Effect of hydrocolloids addition on rheological properties, and sensory quality of tomato ketchup during storage

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ABSTRACT

The effect of two different hydrocolloids on rheological properties and sensory quality of tomato ketchup during storage was studied. The starch was add to tomato ketchup at level of 0 ,1 ,2 and 3% while pectin was add at level 0.5 and 1%. Tomato ketchup was stored at room temperature for six months.

The rheological behavior of tomato ketchup samples contained different ratios of hydrocolloids were measured in shear rate range 0.0 to 100 s^{-1} and studied at a wide range of temperatures (5 - 75 °C) using a Brookfield Digital Viscometer. The results indicated that these tomato ketchups behave as non-Newtonian fluids (pseudoplastic) and have a definite yield stress. Higher significant correlation was found between the viscosity and temperature. The viscosity decreased with increasing in the temperature. All hydrocolloids increased consistency of tomato ketchup. With increasing storage period, viscosity of tomato ketchup decreased. The water separation as important sensory attribute decreased with the addition level of hydrocolloid and increased with increasing storage duration. The effect of temperature on their viscosity can be described by means of an Arrhenius-type equation. The activation energy for viscous flow depends on the chemical composition; the activation energy decreased with increasing hydrocolloids addition. Sensory tests for tomato ketchups were done during storage and the results indicated that the hydrocolloid addition improved the quality of tomato ketchup in zero time and during storage period.

Keywords Tomato ketchup. Hydrocolloids. Chemical composition. Starch and pectin addition. Water separation. Rheological parameters. Sensory evaluation. Ketchup storage.

INTRODUCTION

Of all vegetables, tomato is both qualitatively and quantitatively an important component of the Mediterranean diet, whether consumed raw or as processed tomato products (juice, tomato paste and tomato sauces). Tomatoes are regarded as the most important source of the carotenoid, lycopene, and a tomato-rich diet is reported to provide protection against some types of cancer and cardiovascular diseases (Sesso *et al.*, 2004; Walfisch *et al.*, 2007 and Willcox *et al.*, 2003). However, the healthy effects attributed to tomato consumption might not be limited to lycopene content alone (Jacob *et al.*, 2008).

The consistency of tomato products depends on the amount of suspended particles (pulp) in a dispersing medium and is directly related to the tomato fruit constituents such as pectin. Other factors such as enzymatic degradations, pulp network, homogenization process and concentration also play an important role in determining the consistency of tomato products (Valencia *et al.,* 2003 and Vercet *et al.*, 2002).

Technological characteristics, such as chemical composition, rheological properties, physical properties and sensory properties play an important role in the formation of the processing steps, which are necessary for the production of tomato ketchup. Ketchup is a descriptive term for a number of different products, which consist of the pulp, strained and seasoned, of various fruits; the variety made from tomatoes being the most popular condiment. Good ketchup is judged by flavor, consistency, uniformity and attractiveness of color. Tomato ketchup is a clean, sound product made from properly prepared strained tomatoes with spices, salt, sugar and vinegar with or without starch, onion and garlic and contains not less than 12 per cent of tomato solids. It is the most important product of tomato and is consumed extensively. A major part of the tomato processed is used for making ketchup compared to other tomato products (Gupta, 1998). Many newly developed tomato products with or without other vegetable juices are now appearing on the market, and among these new products with 'high service content' tomato ketchup has been probably the first to meet with the consumer favour and it still represents a large share of the market, Porretta and Birzi (1995). Even though ketchup is known worldwide, information on this product in technical/scientific literature is limited, Porretta (1991). Commercial ketchup can have an extremely variable composition; nearly every manufacturer has a formula of his own which differs in some respects from those of other manufacturers. These differences are mainly in the quantity, number and amount of spices or other flavoring agents used. Thus, it is difficult to establish the analytical parameters on which quality depends. Viscosity is usually considered an important physical property related to the quality of food products. Viscometric data are also essential for the design evaluation of food processing equipment such as pumps, piping, heat exchangers, evaporators, sterilizes filters and mixtures. Many foods of commercial importance, such as tomato paste and tomato ketchup are concentrated dispersions of insoluble matter in aqueous media. Their rehological behavior, especially the yield point, is important in the handling, storage, processing and transport of concentrated suspensions in industry, Rao (1987). The viscosity of fluid foods is an important parameter of their texture. It determines to a great extent the overall mouth-feel and influences the intensity of flavor, Thomas, *et al*. (1995). Therefore, for many years, the viscosity of liquid and semi solid foods has been of interest to researchers and industrialists. Correlation between sensory and instrumental values of texture parameters can be used for industrial quality control to keep the sensory viscosity within a range assuring good consumer acceptance Szczeniak (1987) and Houska, *et al*. (1998). A complete outline of the physicochemical and sensory characterization of ketchup has been reported previously Porretta, *et al*. (1989). The yield point values of ketchup were correlated with pectin content Rani and Banins (1987). Ketchups are time-independent, non-Newtonian fluids that show a small thixotropy, Bottiglieri, *et al*. (1991). The different brands examined differed essentially only in viscosity and yield point values. The quality of ketchup is strongly dependent on its preservation. The most typical use of ketchup is in 'fast-food' restaurants where it is normally stored at room temperature after the opening of the container, the classic black ring which forms in the bottle neck is a definite sign of the result of a Maillard-type degradation which implies other important quality changes Porretta and Birzi (1995). All the test models discussed so far involve subjecting the foodstuff to a step change in share rate ($\dot{\gamma}$) or share stress (τ) and measuring the stress as s function of time. A useful procedure in the study of food rheology is to subject.

