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ANALYSIS OF THE RHEOLOGICAL PROPERTIES OF KETCHUP ACCORDING TO DIFFERENT HYDROCOLLOIDS AND TEMPERATURE

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Abstract

The present paper presents the analysis of the effect of temperature on the rheological properties of house made ketchup with different content of thickening agents. The viscosity data showed that all the samples under examination were non-Newtonian fluids, which was indicative by the pseudo-plastic (shear thinning) nature of tomato ketchup.

The results of this study showed that ketchup supplemented with hydrocolloids (xanthan, guar, CMC) behaves as a non-Newtonian thinning liquid, in the temperature range of 30-60°C. Increased gum concentration increased the apparent viscosity compared to control; however, the effect of xanthan gum on viscosity was greater than that of guar and CMC gums.

Key words: Ketchup, rheology, temperature, hydrocolloids

INTRODUCTION

Tomato is one of the most important vegetable products mainly marketed in a processed form i.e. pastes, concentrates or ketchup (Mazaheri Tehrani and Ghandi, 2007). Ketchup is a vegetable sauce produced from tomato concentrate and sugar, vinegar, salt, and different spices. Poland is the third largest market of consumption of ketchup in Europe, after Germany and Great Britain (Ochmańska, 2006).

Ketchup is a descriptive term for a number of different products, which consist of various pulps, strained and seasoned fruits; the variety made from tomatoes being the most popular condiment. Tomato ketchup is a heterogeneous, spiced product, produced basically from either cold or hot extracted tomatoes; or directly from concentrates, purees or tomato paste (Sahin and Ozdemir, 2004).

Knowledge of the rheological properties of fluid and semisolid foodstuffs is important in the design of flow processes in the quality control, storage and the processing stability, and in understanding and designing texture (Vercet et al., 2002; Mazaheri Tehrani and Ghandi, 2007, Hilma E., 2018). Viscosity of the continuous phase is mostly affected by thickening substances, especially polysaccharide hydrocolloids used to produce a ketchup (Gujral et al. 2002; Sahin and Özdemir 2004; Koocheki et al. 2009). Ketchup is non-Netwonian, shear-thinning fluid, with yield stress. It also shows thixotropy and viscoelastic properties (Bottliglieri et al. 1991; Varela et al. 2003; Sahin and Özdemir 2004; Sharoba et al. 2005; Koocheki et al. 2009). The viscosity of tomato ketchup is a major quality component for consumer acceptance.

Usually viscosity is considered an important physical property related to the quality of food products. Therefore, reliable and accurate rheological data are necessary for designing and optimization of various food processing equipment such as pumps, piping, heat exchangers, evaporators, sterilises, filters and mixers (Crandall and Nelson, 1975; Tanglertpaibul & Rao, 1987; Stoforos & Reid, 1992; Vercet et al., 2002).

Rheological properties of ketchup depend not only on the amount of tomato paste used and its rheological characteristics but also on the kind and amount of added thickening substances. Hydrocolloids are water-soluble, high molecular weight polysaccharides that serve a variety of functions in food systems including enhancing viscosity, creating gel-structures, film formation, control of crystallization, inhibition of syneresis, improving texture, encapsulation of flavours and lengthening the physical stability (Dziezak, 1991; Glicksman, 1991; Garti and Reichman, 1993; Dickinson, 2003). Generally, gums and stabilisers have non-Newtonian rheology and they impart non-Newtonian character to the emulsions even when the amount of the dispersed phase is low (Ford et al., 1997). For consumers' acceptability, the long-term stability of sauces is also very important. Thus, hydrocolloids are widely used in the food industry.

The most often used thickening agents are polysaccharide hydrocolloids such as: guar gum, xanthan, tragacanth, pectins, and sodium alginate (Gujral et al. 2002; Varela et al. 2003; Sahin and Özdemir 2007; Koocheki et al. 2009). These substances essentially improve sensory and rheological properties of ketchup. Guar and xanthan gums and their mixtures are found to be the most successful in decreasing serum separation of tomato ketchups (Varela et al. 2003; Sahin and Özdemir 2007).

MATERIAL AND METHOD

The present paper presents the analysis of the effect of temperature on the rheological properties of house ketchup with different content of thickening agents. The objectives I have pursued in this paper were: to establish the influence of the thickening agent on the viscosity; analysis of the ketchup viscosity variation as a function of temperature; analyzing the variation of ketchup density as a function of temperature; pH determination; ketchup stability analysis. The vegetable material used was the ketchup made in the house. The ingredients used for the preparation of homemade ketchup can be found in table 1.

