

Conformational Changes in Serum Pectins during Industrial Tomato Paste Production

JEROME V. DIAZ,* GORDON E. ANTHON, AND DIANE M. BARRETT

Department of Food Science and Technology, University of California, Davis, California 95616

It is well-known that an irreversible decrease in serum viscosity occurs when tomato juice is concentrated by evaporation into paste. Several studies have suggested that the loss in serum viscosity is due to pectin depolymerization, caused by the high temperatures used during industrial tomato paste production. This study demonstrates that conformational changes in pectin may play a more important role than pectin depolymerization in the irreversible loss of serum viscosity during industrial tomato paste production. Samples of tomato juice, processing intermediates, and paste were obtained from a commercial producer in California. After dilution to 5 °Brix, tomato serum was obtained by centrifugation at 15000g for 10 min. Weight average molecular weight (M_w) and root-mean-square (rms) radius of the polymers in the tomato serum were determined using high-performance size-exclusion chromatography with multi-angle laser light scattering and refractive index detectors (HPSEC–MALLS–RI). Serum viscosity decreased throughout the juice concentration process, especially at later stages, where the processing temperature reached a maximum of 90–95 °C. In parallel with this decrease in serum viscosity, there was an increase in the soluble pectin concentration. Analysis of the M_w distribution of the tomato serum showed that solubilization of pectin occurred across the entire polymer distribution range. The M_w changed from 2.62×10^5 g/mol in the juice to 2.61×10^5 g/mol in the paste, indicating that minimal depolymerization occurred. However, the rms radius distribution indicated that the pectin conformation became more compact as the juice became more concentrated. Conformational plots revealed that serum pectins in the hot-break tomato juice and at the early stages of concentration behaved as extended coils, having shape factors of about 0.40. In processing intermediates taken from later stages in the process and in the paste, the shape factor changed to about 0.25, indicating a more compact conformation. This conformational change correlated with the observed decrease in serum viscosity in the paste production process. This result is consistent with a Flory–Fox-type relationship between viscosity, rms radius, and M_w . The conformational change may be due to increased polymer–polymer interaction brought about by the concentration process.

KEYWORDS: Tomato paste; serum viscosity; pectin; conformational changes

INTRODUCTION

Tomato paste is widely used as an ingredient in the food industry. It serves as a base material for formulated products, such as sauces and ketchups. It has been shown that the properties of tomato paste used in formulation affect the quality of remanufactured food items (1). One of the most important quality characteristics of tomato paste is consistency. For both tomato paste manufacturers and food processors that use tomato paste as an ingredient, understanding the nature of consistency changes during concentration may lead to better and more consistent products from a quality assurance point of view.

The industrial production of tomato paste typically involves a series of concentration steps to achieve the final concentrated tomato material. While in recent years new methods of concen-

tration, such as reverse osmosis, freeze concentration, and centrifugation followed by serum concentration, have been used, tomato pastes are still widely produced from industrial plants that employ evaporators. When pastes produced by such industrial evaporators are diluted with water, the resulting juice has a lower consistency than the original juice from which it was concentrated (2). This consistency loss has been attributed to thermal degradation of pectic materials (3), the result of the high temperatures used in commercial evaporators. However, we have recently shown that the total pectin content changes little through industrial processing (2), and a consistency loss from concentration and dilution of juice has also been observed in small-scale benchtop concentrators that involve milder conditions than those in commercial evaporators (4–6). Consistency loss occurs regardless of the type of processing technique used, degree of concentration, or initial solids content of the juice (7).

*To whom correspondence should be addressed. E-mail: jeromevdiaz@gmail.com.

Table 1. Processing Parameters during Hot-Break Paste Production

process stage	sampling point	average soluble solids (°Brix)	approximate temperature (°C)	approximate res. time (min)	water added to adjust to 5 °Brix (% w/w)
whole tomato	1		ambient		
break tank			90–95	5	
flash evaporators	2	5.1	60–75	10	1.9
third-effect evaporator	3	7.7	50	30	35.1
second-effect evaporator	4	10.9	74	40	54.0
first-effect evaporator	5	20.3	91	40	75.4
high-density evaporator			80–90	30	
paste	6	28	ambient		82.0

Tomato juices and pastes can be roughly viewed as consisting of two major systems, an insoluble pulp dispersed in a serum (8, 9). The bulk of the overall consistency of tomato juices and pastes can be attributed to the insoluble tomato pulp that is comprised primarily of cell walls. Cell wall components in the pulp of tomato products may exist as pieces of tomato tissue and fractured cells. The serum consists primarily of soluble materials, primarily the pectic polymers, which impart viscosity, but also other monosaccharides, organic acids, and various ions. It has been suggested that the interaction between the insoluble pulp and the soluble serum is important to overall consistency, especially in reconstituted juices and formulated products (6, 10). Several authors have indicated that serum properties may influence serum separation (5, 11). Serum pectins have previously been used as an indicator of changes in the insoluble pulp (8, 12) because, during processing, pectin is solubilized from the pulp into the serum (3, 13). The influence of serum properties on the overall consistency of tomato juices, pastes, and products derived from them is not yet clearly understood. Because the tomato serum serves as a final repository for solubilized material, following the changes in the physicochemical properties of the tomato serum occurring during the process provides a simple system for monitoring overall pectin changes in the tomato juice concentration process.

