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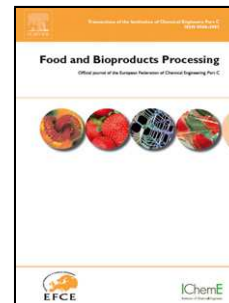
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Highlights

- Fresh tomato pomace was used to create ketchup with increased fibre content.
- Value-added ketchup contained 3.18 g/100 g of total dietary fibre.
- Rheological properties are in the limits of standard tomato products.
- Sensory properties of ketchup were similar to fresh tomato.
- Flavour, viscosity and colour could be modified according to consumers' demands.

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Nutritional, rheological, and sensory evaluation of tomato ketchup with increased content of natural fibres made from fresh tomato pomace

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Abstract

The aim of this study was to upgrade the tomato pomace by its conversion into a value added product – ketchup with increased content of natural fibre and optimal sensory properties, produced using standard processing equipment. Fresh tomato pomace was homogenized with other ingredients (water, sugar, salt, vinegar, glucose syrup, xanthan gum, guar gum) at 30 °C, then heated at 60 °C, packed and pasteurised. The end of process was determined according to Bostwick consistency value. Chemical composition, colour and rheological properties were measured at six production steps. Ketchup with increased nutritional value was compared with five commercial products in terms of colour, rheological and sensory properties. Tomato ketchup with increased content of natural fibre contained 3.18 g/100 g of total dietary fibre. Although the rheological properties of ketchup with increased fibre content depend mostly on total solids and insoluble particles content, they remained in the limits of standard tomato products. The obtained results are encouraging in terms of the applied technological process since it resulted in a product with sensory properties more similar to fresh or slightly processed tomato. Flavour, viscosity and colour of ketchup with increased nutritional value could be modified to meet the demands of consumers from different markets.

Key words: fresh tomato pomace, tomato ketchup, rheological properties, fibre, sensory properties

Introduction

Tomato (*Solanum lycopersicum* L.) is the second most important cultivated vegetable crop worldwide, especially in Mediterranean countries (Kalogeropoulos et al., 2012; Lenucci et al., 2013). All over the world, tomato is consumed mostly as fresh fruit, and after processing into various products such as tomato juice, paste, sauce, puree and ketchup (Capanoglu et al., 2008; Lenucci et al., 2013). The industrial processing of tomato is accompanied by the generation of waste – tomato pomace (seeds, pulp and skins) which comprise about 1–5% (w/w) of the total tomato processed into tomato products (Albanese et al., 2014; Capanoglu et al., 2008; Lenucci et al., 2013; Ruiz Celma et al., 2009). Large quantities of tomato processing by-products (mainly peels and seeds) are generated by tomato industrial processing plants, in which the most serious problem is the accumulation, handling, and disposal of processing wastes and by-products (Lenucci et al., 2013). On the other hand, they are available at no additional raw material cost, and their utilization can contribute to the creation of value added products and their commercial valorisation, which is the latest trend in development of functional food of vegetable origin (García Herrera et al., 2010; Sarkar and Kaul 2014). Attempts of tomato waste reuse streams resulted in producing of feed stuff and biocolourants (Laufenberg et al., 2003) or in adding of tomato pomace as a potential thickener to tomato ketchup as hydrocolloids replacer and improver of colour and texture of the product (Farahnaky et al., 2008). Also, the drying process (convection or freeze drying) has been shown to be the most favourable pre-treatment, followed by milling and frozen storage at $-20\text{ }^{\circ}\text{C}$ (O'Shea et al., 2012).