Table .	1
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Raw materials	MU	Raw quantity
Tomatoes	g	1000
Sugar	g	75
Salt	g	10
Vinnegar	ml	25
Onion	g	50
Garlic	g	5
Cinnamon	g	5
Black pepper	g	0.15
Sodium benzoate	g	0.25
Hidrocolloids ¹	g	

Ingredients used to make homemade ketchup

Healthy and ripe tomatoes were purchased from the local market, sorted by color, size and lacking in bruises/green spots. The tomato pulp was placed in a laboratory vessel. The spices (cinnamon, black pepper) were wrapped in a cloth and dipped in tomato paste. The onion and garlic were added directly over the tomato pulp.

The mixture was then heated to a moderate temperature and stirred constantly until it reached a temperature of between $75^{\circ}C$ and $80^{\circ}C$, at which time vinegar and salt were added. Finally, sodium benzoate was added as a preservative. Hydrocolloids were then added to each 100 g of ketchup at different levels and stirred for 2 minutes. The final level of each hydrocolloid by weight in the ketchup samples was 0.5%, 0.75% and 1%. Each sample was immediately poured into glass containers and then stored at ambient temperature ($20^{\circ}C - 22^{\circ}C$) for 24 hours before analysis.

The physical properties of ketchup were evaluated after the addition of three commonly used food thickening agents: guar, xanthan and CMC of different concentrations (0.5%, 0.75% and 1%) and four temperatures (30, 40, 50 and 60°C). Ketchup without supplements served as a control.For physical determinations, I prepared 10 samples as follows: ketchup with 0.5% (2.89 g) guar gum, ketchup with 0.75% (4.33 g) guar gum, ketchup with 0.5% xanthan gum, ketchup with 0.75% xanthan gum, 1% ketchup 1% xanthan gum, ketchup with 0.5% CMC, ketchup with 0.75% CMC, ketchup with 1% CMC gum.

Different concentrations of gums were added to the samples. These were stirred continuously until boiling. Upon completion, the samples were poured into glass jars, and then stored at ambient temperature $(20 - 22^{\circ}C)$

¹ Gums are added to concentrations of 0 ,5%, 0,75% ans 1%.

for 24 hours before analysis. The hydrocolloid-free sample was considered as a control.

In order to achieve the objectives, taking into account the physical properties of the analyzed product, I made the following determinations: pH determination; density determination; viscosity determination and stability of the samples. The pH determination was performed using the Inolab WTW pH meter, pH 720. The viscosity analysis was performed after one day storage at ambient temperature using the Brookfield viscometer. In the preparation of ketchup I used a hand mixer with 7 steps, power 250 W, Hausberg brand.

RESULTS AND DISCUSSION

The rheological assessments of ketchup were made after one day storage at ambient temperature. Thickening agents: guar, xanthan and CMC were added in ketchup at different concentrations (0.5%, 0.75% and 1%).

The prepared samples were allowed to equilibrate for 10 minutes at the desired temperature (30, 40, 50 and 60°C), after which they were used in the determinations listed above.

The first determination consisted of measuring the ketchup viscosity as a function of temperature.



Fig. 1. Variation of ketchup viscosity as a function of temperature with thickening agents 0.5%

The ketchup viscosity in which 0.5% Xanthan gum was added depends on both the measurement temperature and the dissolution temperature of the gum. The viscosity decreases with increasing temperature. This behavior is completely reversible between 30 and 60°C. Although the viscosity decreases, the dissolution temperature increases up to 40°C. Between 40 and 50°C, the viscosity increases with a higher temperature.

At temperatures above 50°C, the viscosity decreases with increasing temperature. This unique behavior is associated with the conformational changes (the ordering-disturbance transition) of the xanthan molecule.

The highest viscosity was recorded at 60° C, by the addition of 0.5% CMC - a more active thickening agent, CMC is a ionic polymer and forms

complexes with the soluble proteins in tomatoes, which increases the product's viscosity.

The following samples analyzed were those with the addition of 0.75% concentration thickening agents.



Fig. 2. Variation of ketchup viscosity as a function of temperature with thickening agents 0.75%

The control sample recorded, with increasing temperature, the lowest viscosity compared to the samples with thickening agents, so the values increased for all samples containing hydrocolloids compared to the control. Therefore, the control had the lowest temperature dependence and the ketchup containing 0.75% CMC the highest, at 40°C.

The addition of 0.75% **Guar gum** resulted in a significant increase in the apparent viscosity of tomato ketchup. When adding **Xanthan** gum 0.75% the consistency of the ketchup fluctuates, the highest being at 50°C, 308 cP. At temperatures above 50°C, the viscosity decreases with increasing temperature. This unique behavior is associated with the conformational changes (the ordering-disturbance transition) of the xanthan molecule.