In a previous study, we looked at the irreversible changes in pectin solubility and juice consistency that occur during industrial processing, as tomato juice is concentrated to paste (2). This study examines the physical and chemical changes that occur to the soluble pectins in the tomato serum during industrial tomato paste processing. This paper also aims to give insight into the role of tomato serum in overall tomato juice and paste consistency.

MATERIALS AND METHODS

Materials. Alcohol oxidase (from *Pichia pastoris*) and Purpald (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole; catalog number 162892) were obtained from Sigma Chemical Co., St. Louis, MO. Dextran T40 and T200 with average molecular weights of 39 000 and 200 000 g/mol, respectively, were obtained from Pharmacia, Uppsala, Sweden.

Sample Collection. Samples from different steps of the tomato paste manufacturing process were obtained from the Morning Star Processing plant located at Williams, CA, as described previously (2). The tomatoes used were a mixture of Heinz tomato processing varieties (*Solanum esculentum* M.). Samples were collected at 5 points in the process: immediately after the juice passed through the finisher (step 2), third-effect evaporator (step 3), second-effect evaporator (step 4), first-effect evaporator (step 5), and final paste product (step 6). Samples of the raw whole fruit (designated step 1) were not analyzed. Process conditions are summarized in Table 1. After collection, samples were immediately cooled in an ice bath, transported to the laboratory, and reconstituted with water on the same day.

Sample Preparation. Samples were adjusted to 5.0 °Brix levels by adding the appropriate amount of distilled water (Table 1). Visual inspection and hand mixing were carried out to ensure that no agglomerated particles were present. The samples were centrifuged at 15000g at

5 °C for 10 min (Sorvall refrigerated centrifuge, RC5C, Waltham, MA). Tomato serum (supernatant) was collected and analyzed for relative viscosity, molecular weight, and root-mean-square (rms) radius. Cell wall material (CWM) and various pectin fractions were also isolated from the diluted juice samples as described below and analyzed for galacturonic acid content. Water-soluble tomato pectin fractions were collected and analyzed for molecular weight and root-mean-square (rms) radius. All analyses were conducted in triplicate. Representative M_w and rms radius distribution curves for each sample analyzed were chosen and presented in the figures.

Isolation of CWM. Tomato juice samples obtained from the various stages of tomato paste manufacture were freeze-dried (Labconco Freeze-Dryer, Kansas City, MO) to remove water and concentrate the insoluble solids. The CWM was isolated from this material according to a modified procedure from Huber and O'Donoghue (14). Approximately 100 g of freeze-dried tomato juice was homogenized (Polytron PT 3000, Brinkmann, Switzerland) briefly in 200 mL of 95% ethanol and allowed to settle overnight. The precipitate was collected through filtration using Whatman glass fiber filters (GF/A). The precipitated material was decolorized by adding a mixture of 2:1:1 hexane, acetone, and ethanol intermittently. When the precipitate was white, it was air-dried under a fume hood overnight and subsequently vacuum-dried (Isotemp vacuum oven, Model 280A, Fisher Scientific, Pittsburgh, PA) for 48 h.

Fractionation of Various Pectins. Sequential extraction of various tomato pectins was made from the isolated CWM according to the procedure used by Hurtado et al. (3). Briefly, 300 mg of isolated CWM was suspended in 100 mL of distilled water and stirred continuously for 16 h. Sodium azide was added to a final concentration of 0.2 g/L prior to stirring to prevent microbial growth. After extraction, the samples were centrifuged (Sorvall refrigerated centrifuge, RC5C, Waltham, MA) at 15000g at 5 °C for 5 min. The supernatant was decanted and saved. A second 100 mL aliquot of extractant was added to the residue. The resulting suspension was mixed until the pellet was resuspended and, subsequently, was centrifuged as above. The supernatant was added to the initial supernatant obtained, and this was called the water-soluble pectin fraction. Sequential extraction with 50 mM CDTA in 50 mM sodium acetate and then 50 mM sodium carbonate with 20 mM sodium borohydride followed the same fractionation procedure using the residue from the previous extraction. These fractions were called the chelator- and sodium carbonate-soluble fractions, respectively. All of the fractionated pectins were dialyzed against several changes of distilled water using Spectrophor dialysis tubing (Spectrum Laboratories, Inc., Rancho Dominguez, CA), with a molecular cutoff weight of 6000–8000 g/mol. After dialysis, the fractions were freeze-dried and stored at –10 °C in a sealed container prior to physical and chemical analyses. The entire process of isolation of cell walls and fractionation of pectins was carried out on different tomato juice samples at least 3 times. The amount of pectin galacturonic acid in each of the fractions was determined as described previously (15).

