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Effect of Carboxymethylcellulose and Starch as Thickening Agents on the Quality of Tomato Ketchup

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Abstract: The objective of this study was to evaluate the effect of thickening agents such as carboxymethylcellulose and starch on the quality parameter of tomato ketchup during storage at 30°C. The carboxymethylcellulose was used at the rate of 0.75-1.25% while, starch was 3-4% in the formulation of tomato ketchup. The moisture content of ketchup was increased by the addition of both the thickening agents. The protein, fibre, ash, acidity and total soluble solid of tomato ketchup were decreased gradually when higher percentage of starch and carboxymethylcellulose were added. Amounts of lycopene, vitamin C and reducing sugar content were higher in the ketchup where starch was used. Starch and carboxymethylcellulose had <10 cfu/g of molds and total viable bacteria throughout storage at 30°C for 60 days. Carboxymethylcellulose treated ketchup was found more suitable than the starch treated through sensory evaluation.

Key words: Tomato ketchup, carboxymethylcellulose, starch, chemical composition

INTRODUCTION

Tomatoes (*Lycopesicon esculentum* Mill) are one of the most popular and nutritious fruit in human diet and widely grown in the tropical regions. They are rich in food components necessary for the normal growth of human such as carotenoids (lycopene), ascorbic acid (vitamin C), vitamin E, folate and dietary fibre (Davis and Hobson, 1981). The global production of tomatoes (fresh and processed) has been increased by 300% in the last four decades (FAO, 2005) in both tropical and temperate regions. Tomatoes are highly perishable fruits and it rapidly deteriorates after ripening. They are available in plenty at a particular period of time in specific regions often resulting in market glut. Due to glut during peak season large quantity of tomato gets spoiled. The post harvest loss in vegetables has been estimated to be about 30-40% due to inadequate post harvest handling, lack of infrastructure, processing, marketing and storage facilities (Karim and Hawlader, 2005). So, if these perishable fruits are processed into shelf stable products at rural level, the financial return is expected to be more for the growers while, post harvest loss of fruits will be reduced to a great extent. Therefore, the food-processing sector can play a vital role in reducing the post harvest losses by processing and value addition of vegetables and fruits, which will ensure better remuneration to the growers.

To supply throughout the year, it is necessary to preserve tomato and tomato products for a longer period. Tomato can be stored for short time in cold storage by chilling or freezing method. However, these methods are costly and require the availability of cold storages. For long term preservation processing is considered to be the best methods for the developing countries. Therefore, it is essential to develop suitable inexpensive methods for processing and preservation of tomatoes and tomato products. There are number of processed products like tomato paste, tomato ketchup, tomato juice, tomato puree, tomato sauce, tomato mat, tomato pickles, powder and others. Among the various tomato products, ketchup is the most important one as it requires limited equipment and the methods used are inexpensive. Ketchup is a popular condiment, usually made with ripened tomatoes. The basic ingredients in modern ketchup are tomatoes, vinegar, sugar, salt, spices while some times thickening agent are used (Srivastava, 1982). Thickening agents are natural or chemically modified carbohydrates that absorb some of the water present in the food, there by making the food thicker (Sahin and Feramuz, 2004).

Commonly used thickening agents are starch, Carboxymethylcellulose (CMC), guar gum, roux, browned flour, flour paste, arrowroot, split peas, egg yolks etc. (Sidhu *et al*., 1997; Srivastava, 1982). Starch can assume a multifunctional role in a condiment system, providing viscosity at key processing points, as well as helping to maintain consistent suspension. Starch is added to tomato in industry to achieve good quality of the final product (Hoover and Ratnayake, 2002).

Carboxymethylcellulose provides significant viscosity, excellent suspension ability and clarity. It creates a distinct pour and can have a gummy texture at excessive levels (Sahin and Feramuz, 2004; Hilan and Ozdemir,

2007). The purpose of this research was i) to study the effects of thickening agents such as Carboxymethylcellulose (CMC) and starch on the quality of tomato ketchup ii) to compare the nutritive values of ketchup treated with different thickeners iii) to study the effect of storage on the composition and quality of tomato ketchup prepared with different thickening agents iv) to assess the overall acceptability of the tomato ketchup containing different thickening agents.

