RHEOLOGICAL BEHAVIOUR OF APRICOT PUREES AND CONCENTRATES

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INTRODUCTION

Because the viscous properties of fruit and vegetable purees vary with the rate of shearing, such purees are classed as non-Newtonian fluids. Non-Newtonian fluids present special problems to the engineer in the design of heat transfer and flow equipment. Furthermore, limited data have been published that adequately describe the viscous properties of these purees, and the factors contributing to them are not well understood.

Variable speed single or concentric cylinder viscometers permit the shear stress to be measured over a wide range of shear rates. When the shear stress minus the yield stress is plotted against the shear rate on logarithmic coordinates a straight line relationship is obtained (2). Such lines can be represented by the power-law expression:

$$\tau - \tau_S = K\gamma^n \qquad (1)$$

where τ = shear stress (dynes/cm^2)
n = flow-behaviour index
K = consistency coefficient (dyne-cm sec^{-2})
γ = rate of shearing (sec^{-1})
τ_S = yield stress (dynes/cm^2)

Charm (4) has reported the presence of a yield stress in apple sauce and tomato puree. However, in the present experiments a consistent measurable yield stress was not found. Equation one, therefore, is simplified to:

$$\tau = K\gamma^n \qquad (2)$$

When $n = 1$ the fluid is Newtonian. When $1 < n < \infty$ the fluid is dilatant and when $0 < n < 1$ the fluid is pseudo-plastic. An extensive treatment of non-Newtonian technology is presented by Metzner (10), Wilkinson (18) and Van Wazer (16).

Some materials exhibit a change in shear stress (τ) with time, even though the rate of shearing is constant. Fluids in which τ decreases with time are known as thixotropic, while those where τ increases with time are dilatant. Apricot puree and concentrate tended to change shear stress with time. In these experiments, this tendency was reduced to a negligible level by operating the spindle at high speed for several seconds before making each series of viscous measurements.

For apricot purees and concentrates Harper (8) has reported consistency coefficients (K) values from 54 to 3000 dyne sec cm^{-2} and flow behaviour index (n) values from 0.29 to 0.37 at 80°F. For apricot puree Saravacos (13) has found $K = 68$ at 86° F and 56 at 180°F, while $n = 0.3$ and 0.27 at 86 and 180°F respectively.

Much of the data (5, 6, 7, 9, 14, 15,

TABLE I. VISCOUS PROPERTIES (K and n) AT 40 AND 77°F AND THE CHEMICAL CONSTITUENTS IN APRICOT PUREES AND CONCENTRATES.

Type of Fruit	40°F		77°F		Soluble Solids %	Total Solids %	Insoluble Solids %	Pectin (mg./gm.)			
	K	n	K	n				Total	Water Soluble	Oxalate Soluble	NaOH Soluble
Reliable Puree											
green	210	.34	60	.42	12.2	15.0	2.8	8.9	5.4	1.8	1.8
ripe	140	.35	90	.46	14.0	15.4	1.4	8.7	5.4	1.8	1.2
ripened	210	.33	110	.32	13.4	15.4	2.0	11.1	7.1	2.5	1.7
over ripe	230	.33	200	.30	16.0	19.0	3.0	11.6	8.5	1.8	1.5
Reliable Concentrate											
green	1700	.25	1400	.22	22.0	27.0	5.1	15.5	9.9	3.3	3.3
ripe	670	.25	540	.22	22.0	24.1	2.2	14.1	9.2	3.2	2.2
ripened	850	.24	710	.26	22.0	25.6	3.3	18.0	11.7	3.7	2.5
over ripe	900	.27	670	.30	22.0	26.0	4.1	15.5	11.4	2.3	2.1
Kaleden Puree											
green	200	.29	160	.29	14.0	17.0	3.0	9.3	6.2	1.2	1.9
ripe	230	.29	150	.27	19.0	23.0	4.2	10.9	7.7	1.6	1.6
ripened	450	.25	310	.31	22.0	24.9	2.9	13.1	8.5	2.7	1.7
Kaleden Concentrate											
green	880	.27	700	.30	22.0	26.8	4.7	14.5	9.4	2.1	2.9
ripe	530	.27	270	.26	22.0	26.8	4.8	13.0	9.9	1.8	1.9
ripened	490	.27	400	.30	22.0	24.9	2.9	13.2	8.5	1.8	2.5
Cell Sap	8.2	.91	5.3	.91	22.0	22.0	-	-	-	-	-