Relative Viscosity. Relative viscosity of serum samples was measured using a standard Cannon-Fenske capillary viscometer (Canon Instrument Co., State College, PA) supported in a specialized holder that kept the viscometer in a vertical position in a 25 °C water bath. A 10 mL sample was pipetted into the viscometer, and the time in seconds for the fluid to pass from one to another demarcation line was recorded. Results were reported relative to the time that water at 25 °C passed through the demarcation lines of the viscometer.

Determination of Molecular Weights and rms Radius. Changes in molecular weight profile and rms radius of the serum pectins during the

manufacture of tomato paste were monitored using a high-performance size-exclusion chromatograph equipped with a multi-angle laser light scatter detector (HPSEC–MALLS–RI, DAWN DSP-F, Wyatt Technology Corp., Santa Barbara, CA) and a refractive index detector (ANSPEC Co., Tokyo, Japan). The chromatography was conducted with three Waters columns (Waters, Milford, MA), namely, Ultrahydrogel 250, 1000, and 2000 with exclusion limits of 8×10^4 , 1×10^6 , and 7×10^6 g/mol, respectively. Columns were maintained at a constant temperature of 40 °C. Before injection, serum samples were filtered through 0.45 μm glass fiber filters (Millipore, MA). Injections of 100 μL aliquots of each sample were made using an automatic sampler. The eluant used was 0.01 N sodium nitrate (pH 6.8) plus 0.01% sodium azide, added as a preservative. The separation was conducted at a constant flow rate of 0.6 mL/min, which resulted in 30 bar pressure. Dextrans T40 and T200 were used as standards to verify the accuracy of the system. A value of 0.15 mL/g refractive index increment was used. Data collected were processed using ASTRA software, version 4.73.04 (Wyatt Technology Corp., Santa Barbara, CA) and were expressed as weight average molecular weight, cumulative weight average, and rms radius. The molecular parameters were obtained through the Rayleigh–Debye–Gans light-scattering theory for dilute polymer solutions:

$$\frac{R_{\theta}}{K_c} = M_w P_{\theta} - 2A_2 c M_w^2 P_{\theta}^2$$

where R_{θ} is the Rayleigh excess intensity of scattered light at angle θ , K is the optical constant at concentration c (g/mL), M_w is the weight average molecular weight, P_{θ} is the angular dependence of light scatter, and A_2 is the second virial coefficient. A Zimm plot calculated by the ASTRA software yields a curve with intercept M_w and a slope r_g or radius of gyration. The molecular weights were expressed as weight average (M_w), number average (M_n), and z average molecular weights (M_z) calculated as follows:

$$M_w = \left[\frac{\sum (c_i M_i)}{\sum c_i} \right]$$

$$M_n = \left[\frac{\sum c_i}{\sum (c_i / M_i)} \right]$$

$$M_z = \left[\frac{\sum (c_i M_i^2)}{\sum (c_i M_i)} \right]$$

where c_i is the sample concentration and M_i is the sample mass. The polydispersity index (M_w/M_n) of the population distribution indicates the homogeneity or heterogeneity of the polymer distribution. For example, a monodisperse population has a polydispersity index of 1.

The weight average rms radius was calculated using the following equation:

$$\text{rms radius (nm)} = \left[\frac{\sum c_i (r_i^2)}{\sum c_i} \right]$$

where c_i is the sample concentration and r_i is the radius of gyration. Conformational plots were constructed from the M_w and rms radius data for each of the processing steps. Shape factors were calculated from the slopes of these plots.

RESULTS

Serum Viscosity. Samples taken at the various steps in the paste concentration process were reconstituted with water back to 5 °Brix and then separated into a soluble serum and an insoluble residue. Viscosity of the serums decreased through the course of the process (Figure 1), with a 35% decrease in serum viscosity in the final product as compared to the original 5 °Brix tomato juice. While the loss in serum viscosity starts after step 3, the greatest change in serum viscosity occurred between processing steps 4 and 5. At this step, the juice is concentrated from 10 to 20 °Brix and there is an increase in the temperature from approximately 74 °C (second-effect evaporator) to 91 °C (first-effect evaporator).

