Rheological characteristics of commercial tomato concentrate and corresponding ketchup

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ABSTRACT

Several studies have investigated effects of homogenization and thermal processing of tomato concentrate. Many of these works are based on pilot plant studies regarding both the processing and the composition of the concentrate. This study focuses on rheological characterization of commercial tomato concentrate (paste) and ketchup from real industrial manufacturing.

From a physical point of view, ketchup is two-phase system in which solid particles of tomato concentrate and added spices are dispersed in a colloidal continuous phase. The colloidal phase consists of sugars, salts, organic acids, a fraction of soluble pectin, and other compounds of extract dissolved in water. Industrial challenges when producing this product, are to have adequate knowledge feasible methods to characterize and properties of one concentrate to predict properties of its corresponding ketchup.

This study use modern rheological equipment measurement in order to investigate and get hold of some of the mentioned challenges. Since the texture of the tomato ketchup is a major quality component for consumer acceptance, the focuses results in this study on measurements of consistency and viscosity. Consistency and viscosity of ketchups are also main attributes from a technologically point of view, during production and storage to determine stability and quality control in general.

INTRODUCTION

Traditional devices used for quality control of tomato products are the Bostwick consistometer and the Brookfield viscometer. The former is an empirical measurement of the distance that a specific volume of fluid can flow under its own weight in a known interval of time.

This device provides a single point measurement and is thus not suitable for concentrated products. The Brookfield viscometer requires a discrete number of measurements at different velocities to determine the complete apparent flow curve. The measurements involve a non-welldefined shear rate profile throughout the fluid tested, which makes it difficult to measure non-Newtonian fluids. However, despite these problems, both methods are extensively used by the food industry¹.

Another measurement system often used by the industry, is based on the serum viscosity of the product. The measurements are determined by a capillary viscometer (Ostwald). Such a viscometer can be divided into three groups according to how it works; gravitational forces, hydrostatic forces or by a pressurized gas / piston movement².

This study uses a rheometer instrument equipped with a bob/cup system, having accurate control with shear rate, to investigate and characterize viscosity and

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viscoelasticity in tomato paste and its corresponding ketchup.

A Flow diagram for tomato paste production is given in Fig. 1. The proximate gross chemical composition of tomato and some products are given in Table1.



Figure 1. Flow diagram for tomato paste/concentrate production³.

Table 1. Approximate composition of tomato and some products in $\%^4$

Constituent	Tomato	Ketchup ⁵	Juice
Moisture	92.57±1.32	71.43±0.6	93.6±1.05
Protein	1.2±0.09	3.0±0.25	0.8±0.1
Fat	0.22±0.01	0.5±0.02	0.23±0.10
Ash	1.28±0.03	1.4±0.01	1.1±0.1
Carbohydrate	4.5±0.2	22.7±0.3	4.3±0.2

Ketchup is a vegetable sauce produced from tomato concentrate normally named paste⁵. Tomato paste is the product resulting from the concentration of tomato pulp, after the removal of skins and seeds. It contains 24% or more natural tomato soluble solids. When producing ketchup, this paste is added sugar, vinegar, salt, and different spices⁶. From a physical point of view, ketchup is two-phase system in which solid particles of tomato concentrate and added spices are dispersed in a colloidal continuous phase. The continuous phase consists of sugars, salts, organic acids, a fraction of soluble pectins, and other compounds of extract dissolved in water.

Regarding commercial production of Ketchup high pressure homogenization is commonly used followed by some sort of thermal processing. The effect on the microstructure of the tomato products is however poorly documented⁷.

Viscosity of the continuous phase is mostly affected by thickening substances, especially polysaccharide hydrocolloids used to produce the ketchup. Ketchup is a non-Newtonian, shear-thinning fluid, with a yield stress. It also shows thixotropic- and viscoelastic properties⁸.

The objectives with this study were as follows:

- Characterize different commercial tomato pastes and their ketchups regarding rheological behavior and particle size measurements after traditional factory processing.
- Investigate the feasibility of a rotational rheometer instrument equipped with a bob/cup system to study texture characteristics in the colloid tomato systems⁹.
- Investigate the feasibility of laser diffraction particle size measurement using equipment from Malvern Instruments to characterize and distinguish between fine particles and larger flocculated or coalesced particles in paste and ketchup.