17) respecting the viscosity of juices and purees have been obtained using instruments operating at one rate of shearing. Single point measurements cannot adequately describe non-Newtonian fluids. A comparison of several instruments for determining the viscosity of tomato pastes has been made by Davis *et al* (5). They have reported that the Stormer and efflux tube viscometer measure different viscous properties than the Bostwick and Adams consistometers.

Hand *et al* (7) demonstrated that in tomato juices with uniform gross viscosity and particle size, large differences in cell sap viscosity did not impart any detectable difference in consistency. If few suspended particles were present, the viscosity approached that of water. The fragmentation of the predominently spherical cellular particles by homogenization increased the gross viscosity.

Similar results were reported by Whittenberger *et al* (17). They reported that the viscosity of tomato juice was due to the cell walls. Addition of soluble pectin, citric acid or salts caused a marked reduction in the viscosity. Removal of these substances caused the suspended material to thicken to a semi-gel.

Smit *et al* (15) stated that Pectinol treatment caused poorer consistency, lower serum viscosity and higher rate of settling in tomato juice. However, it was pointed out that consistency is not directly related to the pectin content, and that the suspended particles appeared to play an important role.

Luh *et al* (9) reported that San Marzano tomato paste having a pectin content of 1.53% had a thicker consistency than paste of 3.48% pectin made from Pearson tomatoes. It was concluded that the consistency of tomato pastes may vary because of the quality and quantity of the pectic substances, the consistency of the alcohol insoluble solids and the size and shape of the suspended particles. These authors stated that the role of cellulose depended upon the manner in which the cellulose is combined with pectin and other high weight polymers, thus influencing the condition of the insoluble particles.

Simpson (14) showed that the reduction in the viscosity of strawberry

TABLE II. SIMPLE CORRELATION COEFFICIENTS OF SOLIDS CONTENT AND PECTIN CONTENT OF RELIABLE AND KALEDEN APRICOT PUREES AND CONCENTRATES WITH VALUES OF K MEASURED AT 40 AND 77°F.

	Soluble Solids %	Total Solids %	Insoluble Solids %	Pectin (mg./gm.) Total	Pectin (mg./gm.) Water Soluble	Pectin (mg./gm.) Oxalate Soluble	Pectin (mg./gm.) NaOH Soluble
K at 40°F	0.67	0.72	0.64	0.78	0.70	0.66	0.88
K at 77°F	0.66	0.69	0.59	0.79	0.69	0.67	0.89

$r_{.05} = 0.51$ $r_{.01} = 0.65$

TABLE III. EFFECT OF TEMPERATURE UPON THE VISCOUS PROPERTIES (K and n) FOR APRICOT PUREES AND CONCENTRATES.

LOT	40°F		77°F		120°F		140°F	
	K	n	K	n	K	n	K	n
Reliable Puree (ripe)	130	.37	90	.37	45	.45	38	.46
Reliable Puree (over ripe)	220	.32	200	.31	88	.39	88	.39
Reliable Concentrate (over ripe)	860	.26	670	.30	440	.33	400	.32
Kaleden Concentrate (ripened)	490	.28	403	.33	357	.34	297	.34
Kaleden Cell Sap (ripened)	8.2	.91	5.3	.91	3.2	.80	1.8	.74

TABLE IV. THE EFFECT OF "MILLING" AT 70°F OF RIPENED KALEDEN APRICOT CONCENTRATE UPON THE PARTICLE SIZE, AND VISCOUS PROPERTIES (K and n) AT FOUR TEMPERATURES.