The viscosity of tomato ketchup is a major quality component for consumer acceptance. Several parameters contribute to the flow behavior of tomato ketchup, including the quality of the raw material and the processing conditions (Bayoda *et al*., 2008). Tomato ketchup is a heterogenous suspension product, controlling of the phase separation in tomato ketchup is of a major commercial importance due to a high or low degree of serum separation during storage (Gujral, *et al.,* 2002; Stoforos and Reid, 1990).

Sidhu *et al*. (1997) indicated that the consistency of tomato ketchup can be improved by adding polysaccharides such as gums and Gujral *et al.* (2002) reported that hydrocolloids increased the viscosity and reduced the serum loss of tomato ketchups. Also, Sahin and Ozdemir (2004) showed that all tested hydrocolloids can be used to improve consistency/viscosity of tomato ketchups. Hydrocolloids are water-soluble, high molecular weight polysaccharides that find wide application in food industry because of their ability to improve the rheological and textural characteristics of food systems and often used as food additives for enhancing viscosity, creating gel-structures and lengthening the physical stability (Dickinson, 2003).

The present work was done to determine the effect of hydrocolloids addition on rheological properties and sensory quality of tomato ketchup during storage, with relationship of chemical composition and sensory characteristics.

MATERIALS AND METHODS

1. Materials:

Tomato fruits (super strain B), spices, salt, sugar, onion, garlic, and acetic acid were purchased from the local supermarket in Toukh city Quliobia govrnotate.

Starch, pectin and all chemicals used in chemical analysis were purchased from Al-Gomhuria Co. for chemicals, Cairo, Egypt.

2. Preparation of ketchups:

Tomato ketchups including control samples were made in (THE) laboratory.

The ketchup was prepared according to Gujral *et al.* (2002) as follows: The tomato was washed, crushed and then hot pulped (boiled in their owen juice for 5 min). They were then passed through a laboratory pulper to get tomato juice. The tomato ketchup was prepared using ingredient as follows: Tomato juice 1 kg, sugar 80g, salt 10g, onion 3g, ginger 6 g, garlic 6g, mace 0.3g, cloves 0.3g, cinnamon 0.3g, red chilli powder 1.5g, black pepper powder 0.002g and acetic acid 50-60 ml (5-6%). Tomato juice was put into an open pan. Spices were wrapped in a cloth and dipped into the tomato juice. Onion and garlic pulp were added directly to the juice. The mixture was then heated at a moderate temperature, and stirred constantly until the mixture reached a temperature between 75 and 80 °C. At this point, some sugar and all salt were added, and heating was continued until the mixture attained a TSS content of 25% $\pm$1. Then, ginger and acetic acid were added to the mixture, and the ketchup was heated until a TSS of 30% $\pm$1was obtained. Finally, sodium benzoate was added as a preservative, (500mg/kg) and the ketchup was immediately portioned into 6 samples. The hydrocolloids were mixed with a little bit of sugar then added into ketchup (0,1,2 and 3% of starch and 0.5 and 1% pectin), and stirred for 2 min with an electric blender. Each ketchup sample was then immediately poured into the glass jar, while still hot, sealed with screw caps, and then stored at ambient temperature (25-30°C) for 6 months.

3. Analytical Methods:

3.1. Chemical methods:

Moisture content, total solids, fat, protein, ash, ascorbic acid and starch were determined according to AOAC (2000). Total soluble solids were measured at 25 °C by using Abbe refrectometer Model 1T according to AOAC (2000). The pH was measured with a pH meter model Consort pH meter P107. Titratable acidity was determined by titration with NaOH 0.1 N solution using phenolphthalein as indicator according to AOAC (2000). Total and reducing sugars were determined by Shaffer and Hartman method as described in the AOAC (2000). Total pectin content and fractional pectin components were determined by the method of Carre and Hayness, which was described by Pearson (1976). Pulp content was determined according to El-Mansy *et al.* (2000 a,b). Color index of ketchup was determined by the method of Meydov *et al.* (1977). Carotenoids were determined according to Harvey and Catherine (1982). While lycopene was determined according to Ranganna (1997).

3.2. Rheological measurements:

All measurements: Rotational measurements have been performed on by the Brookfield Digital Viscometer Model DV-II+ with 18 rotational speeds for comprehensive data gathering (0.3, 0.5, 0.6, 1.0, 1.5, 2.0, 2.5, 3, 4, 5, 6, 10, 12, 20, 30, 50, 60 and 100 rpm), the up and down curve of a shear rate were done. A temperature-controlled water bath was used to regulate the temperature of the samples. The Brookfield small sample adapter was used. Data were analysed by using Brookfield Software Rheocalc version (1.1). Power Law (PL) and Casson (CA), math models provide a numerically and graphically analyse the rheologic of data sets.

The power law or Casson equations models were used to describes the flow behavior of tomato ketchups because their have a higher correlation coefficient.