Pectin Solubilization. Total polymeric material in the serum was analyzed by HPSEC–MALLS–RI. This method does not discriminate pectic polymers from other polymers that may be

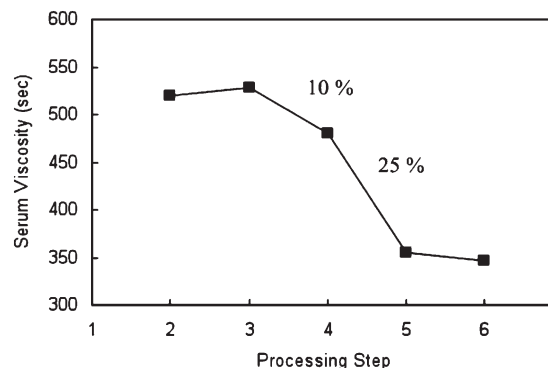


Figure 1. Serum viscosity changes during the concentration of tomato juice to paste. Samples were reconstituted to 5 °Brix prior to analysis. Percent loss in serum viscosity between processing steps is indicated. Standard deviation <0.5% for all measurements made.

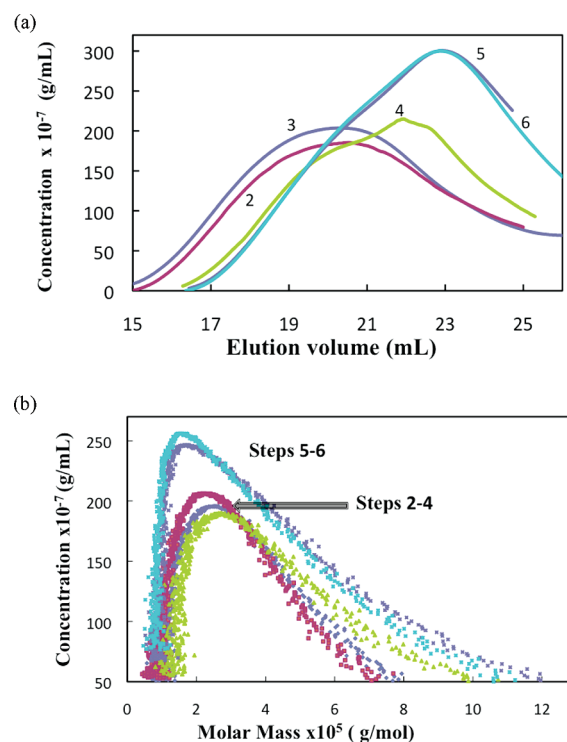


Figure 2. Changes in (a) elution profile and (b) molecular weight distribution of serum pectins obtained during various steps in the tomato juice concentration process.

present in the tomato serum; however, polymeric materials in the tomato serum samples obtained from the tomato juice and the intermediate steps in tomato paste production are composed predominantly of solubilized pectins (16). The assumption is that the changes in the polymer distribution in the tomato serum are primarily due to changes in the pectic polymers.

The total amount of polymeric material in the serum increased through the course of processing, as shown by the increasing peak heights in the elution profiles from the HPSEC–MALLS–RI (panels a and b of Figure 2). These results are consistent with our previous direct measurements of pectin solubilization during tomato paste processing (2), supporting the assumption that the polymeric material is predominantly pectin. Also consistent with our previous direct measurements of pectin solubilization, the polymer solubilization observed here occurred mostly between processing steps 4 and 5. Pectin solubilization coincides with the

Table 2. Changes in the Molecular Weight Moments, Polydispersity (M_w/M_n), and Percent Depolymerization of Tomato Serum Pectins during Industrial Tomato Paste Production

processing step	$M_n (\times 10^5)$	$M_w (\times 10^5)$	$M_z (\times 10^5)$	M_w/M_n	percent depolymerization
2	1.87	2.62	3.89	1.41	
3	1.69	2.37	3.50	1.40	
4	2.21	3.11	4.92	1.41	
5	1.55	2.61	5.12	1.69	
6	1.42	2.41	4.76	1.70	8.12