MATERIALS AND METHODS

Tomatoes (*Lycopersicon esculentum*) used in the studies were collected from the Agricultural Farm of Bangladesh Agricultural University. Only ripe and fresh tomatoes were used in this study. Other materials such as sugar, salt, spices were purchased from local markets in Bangladesh Agricultural University. Two different commercial thickening agents Carboxymethylcellulose (CMC) and starch were obtained from the company of Incom Inc. (Mersin, Turkey).

Formulation of ketchup: The basic formulation of tomato ketchup was prepared following the composition described by Srivastava (1982) and presented in Table 1.

Processing of ketchup: The tomato pulp having a Total Soluble Solids (TSS) content of 4.7% was put into an stainless steel vessel and the spices (cinnamon, red chillies, clove) were wrapped in a cloth and dipped in to the pulp. Onion and garlic pulp were added directly to the dilution. The ketchup was heated on a low flame with constant stirring till a final TSS of 23% was obtained. Then vinegar was added to the mixture and the ketchup was heated until the final TSS was obtained. Finally, sodium benzoate was added as a preservative. The thickening agents were then added to the ketchup at different levels just before the end point. The thickening agents were pre blended with the sugar and salt and then added to the ketchup during the final stages of cooking. The ketchup was filled hot in glass bottles, sealed with crown corks and stored at ambient temperature (30°C) in incubators for 60 days.

Analysis of tomato ketchup: Moisture content, total soluble solids, ash, fibre, titratable acidity and ascorbic acid were determined by AOAC (2000). The pH was measured with a Schott CG840 pH meter. Reducing sugar content was determined by the method of Lane and Eynon (1923). Lycopene was determined by the method of Rangana (1997).

Determination of total viable bacteria yeast and mould count: Tomato ketchup sample (4 g) was aseptically homogenized with 45 ml Ringer powder solution for 2 min. From this, serial decimal dilutions were prepared with same diluent and 0.1 mL aliquots were inoculated. Dilutions of samples were plated for the counting of the following microorganisms: total aerobic mesophilic and psychotropic bacteria, respectively on PCA incubated at 32°C for 48 h and yeast and mould on Sabourand chloramphenicol agar incubated at 25°C for 3 days. The results were reported as log colony-forming units (cfu) per gram.

Sensory evaluation of tomato ketchup: Sensory test was carried out after two months. The 20-panel member's consisted of staff and students from Bangladesh Agricultural University, Bangladesh. There are 15 males and 5 females aged between 19 and 50+. Seven different samples were presented to panelists in random order. Panelists were then asked to evaluate colour, flavour, texture and overall acceptability. Between each sample, panelists were encouraged to rinse their mouth with water. The preference rating was scored on a 9 point scale with 1 = Dislike extremely and 9 = Like extremely.

Statistical analysis: Analysis of variance and the Duncan multiple range test were performed using a statistical software program (SPSS for Windows Version 14.0). Significant of the difference was defined as $p<0.05$.

RESULTS AND DISCUSSION

The experiment was carried out to study the effect of starch and CMC as different thickening agents on the quality of tomato ketchup. Chemical composition of the studied tomato pulp was also investigated and presented in the Table 2.

Effect of thickening agents on composition of tomato ketchup

Moisture content, ash content and acidity: Compositions of tomato ketchup prepared by different concentrations of starch and CMC are presented in Table 3. The results showed that moisture content was increased by the addition of higher percentage of thickening agents compared to the control. The thickening agents act as water-binding (Garti *et al*., 1997) materials, which hold water and prevent moisture removal during the cooking process. Thus the addition of thickening agents increased the consistency of ketchup, because the moisture did not vaporized easily in both cases while, starch and CMC were added.

Ash content was decreased with the increase of the amount of thickening agents. The acidity of tomato ketchup was gradually decreased by the addition of increasing level of thickening agents. There were no significant difference in moisture content, ash content and acidity among the different thickened tomato ketchup during the storage.