Power law model (PL):

$$\tau = K \cdot \dot{\gamma}^{n} \qquad (1)$$

where: τ = Shear stress (N/m^2) $\dot{\gamma}$ = Shear rate (sec^{-1})
K =Consistency index ($Pa.s^n$) **n** = Flow index (dimensionless)

Casson model (CA):

$$(\tau)^{0.5} = (\tau_{0CA})^{0.5} + (\eta_{CA} \cdot \dot{\gamma})^{0.5} \qquad (2)$$

where: τ_{0CA} = yield stress η_{CA} = Casson apparent viscosity (Pa.s)
$\dot{\gamma}$ = Shear rate (sec^{-1})

Flow activation energy and the effect of temperature on viscosity:

Activation energy was calculated using Arrhenius-type equation as mentioned by Koocheki, *et al.* 2009; El-Mansy, *et al.* (2000 a,b) and Ibarz, *et al.* (1996).

$$\eta = \eta_{\infty} \exp (E_a / RT) \qquad (3)$$

where: η is the viscosity, η_{∞} is a constant (is the viscosity at infinite temperature), E_a is the activation energy of flows (J/mol), **R** is the gas constant and **T** is the absolute temperature in °K.

3.3. Sensory evaluation:

Sensory evaluation was carried out by a properly well trained panel of 12 testers. Samples of the different products in arbitrarily identified glasses were ranked in order of acceptability for water separation, texture, colour, taste, odour and overall acceptability by each panellist separately. Twenty degrees for each attribute except overall acceptability which has 100 degrees.the sensory evaluathion was done according to Jimenez *et al.* (1989).

3.4. Statistical analysis:

Data for the sensory tests of all tomato ketchup samples were subjected to the analysis of variance followed by (L.S.D) analysis according to Gomez and Gomez (1984).

RESULTS AND DISCUSSION

Technological characteristics, such as chemical composition, rheological properties, physical properties and sensory properties play an important role in the formation of the processing steps, which are necessary for the production of tomato ketchup. This part deals with some of these aspects, in order to obtain some useful data for the differentiation between the tested tomato ketchup.

Chemical properties of tomato ketchup:

Results recorded in Table (1) show some chemical and physical properties of control tomato ketchup.

Total solids, moisture and ash:

Total solids content is an important factor in the production of tomato ketchup. It is well known that the higher of the total solids the better will be the quality of the end product. As shown in Table 1 total solids was 30.36%, also data of Table 1 represent the ash content of tomato ketchup which was 3.27%. The results are in agreement with those obtained by Sharoba, *et al.* (2005).

Titratable acidity and pH value:

pH and acidity are important factors influencing on the quality of tomato ketchup. The pH value was 3.67. The obtained value was in accordance with that obtained by Rani and Banins (1987) who found that pH value for tomato ketchup ranged between 3.55 to 3.87. The acidity value obtained from the tested ketchup was 1.85%. The results are in agreement with those obtained by Porretta and Birzi (1995).

Ascorbic acid (Vit. C):

Tomato and tomato products are considered as a good source of vitamin C. The results obtained in Table (1) showed that the control tomato ketchup contained 28.12 mg /100g vitamin C. The results are in agreement with Orzaez, *et al.*(1991) who found the vitamin C ranged between 8.11 to 60.04 mg /100g.

Total sugars:

Sugars are one of the most important quality parameter of the tomato ketchup, because it is contribution to the flavour, quality, platability and discoloration of tomato ketchup. The data obtained in Table (1) showed that, the total sugars content of the tested ketchup was 15.82%. While, reducing sugars was 9.88%. The obtained data were in agreement with those observed by Pearson (1976) and Vitacel (2002) they found mean values ranged as: sucrose 9.3 and 4.2-12.7 g/100g glucose 6.1 and 3.7-10.8 g/100g fructose 5.7 and 3.6-11.0 g/100 g, respectively.

Pectic substances and pulp content:

Pectic substances are the main factor which greatly influencing the quality, stability, process ability and viscosity of tomato ketchup. The total pectic contents of ketchup were the sum of the pectin fractions extract; water extract, ammonium oxalate extract and acid extract. The obtained results presented in Table (1) showed that the total pectin for ketchup was the ammonium oxalate extract soluble pectin was the highest content, while the water soluble pectin showed the lowest content. The obtained data were in accordance with that found by El-Mansy, *et al.* (2000a) and Sharoba, *et al.* (2005) they found that the ammonium oxalate soluble pectin was the highest content of pectin in tomato products. Pulp content value also, was 69.17 V/V related to pectin, sugar, fiber and other cheimcal compsition.

Colour index, lycopene and carotenoid content:

The colour index (O.D. at 420 nm) for ketchup was 0.978. Epidemiological studies have shown that increased consumption of fruits, including tomatoes, is associated with reduced risk of lung and other epithelial cancers. It has been suggested that high carotenoid levels in tomatoes and fruits are responsible for this reduced risk Tonucci, *et al.* (1995). Also, increased consumption of tomatoes and tomato products has been associated with decreased cancer risk, one fat-soluble compound identified in tomatoes, which may be responsible for this association is lycopene, Djuric and Powell (2001).

The carotenoids content presented in Table (1) was 1.84 mg/l. The results are in agreement with those obtained by Tavares and Rodriguez (1994) and Sharoba, *et al.* 2005. On the other hand the lycopene content was 11.73mg /100 g. These results are in agreement with those obtained by Wilberg and Rodriguez (1993).