MATERIALS AND METHODS

Tomato paste (concentrate) and ketchup The compositions of tomato paste

and ketchup are shown in Table 2.

Table 2. Approximate composition (% ww) of tomato paste and ketchup tested.

Constituent	Paste	Ketchup
Moisture	66.8	75.3
Protein	5.0	1.7
Fat	0.3	0
Ash	3.4	2.0
Carbohydrate	24.5	21.0

Instrumental analysis and experimental setup

A Physica MCR301 rheometer (Paar Physica, Anton Paar, Stuttgart, Germany, 2010) fitted with a CC27 bob/ cup system was used. The viscosity of the tomato products was measured by rotational viscometry. Rotational shear rate sweeps from 1 1/s to 500 1/s were recorded at +4 °C. Temperature-sweeps from +10 °C to +25 °C were recorded at a shear rate of 100 1/s.

Oscillatory amplitude sweeps were performed at angular frequency of 10 rad/s and with strain varying from 0.01 to 100% to determine the limit of the linear viscoelastic range (LVR). Measurements were performed both at +10 and +25°C.

A Malvern Mastersizer 3000 (S.nr. MAL1083189, Malvern, UK, 2013) fitted with a Hydro LV dispersion unit, was used regarding measuring particle sizes in the different tomato products investigated. The sample was dispersed in Millipore distilled water during measurement with the laser diffraction particle size measurement instrument. Experimental set-up for the tomato products; Refractive Index (RI) 1.461, Absorption Index 0.003, spherical model for particles.



Figure 2. Tomato samples measured by rotational viscometry using a Physica MCR 301 rheometer with a CC27 bob/cup measuring geometry.

Statistical analysis

The results were analyzed by Minitab 16. One-way (unstacked) ANOVA with confidence level 95% was used, added with grouping according to the method of Tukey with a family error rate of 5%.





RESULTS

Typical results from the viscoelastic characterization with the Paar Physica rheometer for different tomato pastes (G, M, O) and different batches from each paste, are shown in Table 3, 4 and 5. All tables are giving the values at both at 10 °C and 25 °C. Samples that do not share a grouping letter are significantly different.

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Table 3. LVR Strain limit results of 3					
different tomato pastes (G, M, O) at 10 and					
25	25 °C. N = number of samples.				
Sample	Ν	Mean	Grouping		
0_10	32	0.057672	А		
G_10	11	0.057088	AB		
G_25	11	0.050851	ABC		
0_25	32	0.049311	BC		
M_10	6	0.041613	CD		
M_25	6	0.037932	D		

The results from the flow measurements were modelled with the power law model. The resulting consistency index and fluid behavior index are shown in Table 6 and 7, here also at temperatures of 10 °C and 25 °C.

Table 4. LVR Stress limit results of 3 different tomato pastes (G, M, O) at 10 and

25 °C.				
Sample	Ν	Mean	Grouping	
0_10	32	16.99	A	
0_25	32	12.33	В	
M_10	6	11.451	AB	
G_10	11	10.383	В	
M_25	6	8.517	В	
G_25	11	7.94	В	

Table 5. LVR Storage Modulus (G') results for 3 different tomato pastes (G, M, O) at 10 and 25 $^{\circ}$ C

		and 23 C.	
	Ν	Mean	Grouping
0_10	32	27043	A
M_10	6	25572	AB
0_25	32	23436	AB
M_25	6	20728	ABC
G_10	11	16975	BC
G_25	11	14737	С

Table 6. Mean Consistency Index results for 3 different tomato pastes (G, M, O) and different batches (G1, G2, G3 etc.) at 10 and 25°C.