Table 1: Recipes used for the preparation of tomato ketchup

Ingredients	Quantity						
	Control S_1	Sample S_2	Sample S_3	Sample S_4	Sample S_5	Sample S_6	Sample S_7
Tomato Pulp	3 kg	3 kg	3 kg	3 kg	3 kg	3 kg	3 kg
Thickening agent	0	3%starch	3.5%starch	4%starch	0.75,CMC	1,CMC	1.25,CMC
Onion (chopped)	37 g	37g	37g	37g	37g	37g	37g
Garlic	2 g	2g	2 g	2 g	2 g	2 g	2 g
Spices	1.2 g	1.2 g	1.2 g	1.2 g	1.2 g	1.2 g	1.2 g
Cinnamon	1.8 g	1.8 g	1.8 g	1.8 g	1.8 g	1.8 g	1.8 g
Red chillies	1.5 g	1.5 g	1.5 g	1.5 g	1.5 g	1.5 g	1.5 g
Clove,whole(deheaded)	1 g	1 g	1 g	1 g	1 g	1 g	1 g
Salt	15 g	15 g	15 g	15 g	15 g	15 g	15 g
Sugar	150 g	150 g	150 g	150 g	150 g	150 g	150 g
Vinegar	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL
Sodium benzoate	700 ppm	700 ppm	700 ppm	700 ppm	700 ppm	700 ppm	700 ppm
Yield of final product	1149 gm	1310 gm	1395 gm	1510 gm	1605 gm	1709 gm	1859 gm

Table 2: Chemical composition of tomato pulp

Components	Amounts
Moisture (%)	93.40
Ash (%)	0.420
Ascorbic acid (%)	0.022
Acidity (%)	0.414
Total soluble solid (%)	4.700
Reducing sugar (%)	2.760
Dry matter (%)	6.600

Vitamin C, pH and total soluble solid: The effects of adding starch and CMC of different levels on vitamin C, pH and total soluble solid are shown in Table 4. The amount of vitamin C in the ketchup was decreased as the concentration of CMC and starch was increased. The vitamin C content ranged between 6.29 to 7.30mg/100 g for starch and 5.68-6.35 mg/100 g for CMC ketchup. The vitamin C content of tomato ketchup was lower than that reported by Sharoba *et al.* (2005) who found the vitamin C content ranged 8.11 and 60.04 mg/100 g and by Yastrebov *et al.* (1979) who found the vitamin C content 10mg/100 g. The lower content of vitamin C in this study was attributed to the pretreatments. It is well known that vitamin C is relatively unstable to heat, oxygen and light (Lin *et al.*, 1998). However, the vitamin C content was highest in starch added tomato ketchup, because starch has resistive power to the oxidation (Rami *et al.*, 2007). pH is very important factor influencing the quality of tomato ketchup. The pH values ranged between 4.05-4.09 for starch and 4.10-4.22 for CMC ketchup. The values obtained are in accordance with that obtained by Janette *et al.* (2007) who found that the pH for tomato ketchup ranged between 4.1 and 4.3. Total Soluble Solid (TSS) decreased in tomato ketchup by the addition of thickening agents, this may be due to the consistency of tomato ketchup raised quickly. There was no significant difference in pH and TSS among the different thickened tomato ketchup during the storage.

Effect of thickening agents on lycopene, reducing sugar, protein and fibre: The effects of adding starch and CMC of different levels on lycopene, reducing sugar, protein and fibre content are shown in Table 5 and 6. Lycopene content decreased gradually with the addition of both starch and CMC, because of the volume of final product increased but the amount of pulp was constant. It was also decreased during the storage period. These results were in agreement with Sharma and Maguer (1996) who reported that loss of lycopene increased at high storage temperature. It is well known that lycopene is relatively unstable to heat, oxygen and light (Giulia *et al.*, 2003). However, the lycopene content was highest in starch added tomato ketchup, because starch has resistive power to the oxidation (Rami *et al.*, 2007). The amount of reducing sugars in the ketchup was found to increase in all samples during storage period. Imtiaz *et al.* (2008) found increased reducing sugar contents in apricot and apple juice during storage. The quantity of reducing sugar decreased with the application of thickening agent, because the volume of the product increased. The amount of protein and fibre content decreased with the addition of thickening agents compared to the control samples. The observation may be explained by the increasing of moisture contents in the ketchup due to the addition of thickening agents. This was supported by Paul *et al.* (2005) who found decreased protein, fat and ash contents in imitation cheese with increased moisture contents.