Table (1): Chemical and Physical Properties of Tomato Ketchup

Components	Values ±SE
Moisture %	69.64±0.04
Total Solids %	30.36
Ash %	3.27±0.01
Ascorbic acid (mg/100g)	28.12±0.41
pH value	3.67±0.01
Titratable acidity % (as anhydrous Lactic acid)	1.85±0.06
Starch %	0.76±0.03
Total sugars %	15.82±0.27
Reducing sugars %	9.88±0.42
Non reducing sugars %	5.94
Total pectic substances %	6.74
Acid Soluble Pectin %	1.59±0.07
Ammonium oxalate soluble pectin %	3.81±0.23
Water soluble pectin %	1.34±0.05
Pulp Content (V/V) %	69.17±1.23
Colour Index (O.D. at 420 nm)	0.978±0.01
Carotenoids (mg/l)	1.84±0.00
Lycopene (mg/100 g)	11.73±0.04

Chemical composition on wet weight basis- Each value is the average of three replicates

Rheological properties of tomato ketchups:

The most important single factor determing the quality of commercially processed tomato ketchup is its viscosity. Flow processes is an essential step in the production of all foods products, and so the flow properties of constitute a body of information essential to the economic design of the most suitable food process equipment and operation that can be selected.

Rheological properties of tomato ketchups were studied at a wide range of temperatures at 5, 25, 50 and 75°C. Tomato ketchup showed non-Newtonian fluids characters. It showed pseudoplastic behaviour at all assayed temperatures. In"Pseudoplastic materials" the apparent viscosity decreases as the rate of shear at which the material is tested increases. This pseudoplastic behaviour is the result of a complex interaction among the pulp, soluble pectin, organic acids, soluble solids and high volume concentration of particles, Rao, (1987)

Used power law Model:

The obtained steady flow curves were well described by the power law model. The experimental values of shear stress and shear rate have been fitted by equation (1). The calculated rheological parameters K, n were, using Brookfield Software Rheocalc version (1.1), are shown in Table 2. The "K" decreased when the temperature increased for the different tomato ketchups brands under investigation. These data are in agreement with those previously reported by other investigators, Chaffai (1991) and Young, *et al*. (1997)

On the other hand, the K value was higher for samples contained hydrocolloids addition and lower for control sample at all assay temperatures . These data are in agreement with those previously reported by other investigators, Canovas and Peleg (1983). The reason for such differences in the flow behaviour constants between tomato ketchups brands might be referred to the variations in their content of hydrocolloids addition and the particles size and shape. Also, Table (2) indicated that the K value was higher in sample contained pectin as a hydrocolloids. These results are in agreement with those obtained by Sharoba (1999) who reported that the higher "K" values could be referred to the presence of more suspended total pectic substances in the tomato products. The consistency index K increased with increasing the total solids and decreased with increasing temperature.

The flow index values n for the tomato ketchup were given in Table (2) with $n < 1$ indicating that the rheological behaviour is pseudoplastic. The n values ranged between 0.261 and 0.342. These results could be confirmed with the data obtained by Canovas, and Peleg, (1983); Young, *et al.* (1997); Sharoba, *et al.* (2005) and Koocheki, *et al.* (2009), they indicated that the n value for tomato ketchup ranged between 0.2 to 0.5. Canovas and Peleg (1983) who indicated that the n values obtained from two tomato ketchups (Heinz and Stop& Shop) ranged between 0.38 and 0.40. It is observed from these results that, K and n decreased as temperature rose. At a given temperature, K increased with increase in hydrocolloids addition. These results could be confirmed with the data obtained by Ibarz, *et al*. (1996) who reported that temperature was found to have a large effect on the consistency index but with a little effect on the behaviour index. The rheological parameters are very important values; from the engineering stand point that they are required to calculate an important dimension less value, which is known as, generalized Reynold's number (G.Re.No.). Solving the problems of fluid flows and pumping need essentially the Reynold's number. Besides calculation of heat transfer coefficient; for non-Newtonian fluids depends upon the consistency of the fluid as indicated by Toledo (1980). The tomato ketchup samples contained pectin had a higher rheological values than the tomato ketchup samples contained starch at the same concentration. The power law confidence degree for all tomato ketchup sample ranged form 92 to 99.81 %.

Used the Casson model:

The Casson model (CA) (eqn. 2) has been used to describe the flow behavior of tomato ketchups in all cases of our examinations. The applicability of the CA model for all tomato ketchups at temperature (5 – 75 °C) was examined by CA parameters. The correlation coefficients indicated reasonably good applicability of the model. The use of the CA model was necessary because this model give the appearance viscosity The values of rheological constants for tomato ketchups, using the CA model were presented in Table (2).

Casson yield stress (τ_{0CA}):

Yield stress (τ_{0CA}) value was higher for samples contained hydrocolloids and lower for the control tomato ketchup sample. The τ_{0C} values at temperature 5 °C were 18.34, 20.96, 23.93, 26.11, 24.77 and 29.48 Pa for all tomato ketchups under studies, 0% hydrocolloids adding ratio, (1, 2 and 3% starch), (0.5 and 1% pectin), respectively. On the other hand the confidence degree for Casson model was lower than that obtained using power law model for the different tomato ketchups brands under investigation. These data were in agreement with those obtained by Correia and Mittal (1999).

Casson dynamic viscosity:

Casson dynamic viscosity decreased as temperature rose for the different tomato ketchups brands under investigation. The results were in agreement with those obtained by Correia and Mittal (1999), Chaffai (1991) and Canovas and Peleg (1983), they found that the Casson dynamic viscosity ranged between 0.321to 0.891 Pa.s.