Sample	Ν	Mean	Grouping
06_10	3	776.63	А
02_10	5	749.91	А
M1_10	4	700.97	AB
06_25	2	660.17	ABCDE
02_25	6	633.13	ABC
01_10	11	624.18	BC
M1_25	3	557.14	BCDEF
01_25	14	502.21	ΕF
05_10	6	489.78	DEFG
M2_10	1	456.02	CDEFGH
05_25	6	417.36	FGH
04_10	3	413.53	FGH
03_10	8	372.21	Н
M2_25	1	364.3	FGH
G1_10	5	348.94	Н
G3_10	3	348.69	GH
04_25	3	334.2	Н
G2_10	4	332.41	Н
03_25	6	319.29	Н
G1_25	5	298.89	Н
G2_25	3	296.29	Н
G3_25	4	295.49	Н

Table 7. Mean flow behaviour index results
for 3 different tomato pastes (G, M, O) and
different batches (G1, G2, G3 etc.) at 10 and
25°C.

Sample	Ν	Mean	Grouping

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M2_10	1	0.220	ABCD
M2_25	1	0.219	ABCDEFGHIJ
04_25	3	0.215	A
04_10	3	0.206	A
05_10	6	0.192	ABCD
05_25	6	0.189	ABCD
M1_25	3	0.186	ABCDEFGHIJK
M1_10	4	0.169	ABCDEFGHIJKL
G2_10	4	0.154	D IJKLM
01_25	14	0.151	H JKLM
G2_25	3	0.148	CD GHIJKLMN
G3_10	3	0.147	BCD FGHIJKLMN
G3_25	4	0.146	EFGHIJKLMN
G1_10	5	0.146	KLMN
03_10	8	0.145	KLMN
G1_25	5	0.143	KLMN
03_25	6	0.133	LMN
06_25	2	0.130	KLMN
02_25	6	0.123	MN
01_10	11	0.121	N
06_10	3	0.119	KLMN
02_10	5	0.116	MN

Fig. 5 shows the particle size distribution in the different tomato samples measured. The results are all obtained from the Malvern Mastersizer 3000 measurements by adding some droplets of the tested diluted paste samples (6 °Brix) into a known volume of distilled water free of air.



Figure 5. Size distribution of particles in the different diluted tomato pastes measured by the Malvern Mastersizer 3000.

Regarding the Dx values expressed in Fig. 6; Dx10 – the size of particle below which 10% of the sample lies. Dx50 – the size in microns at which 50% of the sample is smaller and 50% is larger. This value is also known as the Mass Median Diameter (MMD), or the median of the volume distribution. Dx90 – the size of particle below which 90% of the sample lies.



Figure 6. Groups of particle sizes expressed in the different diluted tomato pastes measured, expressed as Dx values (µm).



Figure 7. Ketchup consistency index versus consistency index of paste (Pa sⁿ).

Fig. 7 illustrates an attempt to characterize a property of one paste with the same property in the corresponding ketchup. The consistency index was selected to illustrate that property in Fig. 7.

DISCUSSION

Tables 1-7 sum up all measurements for each of the three different tomato feedstocks (O, M, G). It is thus the average values for different rheological parameters that are reported in the tables.

By observing the results in the different tables 1-7 it appears that;

- Regarding LVR Strain results Table 3 ;
 - There seems to be effect of temperature on tomato paste O.
 - There seems to be effect of type of tomato paste G, M or O.
- Regarding LVR Stress results Table 4;
 - There seems to be effect of temperature on tomato paste O.
- Regarding LVR Elasticity (G') results Table 5;
 - No effect of temperature is seen on the 3 different pastes.

- No effect of the type of tomato raw material is observed.
- Regarding mean consistency index Table 6;
 - The consistency index varied in the range 295 776 Pa sⁿ for the pastes. At 10 °C it varied in the range 332-776 Pa sⁿ and at 25 °C between 295 660 Pa sⁿ. A decrease in the consistency index was observed with increasing temperature, indicating a decrease in viscosity at higher temperatures. Similar results are reported for ketchup¹⁰.
- Regarding flow behavior index Table 7;
 - \circ The flow behavior index varied less at different temperatures compared with the consistency index. At 10 °C the flow behavior index varied in the range 0.116 – 0.220 and at 25 °C between 0.219 – 0.123.
 - In some cases the flow behavior index of the different pastes showed a decreasing trend with temperature. Similar results are reported for ketchup¹¹.

