Journal of Food Biosciences and Technology,
Islamic Azad University, Science and Research Branch, Vol. 10, No. 1, 27-34, 2020

Physical Interactions between Tomato and Dried Carrot Pomace Components in a Novel Ketchup Formulation

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Received: 18 May 2019 Accepted: 4 November 2019

ABSTRACT: Dried carrot pomace (DCP) may be used as a thickening, coloring agent and also a carotenoid-fiber enriched component in food products formulations. The main objective of this study to investigate the effect of DCP from juice industries waste material on the physicochemical, rheological, nutritional properties of ketchup by partial replacement (0.7-3.5%) of tomato paste and the carboxy methyl cellulose. The physicochemical parameters of DCP, including: the moisture, fat, protein, ash, crude fiber, pectin, phenolic compounds content, water holding capacity and color properties were first analyzed. Then, different ketchup samples, based on DCP content variations, were formulated. The physicochemical properties of the formulations as well as the tomato lycopene and DCP β-carotene synergistic effect were studied. Based on the analytical data obtained, the samples with highest viscosity, lowest syneresis and the best color index with (0-2.1%) carrot pomace powder were selected for more detailed investigations to perform carotenoids measurements, color parameters specifications, rheological properties. Finally the formulation with 28% tomato paste, 3% glucose syrup, 0.4% carboxymethyl cellulose and 0.7% DCP was assigned as the best carotenoid-fiber enriched and healthy ketchup product.

Keywords: *Carotenoid, Carrot Pomace Powder, Fiber, Ketchup, Rheological Properties*.

Introduction

Generally, 30-50% of carrot mass is left as a pulp by-product, after juice extraction (Bao & Chang, 1994). In spite of the fact that carrot pomace is a rich source of nutrients but in most countries, it is not commercially used in food product formulations and is either dumped or fed to animals .On the other hand this by-product is quickly perishable because of its high water content (830 ± 1% (dry weight)) and drying is a routine industrial approach to increase its shelf-life for further use (Alam *et al.*, 2013).

Ketchup is a popular condiment that is usually formulated by tomato paste, vinegar, sweeteners, spices, flavoring agents and some types of hydrocolloids (including carboxymethyl cellulose) (Alam *et al.*, 2009). The global ketchup market has been predicted to grow with a CAGR 4.9% over the period of 2017-2023 (Business Wire, 2017). It is well known that fruits and vegetables are rich sources of fibers and should be included in daily diet for their nutritive and physiological roles. But the

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main key factor in order to achieve a good performance of different types of fibers in a food product is to provide a proper ratio of soluble/insoluble fibers (Khan, 1993). Although, tomato and carrot are both good sources of pectin but an important difference of consideration is that the main part of pectic substances in tomato is water soluble while carrot is rich in insoluble pectin and produces different nutritional/functional properties in the final product (Bengtsson & Tornberg, 2011). Therefore, using carrot pomace in ketchup formulation might not only worth economically for taking advantage of this by-product but also might be a nutritive supplement to produce carotenoids and fiber- enriched condiment.

The main objectives of this research were (a) to develop a new formulation for ketchup by partial replacement of tomato paste as well as CMC by dried carrot pomace considering the physicochemical, rheological properties of the final product; (b) Study the possible synergistic effect of two different types of carotenoids i.e., tomato lycopene and carrot pomace β-carotene in the new formulated ketchup.

Materials and Methods

- Preparation of dried carrot pomace

Carrots (*Daucus carota L. CV* ''*Nantes*''), purchased from a local market, were washed, trimmed and peeled manually and then cut into small cubes. Blanching was accomplished by immersing the cubed samples in a water-bath (80 ℃ for 5 min). The blanched/cooled carrot samples were then processed in fruit juice extractor (Panasonic MJ- M176P) and the remaining pulp was collected for further processing. The pomace was spread uniformly on the trays of an air oven (Memmert UFE 500, Germany) and dried at 75 °C for 5 h. The air valves were kept open in order to provide a good air circulation and the relative humidity was controlled by a hygrometer (TFA Kat.Nr.44.1004, Germany) during drying process. The dried carrot pomace (DCP) was then ground to 80-120 mesh size and stored in freezer in sealed packages at -70 °C for further use.