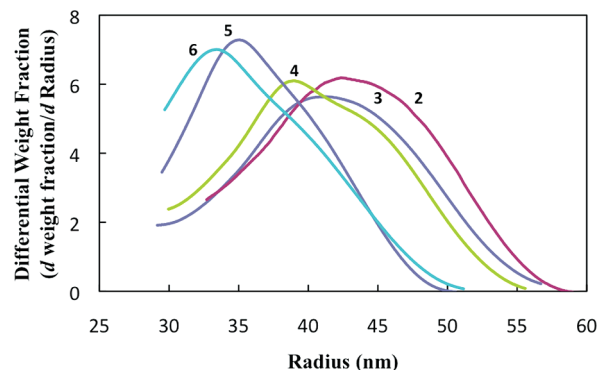
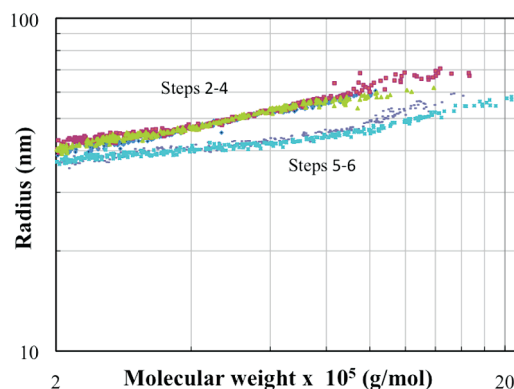
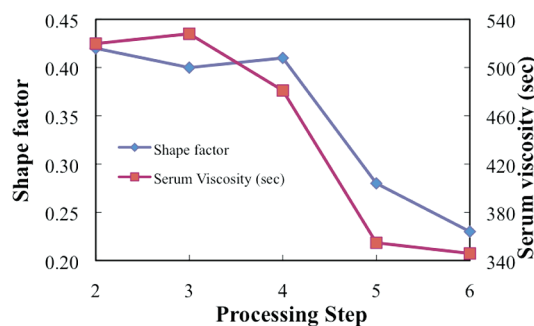
major decrease in serum viscosity, which also occurs between steps 4 and 5 (Figure 1).

Changes in Molecular Weight. The increased serum pectin concentration observed at step 5 is accompanied by later elution from the HPSEC–MALLS–RI system (Figure 2a). This change in elution volume indicates that the polymers in the sample have become smaller. The apparent decrease in polymer size was not due to a decrease in polymer molecular weight, however. Molecular weight distributions of the soluble polymers obtained from the different processing steps were similar (Figure 2b and Table 2). The higher concentrations of pectin in samples collected at steps 5 and 6 indicate that the solubilization of pectin during processing occurred across the entire mass distribution range. The polydispersity index, which is a measure of the hetero- or homogeneity of the polymer distribution in tomato serum, remained essentially the same throughout the process, increasing slightly from 1.41 in steps 2–4 to 1.70 in steps 5 and 6.

Changes in rms Radius. HPSEC–MALLS–RI was also used to elucidate polymer rms radius. The rms radii of serum polymers decreased in the later stages of tomato juice concentration, with the greatest decrease in rms radius occurring between process steps 4 and 5 (Figure 3). This corresponds to the same point at which the pectin concentration increases (Figure 2b) and the serum viscosity decreases (Figure 1). Figure 4 shows the relationship between molecular mass and rms radius at each step in the tomato juice concentration process. At all molecular weights, the rms radius values for samples obtained at steps 5 and 6 are smaller than those in the earlier processing steps.

The slope of the log–log plot of the rms radius versus molecular weight, also called the shape or scale factor, provides information on the conformation of the polymers. Theoretical values for shape factors include 1.0, 0.5–0.6, and 0.3, corresponding to a rigid rod, a flexible coil, and a sphere, respectively (17, 18). Shape factors were calculated for the serum pectins from the slopes in Figure 4. Early in the process, e.g., at steps 2, 3, and 4, the pectins behaved more like flexible extended coils, with slopes of 0.44, 0.39, and 0.41, respectively, while at steps 5 and 6, the slopes decreased to 0.28 and 0.23, indicating a more compact conformation. Water-soluble pectins derived from the CWM also followed similar conformational changes; i.e., a decrease in the shape factor was also observed at steps 5 and 6 (data not shown). The changes in the shape factor during the process are similar to those in serum viscosity (Figure 5).

Galacturonic Acid Content Changes in Pectin Fractions during Processing. The pectin analysis described thus far was performed by starting with the total polymeric material found in the serum obtained by centrifuging tomato juice. An alternative approach is to ethanol precipitate the CWM from whole juice (serum plus insoluble solids) and then extract the pectins from this residue. A simple water extraction of this residue yields a set of water-soluble pectins that are generally presumed to be the same as the water-soluble pectins found in the serum. Additional extractions with chelators and then high pH solubilize additional pectins that

**Figure 3.** Changes in rms radius of serum pectin obtained during various steps in tomato juice concentration.**Figure 4.** Conformational changes in rms radius and molecular weight of serum pectins during tomato juice concentration.**Figure 5.** Relationship between serum viscosity and pectin conformation. Shape factor or scaling factor indicates the general conformation of the polymer, either extended or coiled.

would not normally be water-soluble and thus not normally found in the serum.