Looking at the size distribution of the particles of diluted tomato pastes, one observe from Fig. 5 the same approximate size distribution either the raw material has been frozen at -20 °C or not. Considered grouping of particles of tomato paste as shown in Fig. 6, it appears that there are differences between the feedstock O and G.

This is also as expected since it can be differences between the feedstocks, depending on where in the world the tomatoes are produced, type of tomatoes, climate etc.

Regarding Fig. 7 one observe a clear correlation between the viscosity of tomato raw material (paste G, M, O) and the

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corresponding ketchup. This is also as expected since from a physical point of view, ketchup is two-phase system, in which solid particles of tomato concentrate and added spices are dispersed in a colloidal continuous phase. Both paste and ketchup are also shear thinning with n having values between 0.1 and 0.2.

In colloids like ketchup, several types of instability can occur; like flocculation, coalescence, aggregation and disruption. These processes often take place simultaneously. To prevent the phases from separating, ketchup is of course homogenized.

CONCLUSIONS

Using a rheometer to characterize different tomato products, the conclusions from this study can be summarized as follows:

- All pastes and ketchups were shear thinning with n between 0.1 and 0.2.
- The consistency index of the paste was approximately eight times larger than for the ketchup.
- No large differences on LVR strain were observed. Some effects of temperature and type were observed.
- Some effects of temperature were observed regarding LVR stress.
- No effects of temperature and type were observed for LVR elasticity.
- A clear correlation between the viscosity of the tomato raw material and the corresponding ketchup was observed. A high viscosity paste gave a high viscosity ketchup.

Based on the laser diffraction particle size measurements, the conclusions can be summarized like:

- No large differences were observed between the pastes tested.
- Freezing did not give large effects on the size distributions.

REFERENCES

1. Bayoda, E., Willers, E.P. and Tornberg, E. (2008) "Rheological and structural characterization of tomato paste and its influence on the quality of ketchup". LWT -Food Science and Technology 41:1289– 1300.

2. Barret, D. M., Garcia, E., & Wayne, J.E. (1998) "Textural Modification of Processing Tomatoes". Critical Reviews in Food Science and Nutrition, 38 (3): 173-258.

3. Moresi, M. and Liverotti, C., (1982) "Economic study of tomato paste production", *J. Food Technology*, **17:** 177– 192.

4. Kamil, M.M., Mohamed, F.G., and Shaheen, M.S. (2011) "Fourier Transformer Infrared Spectroscopy for Quality Assurance of Tomato Products". *Journal of American Science* 7 (6): 559-572.

5. Hayes, W.A., Smith, P.G. and Morris, A.E. (1998) "The Production and Quality of Tomato Concentrates". *Critical Reviews in Food Science and Nutrition*, 38(7):537–564

6. CFR - Code of Federal Regulations "Definition of ketchup" Title 21, Revised as of April 1, 2015

7. Colle, I., van Buggenhout, S., van Loey, A. and Hendricks, M. (2010) «High pressure homogenization followed by thermal processing of tomato pulp:

Influence on microstructure and lycopene in vitro bioaccessibility", *Food Research International* 43: 2193–2200

8. Juszczak, L., Oczadly, Z., and Galkowska, D. (2013) "Effect of modified starches on rheological properties of ketchup", *Food Bioprocess Technol* 6:1251–1260.

9. Kontogeorgis, G.M. and Kiil, S. (2016) "Introduction to applied colloid and surface E.-O. Rukke et al.

chemistry", John Wiley & Sons, ISBN 9781118881187, p 195.

10. Koocheki, A., Ghandi, A., Razavi, S.M.A., Mortazavi, S.A. and Vasiljevic, T. (2009) "The rheological properties of ketchup as a function of different hydrocolloids and temperature", *Int. Journal of Food Science and Technology*, 44, 596-602.

11. Sharoba, A.M., Senge, B., El-Mansy, H.A., Bahlol, H. and Blochwitz, R. (2005) "Chemical, sensory and rheological properties of some commercial German and Egyptian tomato ketchups", *European Food Research and Technology*, 220, 142-151.