mL and 0.96 mL/mL ethanol, respectively. Pectin precipitate was then filtered through Whatman No. 4 filter paper and dried under vacuum at 45 °C to constant weight. Dry pectin was ground to pass a 100-mesh sieve.

Pectin characterization

Ash content was determined according to AOAC (1984) method 14.006. The concentration of Ca, Cu, Mg, Na and Zn was determined with a GBC AA Spectrophotometer (GBC Scientific Equipment, Victoria,
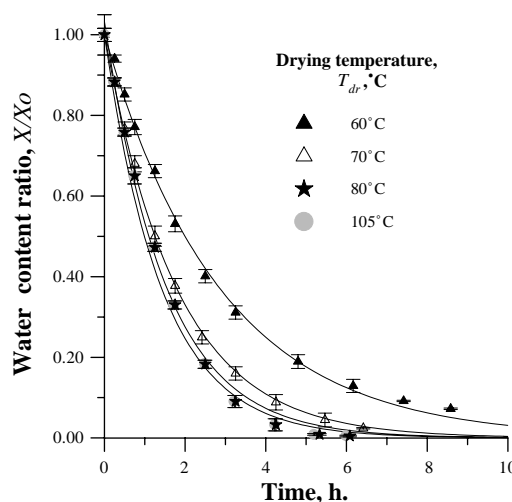

Fig. 1 Apple pomace drying curve as a function of air drying temperature

Australia), after digestion with concentrated HCl (Osborne and Voogt, 1996).

Color was determined as Hunter L, a and b parameters with a Hunter Ultrascan XE Spectrophotometer (Hunterlab, Inc., Reston, VA, U.S.A.) in the reflection mode. Color of pectin samples (powder) was measured in duplicate in black painted glass cells ($40\,cm^3$). Color difference, ΔE, was calculated from a, b and L parameters, using Hunter–Scotfield's equation:

$$\Delta E = (\Delta a^2 + \Delta b^2 + \Delta L^2)^{1/2} \qquad [1]$$

where $\Delta a = a - a_0$; $\Delta b = b - b_0$; and $\Delta L = L - L_0$; Subscript "0" indicates color of pectin powder dried at 60 °C.

Apple pectin gels

Pectin gels were prepared as suggested by the IFT Committee (1959) Method 5–54. Pectin dispersions were prepared under agitation and heating during 5–10 min until the calculated weight was reached. Pectin and soluble solids concentrations were 2 mg/g and 0.65 g/g, respectively. Selected pH (2.0–2.8) was adjusted in the hot solution (Orion pH meter with high-temperature electrode) with the addition of few drops of tartaric acid solution. Soluble solids were determined with a bench top Abbe refractometer. All the other reagents were analytical grade and used without further purification.

Determination of AGA content (% AGA)

Galacturonic acid (AGA) was qualitatively determined by the colorimetric phenyl-phenol method (Blumenkrantz and Asboe-Hansen, 1973) with a UV/VIS Perkin-Elmer Lambda 3 Spectrophotometer, at 520 nm (Abs_{520}) in a 1 cm quartz cell. The colorimetric procedure was as follows: 6 mL sulfuric acid was added to 1 mL of sample in a test tube, agitated with a Vortex mixer and cooled in an ice bath. Following cooling, 100 μL of meta-hydroxydiphenol reagent (150 mg meta-hydroxydiphenol in 10 mL 0.125 N NaOH) was added in each tube and the

Abs$_{520}$ read at its maximum value (4–6 min), against the appropriate blank.

Determination of the degree of methoxylation of pectin (DM)

A stock solution of pectin was prepared at a concentration of 8.33 mg/mL in distilled water. Pectin methyl esters were hydrolysed as follows: 1 mL of NaOH (1 N) was added to 12 mL of pectin solution. This solution was incubated for 30 min at room temperature and neutralized with HCl 0.1 N, using a pH meter. Finally, the solution was diluted with distilled water to a final weight of 20 g. Aliquots of the hydrolysed pectin samples were then analysed for methanol. A Varian 3700/Vista 402 gas chromatograph/data system equipped with an Inox-filled column (Porapak N 80/100 mesh) of 2 m × 2 mm i.d. was used. The oven temperature was fixed at 115 °C and the injector and detector (FID) temperatures were 210 and 220 °C, respectively. The carrier gas (N$_2$) flow rate and sample volume were 20 mL/min and 2 μL, respectively. Solutions of methanol (HPLC degree) in water were used for calibration purposes. Fitting the calibration curve resulted in a straight line through the origin with a regression coefficient $R^2 = 0.9975$.