Effect of thickening agents on weight of tomato ketchup: The yield of final product different tomato ketchup is shown in Table 1. It was found the weight of tomato ketchup was increased by the addition of the thickening agent. It was also found that the 1.25% level of addition of CMC gives the highest weight in all samples, as CMC is more active thickening agent than starch and in the sample percentage of CMC was high. Sahin and Feramuz (2004) have reported that addition of hydrocolloids (CMC, guar gum, xanthan gum) increase in the amount of tomato paste.

Table 3: Effect of different levels of starch and CMC on moisture, ash and acidity of tomato ketchup

		Storage time (days)				
Ketchup	Parameters	0	15	30	45	60
S_1	Moisture (%)	75.33	75.05	74.600	74.10	73.35
	Ash (%)	0.88	0.87	0.870	0.85	0.85
	Acidity (%)	1.28	1.30	1.300	1.33	1.36
S_2	Moisture (%)	79.60	79.25	78.950	78.50	78.29
	Ash (%)	0.80	0.79	0.790	0.78	0.78
	Acidity (%)	1.12	1.14	1.150	1.17	1.20
S_3	Moisture (%)	80.55	80.20	79.930	79.45	79.05
	Ash (%)	0.771	0.767	0.762	0.759	0.754
	Acidity (%)	1.05	1.08	1.110	1.14	1.16
S_4	Moisture (%)	81.20	80.94	80.600	80.32	79.95
	Ash (%)	0.77	0.76	0.760	0.75	0.75
	Acidity (%)	1.02	1.05	1.050	1.09	1.12
S_5	Moisture (%)	81.15	80.85	80.550	80.35	79.98
	Ash (%)	0.75	0.748	0.740	0.740	0.73
	Acidity (%)	0.97	0.99	1.000	1.02	1.05
S_6	Moisture (%)	81.97	81.60	81.320	80.93	80.78
	Ash (%)	0.742	0.740	0.739	0.738	0.736
	Acidity (%)	0.95	0.97	0.970	0.99	1.03
S_7	Moisture (%)	82.93	82.63	82.310	81.97	81.69
	Ash (%)	0.72	0.71	0.717	0.71	0.710
	Acidity (%)	0.90	0.92	0.930	0.95	0.97

Table 4: Effect of different levels of starch and CMC on vitamin C, pH and TSS of tomato ketchup

		Storage time (days)				
Ketchup	Parameters	0	15	30	45	60
S_1	Vitamin C (mg/100g)	8.37	8.29	8.20	8.11	7.99
	pH	4.03	4.01	4.01	3.99	3.98
	TSS	23	23	23	23	23
S_2	Vitamin C (mg/100g)	7.30	7.25	7.21	7.16	7.12
	pH	4.07	4.07	4.06	4.06	4.05
	TSS	18	18	18	18	18
S_3	Vitamin C (mg/100g)	6.90	6.82	6.74	6.67	6.57
	pH	4.08	4.02	4.07	4.06	4.04
	TSS	17	17	17	18	18
S_4	Vitamin C (mg/100g)	6.53	6.48	6.43	6.37	6.29
	pH	4.09	4.08	4.08	4.06	4.05
	TSS	16	16	16	16	17
S_5	Vitamin C (mg/100g)	6.35	6.27	6.2	6.17	6.12
	pH	4.14	4.13	4.12	4.12	4.10
	TSS	16	16	16.5	16.5	17
S_6	Vitamin C (mg/100g)	6.05	5.97	5.95	5.86	5.81
	pH	4.17	4.16	4.15	4.13	4.12
	TSS	16	16	16	16	16
S_7	Vitamin C (mg/100g)	5.90	5.85	5.79	5.73	5.68
	pH	4.22	4.21	4.21	4.20	4.17
	TSS	15	15	15	16	16

Effect of thickening agents on total viable bacteria, total mould and yeast: The counting total numbers of viable bacteria in different sample are shown in Table 7. The result shows that bacterial count increased with the increasing of thickening agent and storage time. The lowest score was observed in sample S_1 (3.67 log cfu/g), highest was in sample S_4 (3.82 log cfu/g). CMC thickened tomato ketchup contained slightly lower bacterial count than that of the starch. Mould and yeast found in tomato ketchup are shown In Table 8. During the experiment there was no countable yeast present in any ketchup. The maximum mould was found in sample S_4 (1.94 log cfu/g) and the minimum was found in sample S_1 (1.60 log cfu/g). Similar, finding was obtained by Lucia *et al.* (2003) that untreated tomato puree without additives had initial total microbial counts of 4.26 log cfu/g and initial yeasts and moulds of 2.39 log cfu/g.