Effect of Storage on rheological properties of tomato ketchups:

The nature of the components of tomato ketchup (i.e., starch, sugar, pectin, organic acids, etc.,) plays a significant role in viscosity. From such point of views, the viscosity could be used as a mirror to reflect the changes in tomato ketchups components as a result of storage at different conditions of time. Data in Tables (3-5) showed the changes in rheological behavior (power law and casson models parameters) of the presented tomato ketchups after 2, 4 and 6 months of storage. It was clear that the all tomato ketchups samples affected by storage time. Also all tomato ketchups samples exhibited pseudoplastic characteristics with n less than one.

Starch at different ratio (1, 2 and 3%) and pectin at ratio (0.5 and 1%) were used as additives to make tomato ketchup and their effects on the rheological properties of the tomato ketchup were examined. The magnitudes of the consistency index, flow index, yield stress and appearance viscosity of the tomato ketchup with the additives, regarded as a for tomato ketchup with pectin adding had rheological parameters greater than tomato ketchup made with starch adding, and both had rheological pramters greater than control sample (no starch or pectin added).

The power law and casson models equations were found a good models to describe the flow behavior of ketchups samples at storage condition Tables (3-5). Values of confidence degree were high. After 2, 4 and 6 months storage power law and Casson models parameters were highly affected by storage time. These results are in agreement with Harnanan *et al.*, (2001).

All rheological parameters increased with the addition of hydrocolloid and decreased with increasing storage duration. These results are in agreement with those obtained by Koocheki, *et al.* (2009); Sharoba (2004); Varela, *et al.* (2003)and Singh, *et al.* (2002).

Table (2): Power law and Casson parameters of tomato ketchup at 0 month storage time

Hydrocolloids adding Ratio	T °C	Power law			Casson		
		K	n	Con%	τ_0	η_{CA}	Con%
		Pa.s^n	-	-	Pa	Pa.s	-
0% Hydrocolloids (Control)	5	20.04	0.298	99.52	18.34	0.321	98.18
	25	18.87	0.294	99.77	16.15	0.305	98.42
	50	15.61	0.292	99.29	14.38	0.284	98.53
	75	14.26	0.286	98.58	12.91	0.261	98.27
1% Starch	5	22.63	0.287	99.47	20.96	0.384	98.11
	25	21.18	0.281	98.89	18.75	0.361	98.07
	50	20.33	0.282	98.96	17.00	0.344	98.23
	75	19.07	0.276	99.74	15.86	0.321	97.45
2% Starch	5	24.13	0.279	99.81	23.93	0.412	98.27
	25	23.08	0.277	98.73	21.21	0.396	98.06
	50	22.27	0..274	99.31	20.07	0.389	98.51
	75	21.51	0.272	98.79	19.01	0.352	97.82
3% Starch	5	27.05	0.263	99.41	26.11	0.502	98.75
	25	25.87	0.262	98.60	23.51	0.471	98.27
	50	23.91	0.262	98.73	22.32	0.431	98.00
	75	23.14	0.261	97.84	19.87	0.417	97.34
0.5% Pectin	5	25.69	0.338	98.72	24.77	0.645	98.05
	25	24.27	0.333	98.51	23.19	0.581	98.12
	50	23.61	0.332	97.96	21.99	0.479	97.76
	75	22.84	0.329	97.63	21.04	0.409	97.89
1% Pectin	5	29.03	0.342	98.37	29.48	0.891	98.57
	25	27.42	0.341	98.53	27.83	0.804	98.50
	50	25.66	0.339	98.96	26.17	0.769	97.77
	75	24.94	0.339	97.41	25.31	0.681	97.28

Table (3): Power law and Casson parameters of tomato ketchup at 2 month storage time

Hydrocolloids adding Ratio	T °C	Power law			Casson		
		K	n	Con%	τ_0	η_{CA}	Con%
		Pa.s^n	-	-	Pa	Pa.s	-
0% Hydrocolloids (Control)	5	19.81	0.295	99.07	17.32	0.322	99.22
	25	18.31	0.291	99.45	15.67	0.301	99.05
	50	15.11	0.290	98.99	14.10	0.276	99.12
	75	14.03	0.281	98.51	12.64	0.249	98.34
1% Starch	5	22.05	0.284	99.08	20.10	0.379	97.64
	25	21.11	0.282	98.78	18.62	0.354	97.91
	50	20.18	0.282	97.14	16.81	0.338	97.62
	75	18.89	0.279	97.54	15.74	0.318	97.37
2% Starch	5	24.02	0.277	99.07	23.51	0.411	98.67
	25	23.00	0.275	98.33	21.03	0.379	98.08
	50	22.31	0.273	97.28	20.00	0.352	97.89
	75	21.32	0.274	97.37	18.87	0.344	97.30
3% Starch	5	26.90	0.261	98.33	26.02	0.500	98.10
	25	25.54	0.260	98.14	23.56	0.470	98.53
	50	23.22	0.260	98.07	22.41	0.429	98.59
	75	23.01	0.258	97.92	19.53	0.412	97.34
0.5% Pectin	5	25.33	0.330	99.00	24.60	0.630	97.96
	25	24.03	0.327	98.93	23.31	0.567	98.95
	50	23.27	0.324	98.37	22.02	0.471	98.10
	75	22.81	0.322	98.39	21.01	0.401	97.67
1% Pectin	5	29.00	0.344	98.91	29.10	0.832	98.25
	25	27.45	0.340	98.22	27.52	0.764	98.01
	50	25.41	0.337	98.57	26.00	0.711	97.50
	75	24.39	0.335	97.94	25.34	0.673	97.51

Table (4): Power law and Casson parameters of tomato ketchup at 4 month storage time