- Physiochemical analysis of DCP

Moisture content of the DCP was measured by in an infrared moisture analyzer (Sartorius MA 30, Germany) at 130 ℃ for 5 min. Total ash, crude protein and crude fiber contents were determined according to AOAC-942.05, AOAC- 978.02 and AOAC-973.18, respectively. Crude lipid, pectin and total phenolic compounds contents were determined according to Chantaro and co-workers (2008) method. Water holding capacity of the sample was analyzed by centrifuge technique (Robertson *et al*., 2000). The color properties ('L*', 'a*' 'b*' values and the yellow index) of the DCP were analyzed by a Hunter Lab (DP 25 with DP 9000 system, USA).

- Preparation of ketchup samples

Ten different formulations of ketchup samples with/without CMC have been prepared according to Table 1. In the first five designated group (K_0-K_4), the tomato paste and CMC contents were gradually decreased and replaced by DCP as well as glucose syrup. While in the second group designated as K_6-K_{10}, CMC has been completely eliminated and instead it is replaced by tomato paste and DCP in the formulations. K_5 in this list is the sample formulated without tomato paste. All other ingredients including sugar (16%), vinegar (8.5%), salt (2.2%) and spices (0.55%) were kept constant in all samples.

- Physicochemical analysis of ketchup formulations

The pH of each formulation was determined using a Hanna pH meter (pH 211, UK) and their soluble solids (brix) were analyzed in an Eclipse hand refractometer (UK). The total solid content was recorded

Table 1. Ketchup formulations

Ingredients (%)	K_0	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}
Tomato paste	35	28	21	14	7	0	35	28	21	14	7
Glucose syrup	0	3	6	9	12	15	0	3	6	9	12
CMC	0.5	0.4	0.3	0.2	0.1	0	0	0	0	0	0
DCP[1]	0	0.7	1.4	2.1	2.8	3.5	0.5	1.1	1.7	2.3	2.9
Water	37.25	40.65	44.05	47.45	50.85	54.25	37.25	40.65	44.05	47.45	50.85

[1] DCP: dried carrot pomace

after drying each sample at 105 °C until constant weight was obtained. The insoluble solid was obtained by deduction of the soluble solids from the total solid content. Viscosity measurements were accomplished by a rotational viscometer (Brookfield Engineering Inc. model DV3T, programmable USA) with disk spindle (no 5) in ω=100 RPM after 7 days of storage of the samples at ambient temperature (Brookfield Engineering Inc.).

Syneresis of each ketchup sample was studied using centrifuge method (Şahin & Özdemir, 2007). The color characteristics (L*, a*, b*, a/b) were determined by Hunter Lab method (DP 25 with DP 9000 system, USA) and tomato catsup score (TCS) has been measured according to the following equation (HunterLab, 2008)

In the next stage, the most acceptable formulations were selected, based on the above test results and the selected samples were further analyzed in detail by the following tests:

The total carotenoids of 5 g of the selected samples have been determined according to Gama *et al*. (2009) procedure. Rheological properties were studied by steady flow behavior tests using an Anton Paar rheometer (MCR 300, GmbH, Austria) at 25 ℃ with parallel plates measuring system (diameter =25 mm, gap = 1 mm). The experimental data were fitted with Herschel-Bulkley model ($\tau = m\,\dot{\gamma}^{\,n} + \tau_0$), where ($\tau_0$) is the yield stress, (m) and (n) representing consistency and flow behavior indices, respectively. Thixotropic tests were performed by increasing the shear rate up to 300 s^{-1}, keeping constant for 45 s and then decreasing down at the same rate to zero. The hysteresis loop area (A_{up}-A_{down}) was calculated by Matlab Software version 7.13 (Matlab R 2011).

- *Statistical analysis*

Statistical analysis of the results was performed by Minitab statistical software (version17) using one way analysis of variance and then Tukey's test ($p<0.05$).