An analysis of the pectins extracted from cell wall residues prepared from juices obtained at the different steps in paste processing showed that through the process there was an increase in the water-soluble pectins accompanied by a concomitant decrease in the chelator- and sodium carbonate-soluble fractions (Figure 6). Total pectin, which is the sum of the three fractions, decreased only slightly. The change in pectin solubility was greatest late in the process, primarily between process steps 4 and 5. The increase in pectin solubility at step 5 is consistent with the observed increase in polymeric material obtained in the supernatant at this step in the process (Figure 2).

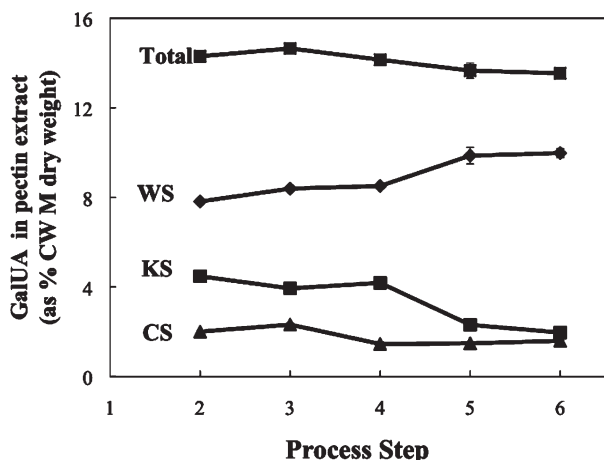


Figure 6. Changes in galacturonic acid content of various pectin fractions obtained from isolated CWM during tomato paste production. Total pectin is composed of the water-soluble (WS), chelator-soluble (KS), and sodium carbonate-soluble (CS) pectin fractions.

DISCUSSION

It is well-known that concentrating tomato juice to paste and then reconstituting it with water back to juice results in a loss of consistency. Several studies have observed a loss in tomato product consistency during the concentration process (2, 4–8), whether consistency is measured as gross viscosity of the whole juice or the fluid viscosity of the juice serum. Previously, we showed that the gross viscosity of the whole juice (measured as Bostwick consistency) changed primarily early in the process, before step 4. Here, we show that the serum viscosity also decreases but later in the process, at step 5. It thus appears that the decrease in serum viscosity is not caused by the same changes to the juice that affect the Bostwick values.

Serum viscosity is determined primarily by the amount and molecular weight of polymeric material in the serum. One might expect that, at the point in the process where serum viscosity decreased, there would also be a decrease in the total amount and molecular weight of the soluble pectin. However, exactly the opposite was observed. At the point in the process where serum viscosity decreased the most (step 5), the amount of serum pectin increased (Figure 2b). While there was a relatively small (8%) change in molecular weight peak of the serum pectins from steps 4 to 5, the total amount of high molecular weight material was greater at step 5 than at step 4 (Figure 2b). The loss in serum viscosity is thus not due to a loss of soluble pectin.

The principal change to the pectins through the process was an increase in the amount of water-soluble pectin in the later steps. This increase in water solubility was shown by both the increase in the amount of pectin in the water extract of the ethanol precipitates (Figure 6) and the increased content of polymeric material in the serums (Figure 2b). This result is consistent with our previous direct measurements of the pectin levels through paste processing, which also showed solubilization of pectin, especially at step 5. Step 5 (the first-effect evaporator; Table 1) is the hottest point in the process and shows that the main effect of heat in the process is to increase the water solubility of the pectin.

The results obtained in this study are inconsistent with a previous report claiming that substantial depolymerization of pectins occurs during tomato paste processing (3). In the prior study, conducted at the same processing plant as studied here, it was reported that there was both a loss in total polymeric pectin and a decrease in polymer molecular weight. It was suggested that the heat used in the process caused thermal degradation of tomato

pectins. However, this seems unlikely because the highest temperature used in the process (91 °C) is not high. Beresovsky et al. (6) reported that it would take a long time for tomato pectin to degrade under similar conditions. Furthermore, it has been shown previously by our laboratory that citrus pectin degradation under these conditions is minimal (19). In the present study, the total pectin content of the ethanol-precipitated CWM changed little through the process (Figure 6) and the molecular weight of the soluble pectin decreased only slightly (Figure 2b). This agrees with our previous direct measurement of pectin contents through processing, which also showed no decrease in total pectin (2).

One difference between this study and that reported previously is the protocol used for determining changes in molecular weight. Hurtado et al. (3) used size-exclusion chromatography (SEC) with pullulan as a standard, while this study directly determined molecular weight with HPSEC–MALLS–RI. One limitation of using secondary standards in SEC is that conformational differences may exist between the sample analyte and the standard (20). In this particular case, the conformation of pullulan is vastly different from that of pectin, because of differences in both monomeric units and glycosidic linkages. Because the size of polymers is dependent upon their solution conformation, using secondary standards to ascertain molecular weight may be misleading, especially if conformational changes occur within the sample analyte, as we have shown to occur here. Using HPSEC–MALLS–RI gives a distinct advantage because this protocol gives absolute molecular weight and conformation of polymers without the use of secondary standards (21).