The DM value was calculated from the following equations:

$$\text{Meq MetOH} = \text{Meq ECG} \quad [2]$$

where MetOH is the generated methanol and ECG are the esterified carboxylic groups; then:

$$\text{DM} = \text{Meq ECG}/\text{Meq TCG} \quad [3]$$

where the total carboxylic groups (TCG) were calculated from the galacturonic acid content.

Determination of molecular weight (M_w)

Apple pectin molecular weight was estimated by applying the Mark Houwink–Sakurada equation, relating [η] with M_w (Arslan, 1995)

$$[\eta] = k[M_w]^a \quad [4]$$

where k and a are constants and [η] is the intrinsic viscosity defined as

$$[\eta] = \lim_{C \to 0} \left(\frac{\eta_r - 1}{C} \right) \quad [5]$$

where η_r is the relative viscosity (solution to solvent) and C is the pectin concentration. Both k and a depend on temperature and solute and solvent characteristics. A large number of models have been used to deduce [η]-M_w relationships (da Silva and Rao, 1992). In the case of a pectin solution in sodium phosphate buffer (0.1 mol/L; pH = 7), they may be assumed to be $k = 0.3$ and $a = 0.613$ (Arslan, 1995). Determination was made in the range of pectin concentration 1–4 mg/g. Viscosity measurements were performed at 25 °C with a Bohlin CVO stress-controlled rheometer using concentric cylinders geometry (C25). Constant shear stress ($\sigma = 0.1$ Pa) was selected.

Small amplitude oscillatory test

The same Bohlin model CVO (Bohlin Instruments Ltd., London, U.K.) rheometer but with cone (4 cm dia.; 4 °) and plate system, was used to obtain dynamic rheological data (Arenaz and Lozano, 1998). A solvent trap was placed on top of the cone to minimize moisture loss. Two methods were used to test the pectin/sucrose solution dynamically:

(1) *Controlled cooling*. The hot pectin dispersion was poured on the rheometer plate, set at 95 °C and the cone lowered until the selected gap (150 μm). Dynamic test was immediately carried out (0.1 Hz; 5% strain) while temperature sweeps over 95–20 °C (cooling rate, 3 °C/min). Magnitudes G', G'', complex viscosity (η^*) and phase angle (δ) as a function of temperature were plotted.

(2) *Frequency sweep*. In this case, rheological tests were performed in the range 0.005–1.0 Hz, (initial strain 0.03 Pa) on pectin gels at 25 °C. Formerly, an amplitude sweep to ascertain the linear viscoelastic range was performed on selected samples.

Results and Discussion

Drying curves were fitted to a simple first-order equation:

$$X/X_0 = \exp(-kt) \quad [6]$$

where X is the water content (kg water/kg dry matter); subscript "0" is for initial water content, t is time (h) of drying and k is a coefficient depending on T_{dr}. **Table 1** lists the values of k corresponding to each drying temperature used in this work.

Results indicated that % AGA (60.6 ± 1.8) was practically unaffected by drying temperature ($P = 95\%$). On the contrary, DM increased with T_{dr}, from 60 to 80 °C then remained practically constant at the higher temperature of drying assayed (**Table 2**).

Pectin color as ΔE was also affected by the temperature at which apple pomace was dehydrated (**Fig. 2**). A lighter color was obtained at 80 °C. High pectin color at lower temperatures of drying may be attributed to the time required for pomace dehydration. On the other hand, increase in the color of pectin extracted from apple pomace dried at 105 °C was attributed to caramelization-type deteriorative reactions. It must be noted that, despite the water rinsing of pomace, its soluble solids (mainly fructose and glucose) still remain as high as 2–3 ° Brix. **Table 2** shows that pectin yield was also drastically reduced when apple pomace was dried at

Table 1 Kinetic constants of drying (Eqn [6])

T_{dr} (°C)	k (h^{-1})
60	0.347
70	0.554
80	0.635
105	0.689

Table 2 Effect of pomace drying temperature on pectin yield and composition. Values in parentheses are standard errors