Results and Discussion

- *Physicochemical characteristics of dried carrot pomace*

Moisture content of the original carrot pomace was 7.54 ± 0.07 g/100 g. The other physicochemical properties after drying process are summarized in Table 2. The results of Table 2 show a high protein and fiber content in DCP. The protein level in the whole carrot plant was previously reported in the range of 6.25-7.75 (g/100 dwb) for different cultivars (Sharma *et al*, 2012). Therefore, carrot pomace which included 10% dry weight of the carrot may be considered as a rich protein source. This result may be due to blanching process before juice extraction. It has been previously reported that during blanching, the main part of heat sensitive proteins may be denatured and left in the pulp (Bao & Chang, 1994). The crude fiber of the whole carrot has been reported in the range of 8.6-17.2 g/100 dwb, in previous research attempts (Holland *et al.*, 1991). Fiber is one of the well-known health promoting food components with recommended daily allowance established between 21-38 g for young and adults (men & women) (IFIC, 2008) and ketchup with the fiber-rich components, may be a promising method in providing the daily fiber requirement.

- Physicochemical properties of ketchup formulations

The results of physicochemical analysis of ketchup formulations are presented in Table 3. Syneresis was not observed in K_o as the control sample with the maximum levels of tomato paste (35%) and CMC (0.5%). The syneresis levels were not significantly changed, using carrot pomace powder (by max 1.4%) in ketchup formulations of K_1 and K_2 and lowering the tomato paste to 21% (K_8) and CMC to 0.3% (K_2).

According to the results of Table 3, tomato paste and CMC may be partially replaced by dried carrot pomace (DCP) along with glucose syrup without significant change in syneresis level. It means that the pectin content of carrot may cooperate with pectic compounds of tomato paste in order to provide a stable texture. In addition, since glucose syrup can usually increase the viscosity (Baker *et al*., 1997) it might also be considered as an important factor in preventing serum separation. However, these positive aspects were achieved for K_0-K_2 samples (Table 3). Therefore, by further reduction in the amounts of tomato paste (< 21%) and CMC (< 0.4%) there were significant increases in syneresis, in spite of the higher amounts of DCP (>1.4%) used.

Table 2. Physicochemical characteristics of dried carrot pomace (DCP)

Physicochemical properties	g/100 g of DCP (dwb)[1]
Protein	10.02 ± 0.06
Lipid	1.13 ± 0.01
Fiber	15.27 ± 0.48
Ash	5.5 ± 0.4
Pectin	5.58±0.1
Total phenolics (mg GAE/100 g)	1035.6 ± 345.6
L*	65.34±0.12
a*	14.76±1.02
b*	43.47±1.86
Yellow Index	95.03±8.09

[1] Results are expressed as mean ± standard deviation.

Table 3. Physicochemical properties of ketchup formulations with different formulations

Properties	K_0	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}
pH	3.63^{c}	3.65^{b}	3.67^{b}	3.62^{cd}	3.56^{e}	3.49^{f}	3.70^{a}	3.71^{a}	3.69^{a}	3.61^{d}	3.70^{a}
Total solid (%)	32.6^{d}	33.7^{bcd}	33.8^{bcd}	34.7^{abc}	34.9^{ab}	35.0^{ab}	33.3^{cd}	34.0^{bcd}	34.2^{bc}	35.2^{ab}	36.0^{a}
Brix (%)	32.1^{e}	33.1^{cd}	33.1^{cd}	33.8^{bc}	34.1^{ab}	34.1^{ab}	32.6^{de}	33.3^{bcd}	33.3^{bcd}	34.1^{ab}	34.8^{a}
Insoluble solids (%)	0.43^{b}	0.56^{a}	0.63^{a}	0.86^{a}	0.80^{a}	0.83^{a}	0.64^{a}	0.73^{a}	0.93^{a}	1.03^{a}	1.17^{a}
Viscosity (mpa.s)	2728^{a}	2612.7^{ab}	2037.3^{b}	1997.7^{b}	690.7^{f}	--	1476.2^{c}	1498.7^{bc}	1108^{e}	617.3^{f}	--
Synersis (%)	0.00^{k}	0.08^{k}	0.6^{k}	2.7^{jk}	13.6^{ij}	56.3^{a}	7.5^{j}	6.8^{j}	11.3^{ij}	28.9^{hi}	50.0^{c}
a*	24.9^{c}	31.4^{a}	25.2^{c}	26.2^{c}	24.3^{c}	23.8^{cd}	28.3^{b}	28.4^{b}	28.1^{b}	27.8^{b}	24.0^{c}
b*	13.2^{b}	14.5^{e}	13.3^{a}	12.9^{b}	11.4^{bc}	10.4^{c}	17.0^{d}	19.5^{c}	13.6^{b}	13.4^{b}	11.9^{b}
a*/b*	1.9^{ab}	2.2^{a}	1.9^{b}	2.0^{a}	2.1^{a}	2.3^{a}	1.7^{b}	1.5^{c}	2.0^{a}	2.1^{a}	2.0^{a}
L*	23.4^{d}	24.4^{b}	25.2^{ab}	23.2^{d}	28.1^{a}	28.2^{a}	23.9^{cd}	25.3^{ab}	26.2^{b}	26.6^{b}	27.6^{ab}
TCS[3]	22.07^{b}	22.06^{b}	22.35^{b}	24.22^{a}	21.25^{bc}	23.09^{ab}	20.90^{c}	18.57^{d}	24.04^{a}	24.16^{a}	22.11^{b}