Time of milling	Mean diam. (mm.)	Range of diam. (mm.)	50°F		77°F		97°F		140°F	
			K	n	K	n	K	n	K	n
0 min.	0.181	.021-1.168	490	.26	403	.33	367	.34	297	.34
5 min.	0.172	.021- .589	460	.28	410	.34	375	.34	330	.34
10 min.	0.148	.021- .589	490	.27	450	.25	430	.26	360	.34
20 min.	0.127	.021- .295	580	.27	510	.25	450	.26	380	.34

TABLE V. THE EFFECT OF 100 mg. OF COMMERCIAL PECTIC ENZYMES UPON THE K VALUE AT 77°F OF 15 OUNCES OF RIPENED KALEDEN APRICOT PUREE AFTER HYDROLYSIS FOR PERIODS UP TO 24 HOURS AT 68°F.

Time (hrs.)	Pectin Esterase K @ 77°F	Pectinase K @ 77°F
0	300	300
1.5	370	370
3	400	310
5	-	280
12	310	100
24	220	60

juice with maturity was due not only to the shorter chain length of the pectin, but also to the lesser amount of pectin in the juice. Ezell (6) found that the viscosity of citrus concentrate decreased with fruit maturity.

EXPERIMENTAL METHODS

Viscosity Measurements

A Brookfield model RV viscometer having eight spindle speeds between .5 to 100.0 rpm was used. The use of cylindrical spindles (#2, 3 and 7) permitted the calculation of K values using the equation given by Charm (3):

$$2\pi N = \underset{2}{\frac{n}{2}}\left\{\frac{A}{2\pi\ KLR^2}\right\}^{\frac{1}{n}} \quad ..... (3)$$

N=spindle speed (rps)
K=consistency coefficient
n=flow behaviour index
A=torque (dyne-cm)
L=corrected length of spindle (cm)
R=radius of spindle (cm)

The value of n was established from the slope of the line obtained by plotting torque (A) against spindle speed (N) on log-log graph paper.

A Haake Rotovisco narrow-gap viscometer equipped with spindles MVI (gap width=0.96 mm) and the SVI (gap width 1.45 mm) was also used. With these spindles shearing rates from 3.25 to 1370 sec^{-1} are obtainable. Shear stress can be measured from 15 to 12,500 dyne/cm^2. Calibration factors supplied with the instrument permit ready calculation of τ and γ values. A plot of τ vs. γ on log-log paper allows the values of K and n to be read directly from the graph. A constant temperature (± 0.25°F) water bath was used to control the sample temperature, and measurements were taken at 40, 50, 77, 97, 120 and 140°F.

Preparation of Samples

Reliable and Kaleden apricots were visually graded according to maturity. One lot of green fruit of each variety was storage ripened at 80°F until well colored. All fruit was washed, hand pitted and cooked for 20 minutes at 200°F. The hot pulp was passed through a laboratory pulper-finisher with .045 inch openings. One third of each lot was heated to boiling and filled hot into number 2 enamel cans. The remainder of each lot was concentrated at 128-130°F in a vacuum pan until the soluble solids content reached 22 per cent. The concentrate was heated to 165°F and filled hot into number two enamel cans. All cans were immediately sealed and cooled in running water and stored at 40°F until tested.

The soluble solids content was determined by refractometer at 20°C. The total solids were determined by drying for eleven hours at 115°F under 29 inches of mercury vacuum (1). The insoluble solids were determined by difference. The pectin analyses were performed using the method of Rouse and Atkins (12).

Measurement of shear stress at the rates of shearing available on the two viscometers were taken in duplicate on all samples at 40° and 77°F.

A Waring blender was used to "mill" 600 ml. samples of ripened Kaleden apricot puree at high speed for 5, 10 or 20 minutes. The "milled" samples were deaerated under 28" of mercury vacuum before measuring the viscous properties. Particle size measurements were taken on the original and "milled" samples using the microscopic method of Reeve (11). A Howard cell was used in place of the Sedgewick - Rafter counting chamber. The samples were diluted with 50 volumes of water so that the volume of original sample in each field was 1.98 mm^3. Twenty-nine fields evenly distributed over the entire chamber were counted for each sample.