Dietary fibre includes a mixture of plant carbohydrate polymers, both oligosaccharides and polysaccharides, and is classified as soluble or insoluble in water (Johansson et al., 2000). Dietary fibre intake is similar in Mediterranean and non Mediterranean European countries (about 20 g per capita), but its origin is different – fruits and vegetables are the primary source in Mediterranean countries, while cereals dominate in other countries. In addition, dietary fibre from fruits and vegetables represent a carrier of bioactive compounds (vitamins, carotenoids, polyphenols), which are usually deficient in most diets (Goñi and Hervert-Hernández, 2011). According to Englyst and Hudson (1996), tomato contains 7.4% soluble and 11.4% insoluble fibres (% dry matter). Soluble fibres increase viscosity, while Insoluble fibres are characterised by their porosity and low density and diet supplemented with dietary fibre influences food to be low in calories, cholesterol and fat (Englyst and Hudson, 1996; Johansson et al., 2000). Insoluble and soluble fibres have different roles in disease prevention: insoluble fibre regulates intestinal functions and water absorption, while soluble fibre influences glucose absorption in the small intestine and reduces blood cholesterol (Yangilar, 2013). Therefore, dietary fibre could influence the reduction in the risk to the chronic diseases like cardiovascular disease, obesity, diabetes, and different types of cancer (Alvarado et al., 2001; Rodríguez et al., 2006). Moreover, tomato fibre is rich in minerals, such as K, Mg, Ca and low in Na, Fe and Zn (Navarro-González et al., 2011). Fruits and vegetables are the primary sources of pectin, soluble dietary fibre with health-enhancing properties, thought to lower blood cholesterol and delay gastric emptying

(Yangilar, 2013; O'Shea et al., 2012). Pectin plays an important role in the textural changes of fruits during heat treatment or other processing operations. Total pectin substances include protopectin and pectic acid partly esterified by methyl groups (Prasanna et al., 2007). Two major enzymes that degrade pectin are polygalacturonase (PG) and pectin methylesterase (PME). PG cleaves the polygalacturonic acid chain, reducing its length and thus decreasing the viscosity of tomato juice (Anthon et al., 2002). On the other hand, PME catalyzes the removal of the methyl groups, increasing the number of free carboxyl groups which can bind Ca^{2+} and cross-link pectin chains, leading to increased firmness of final product (Anthon et al., 2002; Cámara Hurtado et al., 2002). Protopectin is water-insoluble, high molecular weight pectin fraction which is converted during ripening, storage and processing operations into soluble polyuronides (Prasanna et al., 2007). Pectic substances have a major influence on the quality, stability, and viscosity of tomato ketchup (Sharoba et al., 2005).

Rheological properties of tomato products are considered as one of the most important quality attributes, since they influence product processing parameters, especially flow properties during transport, as well as consumers' acceptability. Beside agronomic (variety, maturity, etc.) and processing (heat treatment, mashing, storage, etc.) parameters, the differences in rheological behaviour are the consequence of specific tomato products structure. From a structural point of view, tomato products are dispersions consisting of particles suspended in a colloidal serum. While suspended particles (pulp) include aggregated or disintegrated cells and cell wall material such as cellulose, lignin, hemicelluloses and water-insoluble pectic materials, the continuous phase (colloidal serum) is mostly composed of water-soluble pectins and other tomato components soluble in aqueous solution (Bayod et al., 2007; Tiziani and Vodovotz 2005). Tomato ketchup represents a concentrated dispersion of insoluble matter in aqueous media, and due to its complex structure, it exhibits non-Newtonian, shear-thinning and time-dependent rheological behaviour with yield stress (Bayod et al., 2008, Koocheki et al., 2009; Sharoba et al., 2005).

Ketchup is one of the most popular tomato products in the global market and requires limited equipment and simple processing (Alam et al., 2009; Sharoba et al., 2005). In the production process, thickening agents are used for their ability to act as water binding and bodying agents (starch, carboxymethylcellulose, guar gum, xanthan gum), to increase the consistency, and to prevent serum separation from ketchup (Koocheki et al., 2009; Mert, 2012). From the consumers' point of view desirable characteristics of ketchup are intense red color, high consistency, sweet and tomato taste and spicy flavour (Agribusiness handbook 2009; Bannwart et al., 2008). In order to meet such consumers' expectations, avoid ratio change between insoluble-soluble fibres and change of physicochemical properties (Elleuch et al., 2011), as well as to reduce the production costs, the production process used in this study was created in way to avoid long heat treatment.