[1] Results are expressed as mean ± standard deviation.
[2] Values with similar superscript letters represent no significant difference (p<0.05).
[3] Tomato catsup score: $TCS = -99.999 + 9.532\,a - 0.166\,a^2 - 0.936\,b$

Meanwhile, K_6, the sample formulated without CMC and with maximum levels of tomato paste and DCP, showed very good stability. It seems that pectin contents of raw materials may play somewhat more important role than CMC in providing a good texture for ketchup. Similar pattern has been observed for viscosity of the ketchup samples (Table 3). As K_1, K_2, K_6 and K_7, the DCP-containing samples, have produced the highest viscosity. Pectic compounds concentrations, pulp content and pectin / protein interactions have been identified as the most important factors in relation to viscosity and consistency of tomato products (Stoforos & Reid, 1992; Torbica *et al.*, 2016). The results of five different color characteristics (a*, b*, L*, a*/b* and tomato catsup score (TCS)) of the ketchup formulations are shown in Table 3. These results indicate that by reducing the tomato paste and increasing the water contents of the formulations, the lightness (L*) is increased. However, for commercial tomato-based products, including ketchup, two of the above parameters are usually considered as color indices (Bannwart *et al.*, 2008). Although, the tomato paste content is gradually reduced in the ketchup formulations, nevertheless the redness index (a*/b*) of most samples including: K_1, K_3, K_4, K_5, K_8, K_9, K_{10} are in the range of 2-2.2 and represents a top quality ketchup (Farahnaky *et al.*, 2008). Meanwhile the tomato catsup score (TCS) of these samples are also in the acceptable range. It means that, the redness of DCP could compensate the reduced level of tomato paste.

Based on the results obtained from physicochemical analysis of all these ketchup formulations, the K_0, K_1, K_2 and K_3 samples provide the highest viscosity, lowest syneresis and the best color characteristics, which qualify for more detailed analyses by the following tests:

-*Rheological analysis of the selected ketchup samples*

- *Flow behavior tests*

The results obtained from the flow behavior tests were fitted to Herschel-bulkley model and the rheological parameters are given in Table4. A pseudoplastic behavior (n= 0.54-0.8) has been observed with no significant difference in all the samples. As tomato ketchup is structurally a suspension-type system, a shear-thinning phenomenon might result from the orientation of the dispersed solid particles along the flow lines of mainly tomato and carrot fibers (Juszczak *et al.*, 2013). Bengtsson and Tornberg (2011) reported that the level of yield stress in fruits or vegetable fiber suspensions is decreased by increased amount of insoluble fiber. Thus, it may be expected that by adding the carrot pomace powder, the amount of insoluble pectin could be increased and reduces the yield stress as compared to the maximum tomato paste (K_0) sample. These differences are not evident in K_1, K_2, though in case of K_3, formulated with 2.1% DCP and 14% tomato paste, the yield stress is drastically decreased. It means that DCP by 1.4% (K_2) may be acceptable without undesirable changes in rheological properties as compared to K_0.