The last samples were analyzed with the addition of 1% concentration thickening agents.



Fig. 3. Variation of ketchup viscosity as a function of temperature with thickening agents 1%

An increase in the viscosity of the samples with respect to the control was observed in fig.3, as the temperature increased, which indicates that the 1% ketchup samples have higher pseudo-plasticity at high temperatures. The viscosity of the sample with xanthan and guar 1% compared to the control sample was statistically more significant at P <0.05. This was

mainly due to the addition of guar gum and xanthan which, in turn, increases the ketchup's consistency and viscosity. The viscosity was highest for the xanthan 1% sample.

The viscosity data showed that all the samples under examination were non-Newtonian fluids, which was indicated by the pseudo-plastic (shear thinning) nature of tomato ketchup. The addition of different levels of gum has led to a significant increase in the apparent viscosity of the tomato ketchup. The viscosities of the samples increase in proportion to the increase of the gum concentration.

The results of this study showed that ketchup supplemented with hydrocolloids (xanthan, guar, CMC) behaves as a non-Newtonian thinning liquid, in the temperature range of 30-60°C.

Increased gum concentration also increased the apparent viscosity compared to the control; however, the effect of xanthan gum on viscosity was greater than that of guar and CMC gums.

Consistency increased with the concentration of the three hydrocolloids, indicating that the addition of these gums stabilizes the consistency of the ketchup. The activation energy is generally found to decrease with the use of the gum substitute compared to the control sample. Ketchup containing 1% CMC had the lowest temperature dependence which means it had the greatest stabilizing effect on ketchup.

The **ketchup pH** variation according to temperature differs from sample to sample, but it ranges between 4-6, low acid ketchup. pH is a very important factor that influences the quality of tomato ketchup, so the pH values varied: between 4.71-4.74 for the CMC sample of different concentrations; between 4.65-4.73 for the xanthan sample; between 4.6-4.86 for guar sample; between 4.65-4.82 for control.

The density of ketchup at different temperatures does not have major discrepancies between values. The sample with the addition of 0.5% CMC gum recorded a value close to the ideal value of the ketchup of $\rho = 1.092$ g/cm³. The xanthan gum sample 0.5% has lower values than the rest of the samples, both at low and high temperatures, as the ketchup has expanded, the volume has increased, and therefore the density has decreased.

All samples were stable, they did not show separation of the visual phase after 7 days. Consistency indices increased with the concentration of all three hydrocolloids, indicating that the addition of these gums stabilizes the ketchup's consistency.

CONCLUSIONS

The viscosity data showed that all the samples under examination were non-Newtonian fluids, which was indicated by the pseudo-plastic (shear thinning) nature of tomato ketchup. The addition of different levels of gum has led to a significant increase in the apparent viscosity of tomato ketchup. The viscosities of the samples increase proportionally with the increase of the gum concentration.

The viscosity of xanthan solutions depends on both the measurement temperature and the dissolution temperature. The viscosity decreases with increasing temperature. This behavior is completely reversible between 30 and 60°C. Although the viscosity decreases, the dissolution temperature increases to 40°C. Between 40 and 50°C, the viscosity increases with increasing temperature. At temperatures above 60°C, the viscosity decreases with increasing temperature. This unique behavior is associated with the conformational changes (the ordering-disturbance transition) of the xanthan molecule. The viscosity of xanthan solutions is independent of pH changes.

The samples with guar gum have pseudo-plastic or thin behavior. The degree of weight-plasticity of guar solutions increases with the concentration and the molecular weight. Guar gum provides the thickening and increase of viscosity in aqueous solutions due to the large hydrodynamic volume and the specific intermolecular nature. The viscosities of the guar gum samples increase proportionally with the increase of guar gum concentration.

CMC is an ionic polymer and forms complexes with food-soluble proteins, which results in increased product viscosity. Protein complexes are stable at low pH (3-5.5) and at high temperatures. The results of this study showed that ketchup supplemented with hydrocolloids (xanthan, guar, CMC) behaves as a non-Newtonian thinning liquid, in the temperature range of 30-60°C.

Increased gum concentration also increased the apparent viscosity compared to the control; however, the effect of xanthan gum on viscosity was greater than that of guar and CMC gums. Consistency increased with the concentration of the three hydrocolloids, indicating that the addition of these gums stabilizes the consistency of the ketchup.

The activation energy is generally found to decrease with the use of the gum substitute compared to the control sample. Ketchup containing 1% CMC had the lowest temperature dependence which means it had the greatest stabilizing effect on ketchup. pH does not change significantly, at the addition of thickening agents, therefore neither the preservability nor the nutritional quality of the product is affected.

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