Hydrocolloids adding Ratio	T °C	Power law			Casson		
		K	n	Con%	τ_0	η_{CA}	Con%
		Pa.s^n	-	-	Pa	Pa.s	-
0% Hydrocolloids (Control)	5	19.23	0.298	99.03	17.09	0.319	98.11
	25	17.96	0.290	98.52	15.34	0.294	97.05
	50	15.00	0.286	96.81	13.94	0.271	96.36
	75	14.08	0.282	93.88	12.61	0.251	93.91
1% Starch	5	21.76	0.285	98.8	19.60	0.368	96.57
	25	20.86	0.282	99.05	18.02	0.351	95.94
	50	20.01	0.281	96.64	16.11	0.330	93.67
	75	18.64	0.280	94.12	15.13	0.315	91.60
2% Starch	5	23.64	0.271	96.47	22.04	0.404	96.28
	25	22.57	0.270	96.99	20.15	0.372	96.00
	50	22.03	0.267	97.12	19.20	0.350	94.31
	75	21.29	0.265	95.03	18.24	0.335	93.84
3% Starch	5	26.83	0.260	98.70	24.89	0.490	98.34
	25	25.24	0.260	98.11	23.11	0.456	96.03
	50	23.20	0.258	98.81	22.05	0.405	96.75
	75	23.00	0.257	96.52	19.16	0.402	94.66
0.5% Pectin	5	25.04	0.327	99.74	23.96	0.622	93.12
	25	23.74	0.324	96.83	22.67	0.553	96.71
	50	23.05	0.321	94.97	21.40	0.473	93.61
	75	22.60	0.320	94.50	20.45	0.403	93.22
1% Pectin	5	28.63	0.343	94.17	27.58	0.811	96.67
	25	27.14	0.342	95.36	26.31	0.751	95.71
	50	25.21	0.340	96.32	25.40	0.703	93.35
	75	24.27	0.336	92.48	24.05	0.657	92.99

Table (5): Power law and Casson parameters of tomato ketchup at 6 month storage time

Hydrocolloids adding Ratio	T °C	Power law			Casson		
		K	N	Con%	τ_0	η_{CA}	Con%
		$Pa.s^n$	-	-	Pa	Pa.s	-
0% Hydrocolloids (Control)	5	17.02	0.294	98.22	14.67	0.294	97.53
	25	13.64	0.289	97.50	13.08	0.257	95.88
	50	12.41	0.281	96.73	11.91	0.234	94.24
	75	11.03	0.280	96.71	10.24	0.228	94.09
1% Starch	5	21.05	0.287	99.03	19.21	0.361	95.13
	25	20.10	0.283	98.10	17.30	0.342	94.60
	50	19.82	0.280	97.57	16.02	0.324	95.11
	75	18.41	0.280	97.51	14.86	0.314	93.57
2% Starch	5	23.02	0.268	97.30	21.33	0.392	98.32
	25	22.00	0.264	96.38	19.75	0.370	97.51
	50	22.48	0.262	96.61	18.34	0.346	94.78
	75	20.59	0.261	96.17	17.25	0.330	94.11
3% Starch	5	26.24	0.255	97.59	23.14	0.472	97.30
	25	25.01	0.251	95.98	22.41	0.451	96.87
	50	22.81	0.248	94.74	21.45	0.394	93.61
	75	22.41	0.247	94.19	19.02	0.390	92.78
0.5% Pectin	5	24.11	0.329	95.91	22.71	0.613	99.39
	25	23.20	0.325	94.63	21.06	0.541	98.06
	50	22.71	0.320	95.10	20.26	0.470	92.53
	75	21.96	0.318	93.59	18.68	0.404	92.57
1% Pectin	5	28.06	0.340	97.19	26.93	0.791	96.90
	25	26.73	0.340	96.27	25.34	0.706	92.45
	50	25.01	0.337	97.16	24.05	0.676	94.43
	75	24.04	0.336	94.76	22.69	0.633	93.73

Activation energy and the effect of temperature on viscosity of tomato ketchup:

The flow activation energy has been related to some fundamental thermodynamic properties of the Newtonian fluids. For example E_a has been found to be approximately equal to 1/3 or 1/4 the heat of vaporization, depending on the shape and bonding of liquid molecules. Empirical equations have been suggested for the estimation of the activation energy as a function of the viscosity and the temperature of various classes of liquids Vanwazer, *et al.* (1963). Activation energy highly decreased when suspended particles were present in the product, as in cloudy juices and fruit purees. In pseudoplastic fruit products, the activation energy was directly proportional to the flow behaviour index i.e., the more pseudoplastic the product, the less the effect of temperature on its apparent viscosity.

Activation energies of the pseudoplastic products (hydrocolloids addition tomato ketchup) reported on Table (6) were calculated at a constant shear rate (100 s^{-1}). Viscosity decreases with temperature this effect of temperature on the flow behaviour of fluid foods can be described by the Arrhenius relationship according Canovas, and Peleg, (1983); Singh and Eipeson, (2000); Yoo, (2001) and Sharoba, *et al.* (2005).