The aim of this study was to upgrade the tomato juice by-product (tomato pomace) by its conversion into value added product (tomato ketchup) with increased content of natural

fibre and acceptable rheological and sensory properties using standard processing equipment.

Material and Methods

Materials

Tomato pomace used for production of tomato ketchup with increased content of natural fibre was obtained from commercial tomato used in an industrial plant (Selenča, Serbia) for tomato juice production. Beside tomato pomace, this value added ketchup contained other ingredients, listed in Table 1.

Commercial white refined sugar, table salt and vinegar (9% acetic acid) were used in the ketchup production. Glucose syrup was purchased from Jabuka (Pančevo, Serbia), while guar and xanthan gum were purchased from Carl Roth (Karlsruhe, Germany). Ketchup produced in this research (P1 – Ketchup with increased fibre content) was compared in terms of rheological and sensory properties with five commercial products (P2 – “Gurman” professional mild ketchup (Serbia); P3 – “Polimark” mild ketchup (Serbia); P4 – “Tomatello” mild ketchup (Serbia); P5 – “M Tomato ketchup” (Poland); P6 – “Heinz” tomato ketchup (Netherlands)). The choice of commercial samples was based on the market survey conducted prior to sensory evaluation (unpublished results), which marked the above mentioned ketchups as the most popular in the Serbian market.

Table 1 Formulation of tomato ketchup with increased content of natural fibre

| Tomato ketchup | Quantity (kg)* |
|---|----------------|
| Fresh tomato pomace (peel, seed and pulp particles) | 67.49 |
| Water | 83.01 |
| Sugar | 10.08 |
| Salt | 2.33 |
| Vinegar | 3.10 |
| Glucose syrup | 4.65 |
| Xanthan gum | 0.13 |
| Guar gum | 0.13 |

*The quantity is referred to the minimum production batch of the industrial plant (150 kg of final product).

Production process

The production process scheme is represented in Fig. 1. Tomato pomace (tomato seeds, skins and pulp) was obtained during the production of tomato juice from tomatoes in a plant scale tomato processing line. In the homogenization process, ingredients were added successively, and after addition of the last portion of water and total quantity of tomato pomace, the mixture (step 1 – raw slurry) was subjected to vacuum evaporation at 60 °C (step 2 – semi-concentrated slurry).