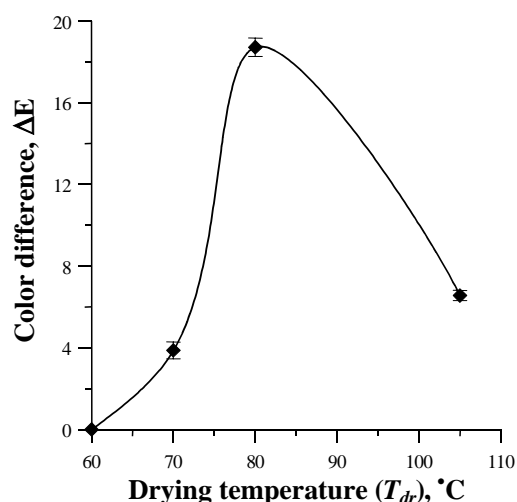| T_{dr} (°C)	Ash (mg/g)	Pectin yield (mg/g)^{a,b}	% AGA^b	% DM
60	29.0 (0.71)	36.3	62.3 (0.75)	72.8 (0.61)
70	36.0 (0.74)	36.3	58.8 (0.84)	73.9 (0.26)
80	44.0 (0.78)	39.6	59.7 (1.82)	79.6 (0.42)
105	25.0 (0.67)	26.3	61.5 (1.02)	79.3 (0.82)

^{a}dry pomace basis.
^{b}Ash-free basis.

Fig. 2 Apple pectin Hunter parameter as affected by pomace drying temperature

Table 3 Mineral content (μg/g) determined in pectin extracted from apple pomace dried at different temperatures (T_{dr})

T_{dr}	Mg	Cu	Na	Zn	Ca	Total
60	406	78.3	900	1827	1796	5067.3
70	316	67.3	655	1190	1206	3504.3
80	383	51.9	778	1057	1267	3616.9
105	124	25.1	—	224	1142	1620.1

105 °C. **Table 3** lists the mineral content of pectin extracted from apple pomace dried at different temperatures. Results showed that in general, mineral content decreased with T_{dr}, particularly at the higher temperature assayed.

Major minerals in apple pectin were $Ca > Na > Mg$. Similar results were reported by Kertetsz (1951) for citrus pectin extracted with ethanol. There are large variations on the content of nonpectic materials (including ash) in solid dry pectin. Arslan (1995) compared the ash content of sugar beet pectin extracted with different agents. This author found that using EDTA solution, ash content resulted three times higher than the same pectin extracted with HCl (0.04 g/g). The ash content increase was connected to the chelating capacity shown by EDTA solutions. Difference level of ash in pectin was considered to be mainly pH dependent (Lin *et al.*, 1976). However, in this work the pH during extraction was practically constant. Differences in ash content were attributed to drying conditions: while pomace dried at the lower temperatures produced porous well-structured pellets easily filtered and pressed after pectin extraction, pomace dried at 105 °C acquired a pulp-like aspect when hydrated, making the processes of filtration and pressing more difficult. Therefore, relative reduction in ash content was attributed to that prolonged contact time with the acidic washing solution.

Intrinsic viscosity
Figure 3 shows intrinsic viscosity of apple pectin solutions extracted from pomace dried under different air temperatures. There was a tendency to decrease [*f*] values when T_{dr} increased. Molecular weights calculated with Eqns [4] and [5] were reduced from approximately 122,000 (60 °C) to 57,000 (105 °C).

Sol–gel transition results
Figure 4 shows a typical plot of G', G'' and δ *vs.* temperature, obtained from small amplitude oscillatory measurements at constant frequency during controlled cooling. In food gels, the temperature where the total phase angle variation is halved ($\Delta\delta_o/2$) can be regarded as a rather good criterion to define the gelpoint (T_g) which is in accordance with the temperature at which $G' = G''$ (Barford and Pedersen, 1990).