The Arrhenius constants for the temperature range 5-75 ^{o}C (η_∞ and E_a), together with regression coefficients are listed in Table 3. For the flow activation energy, the values range from (14.25 to 11.43 kJ/mol) depends on the chemical composition and hydrocolloids addition. The activation energy decreases with the hydrocolloids addition .These results are in agreement with those obtained by Koocheki, *et al.* (2009) , Sharoba, *et al.* (2005) and Rani and Banins (1987). Also these results are trends in accordance with that reported by other authors for different tomato products with similar characteristics Harper and El Sahrigi, (1965) who reported E_a of 3.83 kcal mole^{-1} K for a tomato juice concentrate of 30 % solids using high shear rates of 500 to 800 s^{-1}. Also Rao, *et al.* (1981) found the E_a values for tomato concentrates of 30 to 36 % solids (2.3± 0.3 kcal mole^{-1} K). The E_a decreases with the storage time increasing, these results are in agreement with those obtained by Koocheki, *et al.* (2009); Sharoba, *et al.* (2005). On the other hand E_a calculations may be useful in estimating the effect of homogenisation where it would be hypothesized that the homogenized concentrate would have a higher E_a than the non homogenized control due to an increase in the number of insoluble particles, decrease in particle size and decrease in viscosity.

Table (6): Arrhenius-type constants relating the effect of temperature* and viscosity at 100 RPM on tomato ketchup.

Hydrocolloids adding ratio	Storage period (months)	Coefficient correlation (r)	E_a (J/mol.)	η_∞ (mPa.s)
0% Hydrocolloids (Control)	0	0.997	14.25	2.58
	2	0.993	14.03	2.49
	4	0.995	13.87	2.35
	6	0.991	13.46	2.31
1% Starch	0	0.993	13.34	2.58
	2	0.991	13.08	2.36
	4	0.994	12.74	2.31
	6	0.990	12.40	2.20
2% Starch	0	0.993	13.07	2.37
	2	0.993	12.71	2.14
	4	0.995	12.39	2.03
	6	0.991	12.04	1.88
3% Starch	0	0.972	12.31	2.09
	2	0.978	12.11	2.00
	4	0.981	11.92	1.84
	6	0.977	11.67	1.69
0.5% Pectin	0	0.991	12.85	2.82
	2	0.989	12.32	2.65
	4	0.992	12.07	2.57
	6	0.992	11.80	2.50
1% Pectin	0	0.976	11.43	2.14
	2	0.979	11.27	2.01
	4	0.975	10.94	1.86
	6	0.973	10.62	1.80

- Temperature range for E_a (5-75°C)

E_a (activation energy) η_∞ (constant)

Sensory Evaluation of Tomato Ketchup:

As in all foods, the organoleptic tests are generally the final guide of the quality from the consumer's point of view Jimenez, *et al.* (1989). Thus, it is benefical to make a comparison between tomatoes ketchup. The water separation, texture, and overall acceptability were had high significant difference for all tomato ketchup samples. Also significant difference for tomato ketchup in colour, odour and taste. On the other hand, the scores showed significant differences ($p<0.05$) between control tomato ketchup and hydrocolloids addition tomato ketchup products. The highest scores on texture for ketchup contained 3% starch and lowest scores on texture for control tomato ketchup. The colour of control tomato ketchup, 0.5% pectin addition tomato ketchup and 1% starch addition tomato ketchup had the higher scores than other tomato ketchup samples. The overall acceptability for hydrocolloids addition tomato ketchup had the higher than other control tomato ketchup. Also the results of sensory evaluation scores are showed in Table (7).

The overall acceptability for tomato ketchup samples contained 2% starch and contant 0.5 had the higher scores than other tomato ketchup products. The overall acceptability for tomato ketchup samples contained 3% starch and contained 1% had smaller scores than other ketchup products.

Data in Table (7) indcated also high significant difference for tomato ketchup during storage.

Table (7): Sensory properties of tomato ketchup

Sensory attributes	**Hydrocolloids adding ratio**	Storage period by months				
		0	2	4	6	Average
Water separation	0% (Control)	17.08±0.23	16.25±0.33	15.50±0.25	14.00±0.28	15.70^{d}±0.27
	1% Starch	17.25±0.21	17.00±0.12	16.66±0.34	15.08±0.74	16.50^{c}±0.19
	2% Starch	17.75±0.21	17.91±0.15	16.91±0.23	16.58±0.35	17.29^{b}±0.16
	3% Starch	19.33±0.16	18.50±0.18	18.33±0.16	17.58±0.35	18.45^{a}±0.16
	0.5 % Pectin	18.75±0.21	17.16±0.21	16.66±0.27	16.83±0.10	17.35^{b}±0.19
	1% Pectin	18.75±0.11	18.83±0.27	18.08±0.15	17.25±0.25	18.22^{a}±0.16
	Average	18.15^{a}±0.16	17.61^{b}±0.17	17.02^{c}±0.18	16.22^{d}±0.23	
	$LSD_{(P<0.05)}$(Storage time) 0.261					
	$LSD_{(P<0.05)}$ (addition levels) 0.320					
	$LSD_{(P<0.05)}$ (Storage time * addition levels) 0.641					
Texture	0% (Control)	16.75±0.21	15.91±0.35	15.00±0.46	13.50±0.36	15.29^{e}±0.30
	1% Starch	17.50±0.18	16.38±0.10	16.41±0.37	15.91±0.32	16.66^{d}±0.17
	2% Starch	18.50±0.12	17.83±0.35	17.33±0.16	17.08±0.30	17.68^{c}±0.16
	3% Starch	19.50± 0.18	18.75±0.11	18.83±0.21	18.66±0.16	18.93^{a}±0.10
	0.5% Pectin	18.41±0.15	18.41±0.45	17.83±0.30	17.58±0.20	18.06^{b}±0.16
	1% Pectin	19.08±0.23	18.91±0.27	18.50±0.12	18.50±0.12	18.75^{a}±0.10
	Average	18.29^{a}±0.17	17.77^{b}±0.21	17.31^{c}±0.24	16.87^{d}±0.31	
	$LSD_{(P<0.05)}$ (Storage time) 0.303					
	$LSD_{(P<0.05)}$ (addition levels) 0.371					
	$LSD_{(P<0.05)}$ (Storage time * addition levels) 0.742					
Colour	0% (Control)	19.83±0.10	19.50±0.18	19.16±0.10	19.00±0.18	19.37^{a}±0.09
	1% Starch	19.33±0.16	18.19±0.15	18.33±0.33	17.66±0.16	18.56^{b}±0.16
	2% Starch	17.91±0.15	17.33±0.16	16.25±0.21	15.91±0.37	16.85^{d}±0.20
	3% Starch	17.33±0.24	16.83±0.27	15.50±0.25	14.33±0.24	16.00^{e}±0.27
	0.5% Pectin	18.41±0.15	18.25±0.11	17.58±0.23	17.33±0.30	17.89^{c}±0.13
	1% Pectin	17.75±0.21	17.25±0.17	16.75±0.21	16.41±0.30	17.04^{d}±0.15
	Average	18.43^{a}±0.16	18.01^{b}±0.17	17.26^{c}±0.22	16.77^{d}±0.26	
	$LSD_{(P<0.05)}$ (Storage time) 0.251					
	$LSD_{(P<0.05)}$ (addition levels) 0.307					
	$LSD_{(P<0.05)}$ (Storage time * addition levels) 0.615					