Table 5: Effect of type and level of thickening agents on the lycopene and reducing sugar content of tomato ketchup

		Storage time (days)		
Ketchup	Parameters	0	30	60
S_1	Lycopene content (mg/100g)	8.55	7.40	6.24
	Reducing Sugar (%)	6.87	6.91	6.93
S_2	Lycopene content (mg/100g)	8.15	7.10	5.85
	Reducing Sugar (%)	6.52	6.55	6.59
S_3	Lycopene content (mg/100g)	7.99	6.90	5.55
	Reducing Sugar (%)	6.32	6.38	6.43
S_4	Lycopene content (mg/100g)	7.70	6.50	5.32
	Reducing Sugar (%)	6.21	6.25	6.30
S_5	Lycopene content (mg/100g)	7.54	6.15	4.95
	Reducing Sugar (%)	6.01	6.06	6.11
S_6	Lycopene content (mg/100g)	7.25	5.93	4.70
	Reducing Sugar (%)	5.86	5.90	5.96
S_7	Lycopene content (mg/100g)	6.90	5.74	4.43
	Reducing Sugar (%)	5.70	5.75	5.82

Table 6: Protein and fibre of different tomato ketchup (after two months)

	Sample						
Composition	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Protein (%)	2.42	2.32	2.26	2.23	2.10	2.01	1.91
Fibre (%)	0.70	0.65	0.62	0.59	0.54	0.54	0.51

Values expressed are means of 3 replicates ± SD; $^{a-g}$ Bars with same letter are not significantly different ($p<0.05$)

Table 7: Effect of type and level of thickening agents on the total count of bacteria in tomato ketchup stored at room temperature (30°C)

	After 1 month		After 2 months	
Sample No	No. of Colony	Total log (cfu/g)	No. of Colony	Total log (cfu/g)
S_1	37	3.57	45	3.65
S_2	48	3.68	55	3.74
S_3	53	3.72	62	3.79
S_4	62	3.79	66	3.82
S_5	51	3.71	56	3.75
S_6	49	3.69	59	3.77
S_7	56	3.75	63	3.80

Table 8: Effect of type and level of thickening agents on the total count of mould in tomato ketchup stored at room temperature (30°C) after 2 months

Sample	No. of colony Mould	No. of total Mould	Total (log cfu/g) Mould
S_1	4	4 x 10	1.60
S_2	6	6 x 10	1.78
S_3	7	7 x 10	1.84
S_4	9	9 x 10	1.95
S_5	7	7 x 10	1.84
S_6	8	8 x 10	1.90
S_7	8	8 x 10	1.90

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 Sharoba *et al.* (2005). Results from the sensory panel are presented in Table 9. Pillsbury *et al.* (2004) who reported that colour is a strong driver of overall acceptability and Janette *et al.* (2007) who reported that colour and flavour are the first thing that attract us and then comes the other factors. The perceived colour of the ketchup of S_6 and S_7 were significantly lower than that of S_1 sample. No significant difference in colour was found by the panel between S_1, S_2, S_5 and S_1, S_3 , S_4 samples. The flavour and texture of ketchup S_1 sample was the highest followed by S_2, S_3, S_4 and S_7 samples but not significantly different with S_5 and S_6 samples. The overall acceptability showed that the sample S_1 had the best but was not significant with S_5 and S_6 samples. The samples S_3 and S_4 had least acceptability but was not significant from S_7 sample. There were no significant differences found between the S_2, S_5, and S_6 samples.

Conclusion: The study was carried out to evaluate the effects of CMC and starch as the thickening agents in tomato ketchup. Lycopene and vitamin C and reducing sugar decreased gradually with addition of both starch and CMC. However lycopene, vitamin C and reducing sugar had higher in starch treated ketchup compared to the CMC treated ketchup. The volume of the final product was increased by the addition of thickening agents.

Starch and CMC had <10 cfu/g of molds and total viable bacteria throughout storage at 30°C for 60 days. CMC was found more suitable than the starch through sensory evaluation.

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