Table 4. Herschel-Bulkley parameters of the selected ketchup samples

Sample	τ_0 (Pa)	m ($Pa.s^n$)	n (-)	Thixotropic Area ($Pa.s^{-1}$)	Coefficient of Correlation (r)
K_0	76.94± 13.75^a	14.42±0.6^b	0.8±0.17^a	3176±2157^b	0.95±0.01^a
K_1	83.53±10.12^{ab}	16.17±0.47^b	0.66±0.06^a	3474±1599^{ab}	0.97±0.02^a
K_2	68.25± 5.24^{ab}	18.14±0.74^{ab}	0.59±0.04^a	4775±1155^{ab}	0.94±0.01^a
K_3	46.41± 1.33^b	24.78±0.7^a	0.54±0.01^a	9429.5±135.1^a	0.95±0.02^a

[1] Results are expressed as mean ± standard deviation.
[2] Values with similar superscript letters represent no significant difference (p<0.05).

The consistency coefficients (m) of the samples are in the range of 14.42-24.78 $Pa.s^n$ and K_3 formulation with the highest content of dried carrot pomace has shown the highest consistency. Rani and co-workers (1987) has revealed that the "m" values of tomato ketchup are highly influenced with the contents of pulp and pectin. It seems that this rheological parameter is also more related to water-insoluble pectin (Marsh *et al*. 1980). Hysteresis loop area (thixotropic area) has been also studied in our present research (Table 4). This rheological parameter is especially important for the ketchups packaged in plastic squeeze dispensers (Robinson, not dated) where lower thixotropic area is more preferred to provide rapid structural recovery once it is dispensed out of the bottle. According to the results of Table 4, K_1 is the sample with the lowest hysteresis loop area and exhibits the best stability for dispensing over food.

- *Carotenoid compounds*

Figure 1 represents a typical chromatographic profile of different carotenoid compounds in ketchup samples and the concentration of each compound in the selected samples is given in Table 5. According to the results, lycopene is the major carotenoid pigment along with lesser amounts of β-, γ- and ξ-carotene, phytofluene, and lutein. The total amounts of *cis* and all-*trans* isomers of β-, γ- and ξ-carotenes in K_1 as compared to K_0 were increased by 43.8%, 21.4% and 26.8%, respectively. Synergistic effect of antioxidative properties of lycopene and other carotenoids including β-carotene has been previously reported (Shi *et al*., 2004). Therefore, by using carrot pomace in tomato ketchup formulation not only good physicochemical characteristics but also improved nutritional/antioxidative properties may be provided.