Table (7): Continue

Sensory attributes	Hydrocolloids adding ratio	Storage period by months				
		0	2	4	6	Average
Taste	0% (Control)	19.58±0.20	19.33±0.16	18.33±0.21	17.91±0.27	18.79^{a}±0.17
	1% Starch	19.33±0.10	18.83±0.21	18.33±0.16	17.66±0.16	18.54^{a}±0.15
	2% Starch	18.25±0.17	17.75±0.21	17.25±0.30	17.08±0.32	17.58^{c}±0.15
	3% Starch	16.83±0.10	16.25±0.30	16.16±0.33	15.58±0.39	16.20^{e}±0.17
	0.5% Pectin	18.19±0.15	18.50±0.12	17.58±0.23	16.83±0.38	17.95^{b}±0.20
	1% Pectin	17.33±0.33	17.16±0.21	16.16±0.21	15.58±0.30	16.56^{d}±0.19
	Average	18.37^{a}±0.18	17.97^{b}±0.19	17.30^{c}±0.17	16.77^{d}±0.19	
	LSD$_{(P<0.05)}$ (Storage time) 0.282					
	LSD$_{(P<0.05)}$ (addition levels) 0.346					
	LSD$_{(P<0.05)}$ (Storage time * addition levels) 0.692					
Odour	0% (Control)	19.75±0.11	19.41±0.15	18.33±0.10	17.33±0.16	18.70^{a}±0.20
	1% Starch	19.41±0.20	18.83±0.16	17.83±0.16	16.91±0.23	18.25^{b}±0.21
	2% Starch	18.83±0.27	18.16±0.10	17.50±0.22	16.50±0.12	17.75^{c}±0.21
	3% Starch	17.33±0.33	16.91±0.30	15.50±0.25	14.00±0.28	15.93^{e}±0.30
	0.5% Pectin	19.08±0.20	18.66±0.21	17.50±0.18	16.75±0.21	18.00^{bc}±0.21
	1% Pectin	17.58±0.47	17.16±0.35	16.66±0.35	15.66±0.16	16.77^{d}±0.23
	Average	18.66^{a}±0.18	18.19^{b}±0.17	17.22^{c}±0.17	16.19^{d}±0.20	
	LSD$_{(P<0.05)}$ (Storage time) 0.273					
	LSD$_{(P<0.05)}$ (addition levels) 0.335					
	LSD$_{(P<0.05)}$ (Storage time * addition levels) 0.670					
Overall acceptability	0% (Control)	96.33±0.49	91.83±0.98	88.83±1.22	85.50±1.47	90.62^{b}±0.97
	1% Starch	95.83±0.83	95.08±0.58	90.58±0.55	89.50±0.42	92.75^{a}±0.64
	2% Starch	94.50±0.68	92.66±0.35	91.50±0.40	91.16±0.45	92.45^{a}±0.36
	3% Starch	90.50±0.42	90.66±0.24	88.58±0.49	85.33±0.61	88.77^{c}±0.49
	0.5% Pectin	92.41±0.20	90.91±0.58	91.25±0.28	91.41±0.52	91.50^{b}±0.23
	1% Pectin	89.33±0.65	90.08±0.92	89.08±0.32	89.00±0.90	89.37^{c}±0.35
	Average	93.15^{a}±0.49	91.87^{b}±0.37	89.97^{c}±0.31	88.59^{d}±0.31	
	LSD$_{(P<0.05)}$ (Storage time) 0.772					
	LSD$_{(P<0.05)}$ (addition levels) 0.946					
	LSD$_{(P<0.05)}$ (Storage time * addition levels) 1.89					

Values represent of 12 panellists (Mean ± S.E.)
a, b There is no significant difference ($p \geq 0.05$) between any two means have the same superscripts, within the same acceptability attribute.

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