Increase of T_g with the temperature of drying (T_{dr}) was plotted in **Fig. 5**. Finally, **Fig. 6** shows T_g as a function of pH of dispersion with T_{dr} as a parameter. The values of T_g for samples dried at 60 °, 70 and 105 °C showed a similar tendency, while pectin dried at 80 °C was much more influenced by the pH of dispersion.
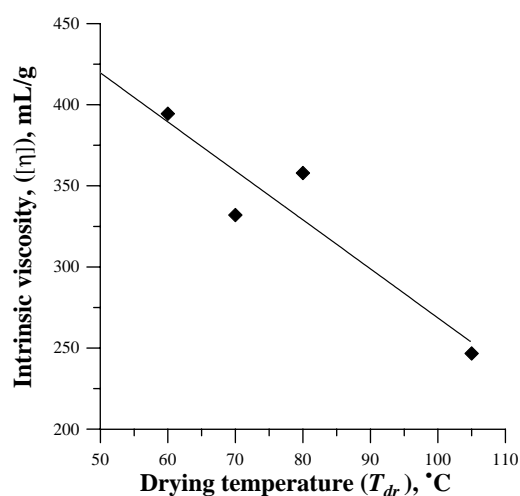

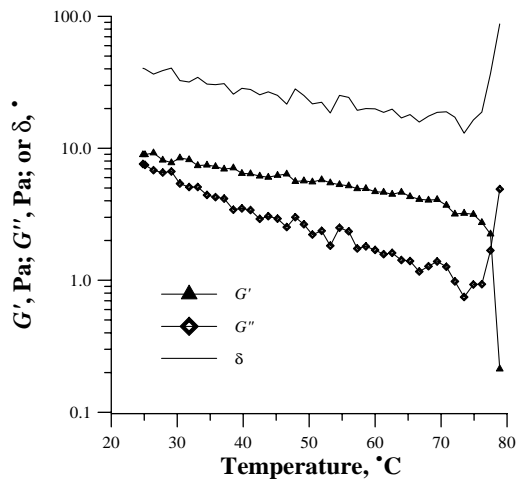**Fig. 3** Apple pectin intrinsic viscosity as a function of pomace drying temperature

Fig. 4 Change of G', G'' and phase angle (δ) with temperature during gelation of apple pectin solution.
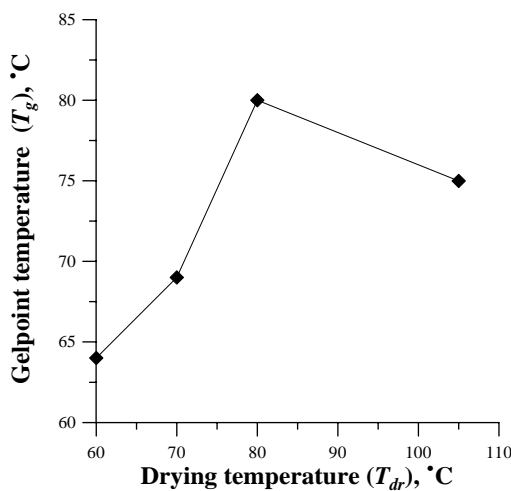

Fig. 5 Gelpoint temperature T_g as a function of drying air temperature T_{dr} (pH = 2.1)
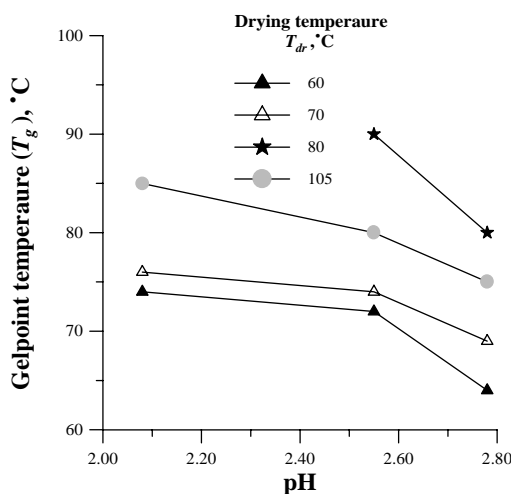

Fig. 6 Gelpoint temperature T_g as a function of pH solution with drying temperature T_{dr}(°C) as a parameter

Conclusions

From a practical point of view, temperature during apple pomace dehydration in a rotary drier affected both the degree of esterification and the degree of polymerization (molecular weight) of extracted pectin. The higher T_g value was obtained with pectin extracted from apple pomace dried at 80 °C. Gel point was shown to be more sensitive to T_{dr} than other quality parameters: while DM had the same value both at 80 ° and 105 °C, minimum T_g occurred at the higher temperature. This behavior may be attributable to the heat-induced reduction in M_w. T_g was also very sensitive to pH. It must be remarked that the gelling temperature of this type of gel is a complex function of several parameters, including number of polymeric chains, solvent interaction and attractive and repulsive forces involved, among others (da Silva and Rao, 1999).

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