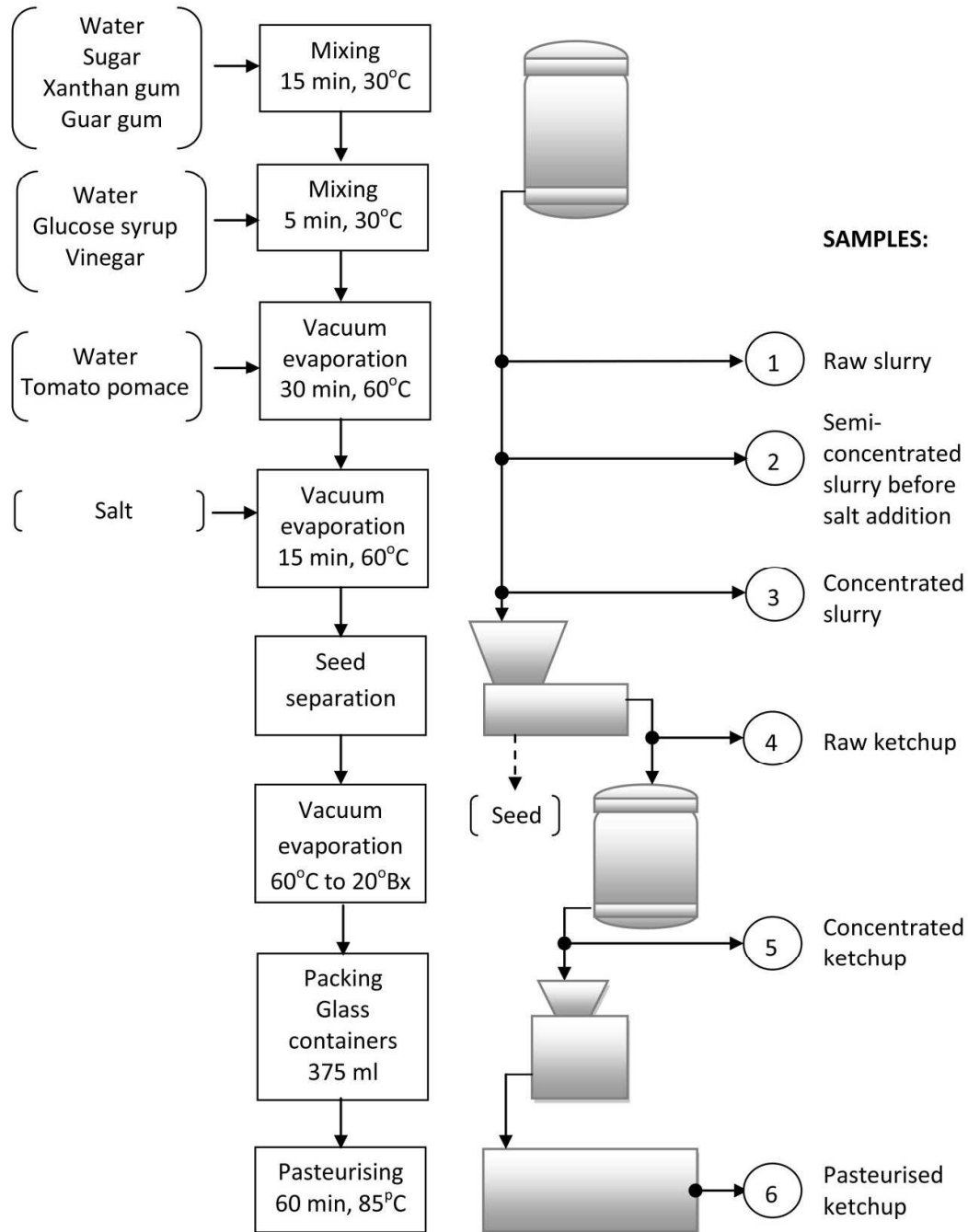


Fig. 1. Production process scheme of tomato ketchup with increased content of natural fibres

After salt addition (step 3 – concentrated slurry), further evaporation and seed separation, raw ketchup was obtained (step 4). Further vacuum evaporation was carried out until a consistency of 9 cm/30 s as measured by Bostwick consistometer was reached (step 5 – concentrated ketchup). Afterwards, the ketchup was packed and pasteurised (step 6).

Chemical analyses

Moisture content, total acids, protein, fat, and total dietary fibre content were analyzed according to Association Official of Analytical Chemists (AOAC 2000) methods 925.10, 925.53, 950.36, 935.38, and 985.29, respectively. Total sugars were determined by Schoorl method (AACC method 80-68 2000). Cellulose content was determined according to Serbian regulative (Regulation of methods of physical and chemical analysis for quality control of grain, milling and bakery products, pasta and quickly frozen dough 1988). Pectin, pectic acids, and protopectin content were determined spectrophotometrically by carbazole method (Regulation of methods of sampling, physical and chemical analysis for quality control of fruit and vegetable products 1983). Total soluble solids (TSS) and pH value were measured instrumentally using table refractometer (ATR ST Plus, Schmidt + Haensch, Germany) and a pH meter with temperature probe (Denver Instrument, USA) in previously filtered samples. In order to determine sodium content all samples were prepared with use of closed vessel microwave oven (Ethos Milestone, Italy) in 7 ml HNO₃ and 7 ml H₂O₂. Determination of sodium was performed on atomic absorption spectrophotometer SpectrAA-10 (Varian, Australia) with addition of caesium solution (EN 15505 CEN/TC 275 , 2008). All analyses were performed in triplicate.