The observed loss in serum viscosity in reconstituted tomato juices obtained from various steps in the tomato juice concentration process may be at least in part due to conformational changes in the serum pectins. Measurements of rms radii showed that, during processing, serum pectins assumed a more compact conformation (Figures 5 and 6). It has previously been shown that the conformation of tomato paste pectins is different from other unheated pectins (22, 23). While depolymerization alone may cause conformational changes in pectins (24), we did not find substantial changes in serum pectin weighted average molecular weight during tomato juice concentration. On top of this, there was an increase in the concentration of serum pectins during the course of processing. Changes in aggregation may also affect conformation because a compact aggregate occupies less space per unit molecular weight compared to a partially or fully dissociated conformation (24). During heating, without concurrent solution concentration, aggregated polymers have been shown to increase in size because they are broken down into asymmetric, less aggregated particles (25). In this study, the opposite trend was found, with a decrease in molecular size and no significant changes in molecular weight occurring during heating. One reason for the difference in observations may be that, in this case, concentration accompanied the heating process.

The rms radius can be related to intrinsic viscosity and molecular weight through the Flory–Fox relationship (26)

$$[\eta] = \phi \frac{R_g^3}{M_w}$$

where η is intrinsic viscosity, R_g^3 is the cube of rms radius, M_w is the molecular weight, and ϕ is a proportionality constant referred to as the draining parameter. This relationship shows that if the M_w remains unchanged, any change in the rms radius is directly proportional to the intrinsic viscosity of the solution. A decrease in rms radius may be due to changes in some intrinsic property in the pectin. For example, Chou and Kokini (22) suggested that

de-esterification of pectin may cause significant conformational changes. There were no changes in the degree of esterification measured through the various steps of the tomato juice concentration process in this study (data not shown). Therefore, one possible explanation for the observed changes in rms radius may be increased inter- and intramolecular associations during the concentration process. Pectins in solution can be viewed as flexible chains that may assume either coiled or extended conformations. As charged polymers, their conformations in solution are affected by factors such as solute concentration and ionic interactions (27–29). During tomato juice concentration, the removal of water may increase these interactions, leading to a more compact conformation. Morris et al. (30) showed that decreased water activity minimizes electrostatic repulsion and promotes chain–chain rather than chain–solvent interactions. It appears that these concentration effects on pectin conformation during tomato juice concentration may affect serum viscosity more so than thermally induced loss in pectin molecular weight.