Two samples of cell sap were obtained from the ripened Kaleden puree by centrifugation at 1000 times gravity in a Servall SS1 super speed angle centrifuge. The volume of cell sap was approximately two thirds the volume of the original sample. Microscopic examination of the cell sap indicated no visible suspended matter.

Four 15 ounce samples of puree from storage ripened Kaleden fruit were treated with 100 mg of either commercial pectinase (polygalacturonase) or pectin esterase. The treated samples were held at 68°F and the rate of hydrolysis was followed by measuring the viscous properties at 0, 0.5, 1.5, 3, 5 12 and 24 hours.

RESULTS AND DISCUSSION

The K and n values at 40° and 77°F for all apricot samples, as well as the results of the chemical analyses, are shown in Table I. Apricot puree and concentrate were both highly pseudoplastic with the concentrates tending to be more pseudoplastic than the purees.

The results of a statistical analyses of the data for apricot purees and concentrates (Table I) are tabulated in Table II. All but one of the parameters studied were correlated at the 99 per cent level with the K values at 40 and 77°F. A multiple regression analyses indicated that the soluble solids, total solids, insoluble solids, total pectin and water soluble pectin together accounted for 94.5 per cent of the variation in K at 40°F and for 91.2 per cent of the variation in K at 77°F.

The purees from green fruit tended to have lower values of K than did the purees from ripened fruit. The green fruit had a lower solids and pectin content. However, the concentrates made from the green fruit purees had higher K values than did the ripe fruit concentrates. This was not unexpected since all the concentrates were finished at 22 per cent soluble solids. Therefore the green fruit purees required the removal of a greater amount of water in order to reach 22 per cent soluble solids. The more water removed, the greater the increase in the solids content.

The change in K and n with temperature is shown in Table III. When the logarithm of K was plotted against the reciprocal of the absolute temperature (°Rankine) an approximately linear relationship was found to exist. In most cases, the puree and concentrate tended to become less pseudoplastic as the temperature increased, whereas the cell sap became more pseudoplastic with increasing temperatures. The viscous properties of the cell sap were more temperature dependent than were the properties of the purees and concentrates. The larger proportion of cell sap in the puree may contribute to the fact that the viscous properties of the purees were more temperature sensitive than were those of the concentrates. However, it is not clear how the small value of K of the cell sap could contribute greatly to the much larger change in K with temperature that occurred in the puree.

The results obtained from the "milled" samples are shown in Table IV. The decrease in particle size in general results in an increase in the value of K although it does not appear to have influenced the pseudoplasticity.

The relatively small change in K with particle size would indicate that the particle size had a limited role in establishing the value of K.

The changes in K due to enzymatic degradation of pectin substances are tabulated in Table V. Both enzymes first caused an increase in the value of K, presumably due to the release of pectic substances from the suspended particles. After 12 hours both enzymes caused a reduction in K. The pectinase caused the greatest reduction, because the pectinase presumably reduced the molecular weight of the pectic substances by splitting the molecules into shorter chains. However, the extent of the reduction in K was greater than would be expected in view of the apparently limited influence of the pectin concentration upon K (as noted in Table I).

SUMMARY

Apricot purees have a pseudoplastic non-Newtonian behaviour which agrees well with the power-law model. The fluid-consistency coefficient was found to decrease substantially and in a linear fashion with increase in temperature. The fluid-consistency coefficient also increased as particle size was reduced by "milling," and decreased when the pectic materials were enzymatically degraded. Viscous properties were significantly correlated with total, soluble, and insoluble solids and with various pectin fractions. Together these chemical constituents accounted for over 90% of the variation in the viscous properties. Further study is required to clarify the fundamental interrelationships contributing to the viscous properties of fruit purees.

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