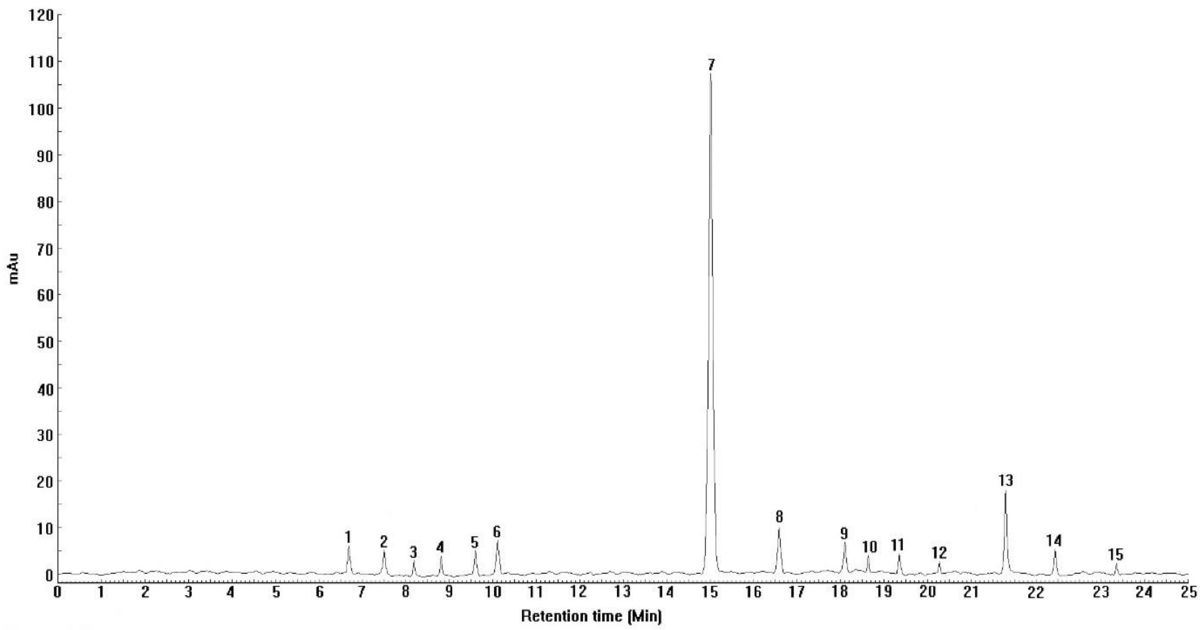

Fig. 1. A typical chromatographic profile of ketchup formulation.

(1: all-*tra*ns-anteraxanthin, 2: all- *trans*- lutein, 3: *cis*-lutein, 4: *cis*-zeaxanthin, 5: *cis*-lycoxanthin, 6: all-*trans*-lycoxanthin, 7: all-*trans*-lycopene, 8: *cis*-lycopene, 9: *cis*-γ-carotene, 10: all-*trans*-γ-carotene, 11: *cis*-ζ-carotene, 12: all-*tran*s-ζ-carotene, 13: all-*trans*-β-carotene, 14: all-*trans*-phytofluene, 15: *cis*-β-carotene)

Table 5. Carotenoids compounds concentrations (μg/g (dwb)) in ketchup samples

Peak n	RT[1] (min)	Carotenoid Compounds	Ketchup samples			
			K_0	K_1	K_2	K_3
1	6.63	all-*trans*-anteraxanthin	4.9	5.2	4.6	4
2	7.50	all- *trans*- lutein	3.71	3.96	4.42	4.81
3	8.23	*cis*-lutein	2.52	2.71	2.38	2.3
4	8.88	*cis*-zeaxanthin	3.86	3.52	3.4	3.07
5	9.66	*cis*-lycoxanthin	5.11	5.27	5.52	5.66
6	10.12	all-*trans*-lycoxanthin	11.66	11.2	10.41	9.83
7	15.17	all-*trans*-lycopene	5122	4940	4507	3938
8	16.65	*cis*-lycopene	24.7	26.1	20.2	15.1
9	18.14	*cis*-γ-carotene	5.12	5.7	6.46	7.23
10	18.63	all-*trans*-γ-carotene	2.91	3.36	3.6	3.88
11	19.37	*cis*-ζ-carotene	3.04	3.52	3.91	4.36
12	20.26	all-*trans*-ζ-carotene	1.92	2.03	2.26	2.51
13	21.84	all-*trans*-β-carotene	31.1	38.8	40.1	45.6
14	22.47	all-*trans*-phytofluene	5.74	5.89	5.58	5.32
15	23.32	*cis*-β-carotene	1.21	1.44	1.82	2.03

[1] Retention time

Conclusion

A promising physical interaction between pectic compounds of tomato paste and carrot pomace has been observed which could provide a new formulation of ketchup with stable texture and low syneresis as a good source of soluble and also non-soluble types of fibers. Increasing the redness index (a*/b*) in DCP-containing ketchup samples, showed another good physical interaction between the carotenoid compounds of tomato paste and carrot pomace. The best formulation may be introduced as K_1, containing 28% tomato paste, 3% glucose syrup, 0.4% CMC and 0.7% carrot pomace. It might be expected that an enhanced antioxidant activity can be observed in the presented carotenoid-fiber enriched ketchup due to the synergistic effect between lycopene and β-carotene that might be concerned with future research works.

Acknowledgement

Authors gratefully acknowledgeand thank the R&D center of Behrouz Food Industries (Tehran, Iran) for technical supports and Mr Asl Rahimi (Iran Polymer and Petrochemical Institute) for his helpful assistance and guideness concerned with the rheological analysis.

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