LITERATURE CITED

- (1) Apaiah, R. K.; Goodman, C. L.; Barringer, S. A. Quality differences between fresh pack and remanufactured tomato sauce. *J. Food Process. Preserv.* **2001**, *25* (6), 431–445.
- (2) Anthon, G. E.; Diaz, J. V.; Barrett, D. M. Changes in pectins and product consistency during the concentration of tomato juice to paste. *J. Agric. Food Chem.* **2008**, *56*, 7100–7105.
- (3) Hurtado, M. C.; Greve, L. C.; Labavitch, J. M. Changes in cell wall pectins accompanying tomato (*Lycopersicon esculentum* Mill.) paste manufacture. *J. Agric. Food Chem.* **2002**, *50* (2), 273–278.
- (4) Kotte, K.; Kalamaki, M.; Ibanez, A. M.; Reid, D. S. The contribution of water removal to the phenomenon of “consistency loss” associated with juice concentrate products. *Proc. 13th World Congr. Food Sci. Technol.* **2006**, DOI: 10.1051/IUFoST:20060664.
- (5) Den Ouden, F. W. C.; Van Vliet, T. Effect of concentration on the rheology and serum separation of tomato suspensions. *J. Texture Stud.* **2002**, *33* (2), 91–104.
- (6) Beresovsky, N.; Kopelman, I. J.; Mizrahi, S. The role of pulp interparticle interaction in determining tomato juice viscosity. *J. Food Process. Preserv.* **1995**, *19* (2), 133–146.
- (7) Heutnik, R. Tomato juices and tomato juice concentrates: A study of factors contributing to gross viscosity. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands, **1986**.
- (8) Tanglertpaibul, T.; Rao, M. A. Intrinsic viscosity of tomato serum as affected by methods of determination and methods of processing concentrates. *J. Food Sci.* **1987**, *52* (6), 1642–1645.
- (9) Yoo, B.; Rao, M. A. Yield stress and relative viscosity of tomato concentrates: Effect of total solids and finisher screen size. *J. Food Sci.* **1995**, *60* (4), 777–779.
- (10) Sahin, H.; Ozdemir, F. Effect of some hydrocolloids on the serum separation of different formulated ketchups. *J. Food Eng.* **2007**, *81* (2), 437–446.
- (11) Thakur, B. R.; Singh, R. K.; Nelson, P. E. Effect of pH and soluble solids on the serum viscosity and serum color of tomato juice at elevated temperatures. *J. Food Qual.* **1997**, *20* (6), 495–500.
- (12) Tanglertpaibul, T.; Rao, M. A. Flow properties of tomato concentrates: Effect of serum viscosity and pulp content. *J. Food Sci.* **1987**, *52* (2), 318–321.
- (13) Lin, H.; Qin, X.; Aizawa, K.; Inakuma, T.; Yamauchi, R.; Kato, K. Chemical properties of water-soluble pectins in hot- and cold-break tomato pastes. *Food Chem.* **2005**, *93* (3), 409.
- (14) Huber, D. J.; Odonoghue, E. M. Polyuronides in avocado (*Persea americana*) and Tomato (*Lycopersicon esculentum*) fruits exhibit markedly different patterns of molecular downshifts during ripening. *Plant Physiol.* **1993**, *102* (2), 473–480.
- (15) Anthon, G. E.; Barrett, D. M. Combined enzymatic and colorimetric method for determining the uronic acid and methyl content of pectin: Application to tomato products. *Food Chem.* **2008**, *110*, 239–247.
- (16) Diaz, J. V. Physical and chemical changes in pectins during tomato (*Lycopersicon esculentum* M.) paste production. Ph.D. Dissertation, University of California, Davis, California, **2008**.
- (17) Striegel, A. M. Multiple detection in size-exclusion chromatography of macromolecules. *Anal. Chem.* **2005**, *77* (2), 104A–113A.
- (18) DeGennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (19) Diaz, J. V.; Anthon, G. E.; Barrett, D. M. Nonenzymatic degradation of citrus pectin and pectate during prolonged heating: Effects of pH, temperature, and degree of methyl esterification. *J. Agric. Food Chem.* **2007**, *55*, 5131–5136.
- (20) Sharma, S. K.; Liptay, A.; Le Maguer, M. Molecular characterization, physico-chemical and functional properties of tomato fruit pectin. *Food Res. Int.* **1997**, *30* (7), 543–547.
- (21) Wyatt, P. J. Light-scattering and the absolute characterization of macromolecules. *Anal. Chim. Acta* **1993**, *272* (1), 1–40.
- (22) Chou, T. D.; Kokini, J. L. Rheological properties and conformation of tomato paste pectins, citrus and apple pectins. *J. Food Sci.* **1987**, *52* (6), 1658–1664.
- (23) Kokini, J. L.; Chou, T. C. Comparison of the conformation of tomato pectins with apple and citrus pectins. *J. Texture Stud.* **1993**, *24* (2), 117–137.
- (24) Fishman, M. L.; Chau, H. K.; Hoagland, P. D.; Hotchkiss, A. T. Microwave-assisted extraction of lime pectin. *Food Hydrocolloids* **2006**, *20* (8), 1170–1177.
- (25) Fishman, M. L.; Chau, H. K.; Hoagland, P.; Ayyad, K. Characterization of pectin, flash-extracted from orange albedo by microwave heating, under pressure. *Carbohydr. Res.* **2000**, *323* (1–4), 126–138.
- (26) Fox, T. G.; Flory, P. J. Intrinsic viscosity–temperature relationships for polyisobutylene in various solvents. *J. Am. Chem. Soc.* **1951**, *73* (5), 1909–1915.
- (27) Fishman, M. L.; Chau, H. K.; Kolpak, F.; Brady, J. Solvent effects on the molecular properties of pectins. *J. Agric. Food Chem.* **2001**, *49* (9), 4494–4501.
- (28) Renard, C. M. G. C.; Jarvis, M. C. Acetylation and methylation of homogalacturonans 2: Effect on ion-binding properties and conformations. *Carbohydr. Polym.* **1999**, *39* (3), 209–216.
- (29) Gidley, M. J.; Morris, E. R.; Murray, E. J.; Powell, D. A.; Rees, D. A. Evidence for two mechanisms of interchain association in calcium pectate gels. *Int. J. Biol. Macromol.* **1980**, *2* (5), 332–334.
- (30) Morris, E. R.; Gidley, M. J.; Murray, E. J.; Powell, D. A.; Rees, D. A. Characterization of pectin gelation under conditions of low water activity, by circular dichroism, competitive inhibition and mechanical properties. *Int. J. Biol. Macromol.* **1980**, *2* (5), 327–330.

Received April 10, 2009. Revised manuscript received July 24, 2009.
Accepted August 4, 2009.