Rheology analysis

Rheological characterization of tomato ketchup samples was performed at 25 °C, with a Haake MARS rheometer (Thermo Scientific, Karlsruhe, Germany).

Flow curve measurements

The cylinder sensor system Z20 DIN (bob diameter = 20 mm and inner cup diameter = 21.7 mm, gap 4.20 mm) was used for thixotropic loop measurements. The absence of the slip effect was firstly confirmed by measuring the same samples with a serrated cylinder system Z38S/Z43S. Thixotropic loop measurements were carried out by first increasing the shear rate linearly from 0 to 100 s⁻¹ for 120 s, then maintaining it at 100 s⁻¹ for 120 s, and finally decreasing it linearly back to 0 s⁻¹ for additional 120 s. The hysteresis loop areas, *S*, were obtained as the difference between the surface area enclosed by the up (ascending) curve and the surface area enclosed by the down (descending) curve in the shear rate range considered (Eq. 1).

$$\text{Hysteresis loop area } (S) = S_{up} - S_{down} \quad (1)$$

where *S*_{up} and *S*_{down} (Pa/s) are obtained surface areas under the ascending and descending flow curves, respectively.

Further quantitative comparison of samples was performed by fitting the experimental data for descending curve to power law equation (Eq. 2).

$$\tau = K\dot{\gamma}^n \quad (2)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K the consistency index (Pa s^n) and n the flow index. Apparent viscosity was recorded from the flow curve as a mean value at 100 s^{-1} .

Yield stress measurements

In order to determine yield stress, stress-controlled (CS) measurements (deformation/stress relationship) were performed using the serrated plates sensor system PP35S (35 mm diameter and 1 mm gap) to avoid slippage. After a waiting period of 300 s, a logarithmical CS ramp in a shear stress range between 0.5 Pa and 100 Pa was measured within 180 s to obtain 50 data points. The intersection of the linear segments in log-log plot of deformation versus stress values indicated the transition from elastic behaviour to flow and was considered as the yield stress value.

Temperature sweep measurements

In order to detect changes in the rheological properties of ketchup samples during thermal treatment, temperature sweep tests were performed using a Haake MARS rheometer (Thermo Scientific, Karlsruhe, Germany) fitted with a serrated plates measuring geometry PP35S (35 mm diameter and 1 mm gap). During the measurements the temperature of the peltier plate, on which the samples were placed, was increased from 25 to 90 °C in 600 s, at a fixed stress of 1 Pa, with a frequency of 1 Hz. A cooling step followed the heating procedure at the same conditions in the temperature range of 90 - 25 °C.

Solvent traps were used in all of the tests in order to prevent sample drying. All of the rheological measurements were performed in triplicates.

Bostwick consistency

Consistency of final product was checked by Bostwick consistometer. The temperature of

Basic statistics was applied in order to calculate mean values and standard deviation for chemical, rheological and colour parameters, and all results are represented as mean \pm standard deviation. The data obtained from the sensory analysis of different ketchups was converted into matrix of selected sensory attributes and ketchup samples and Principal Component Analysis (PCA) was carried out using XLSTAT statistical software suite for Microsoft Excel, version 2012.2.02 (Addinsoft, New York, NY, USA).

Results and Discussion

The production process of ketchup from tomato pomace was created due to aspirations of sustainability of tomato processing. The formulation was developed on the basis of authors' experience in creating formulations for the fruit and vegetable processing industry and harmonized with regulation for ketchup quality (Table 1). In addition, it was adjusted to the process equipment in the industrial plant where the ketchup was produced. The "cold-break" process, during which the homogenized tomatoes are heated only to around 60 °C, has been chosen in order to avoid long heat treatment and losses of natural tomato colour and fresh flavour (Anthon et al., 2002; Goodman et al., 2002). However, during the cold break process pectolytic enzymes might not be completely inactivated, resulting in decreased viscosity of ketchup (Anthon et al., 2002; Goodman et al., 2002). Therefore thickeners (xanthan and guar gums) had to be added in order to ensure its desirable level.

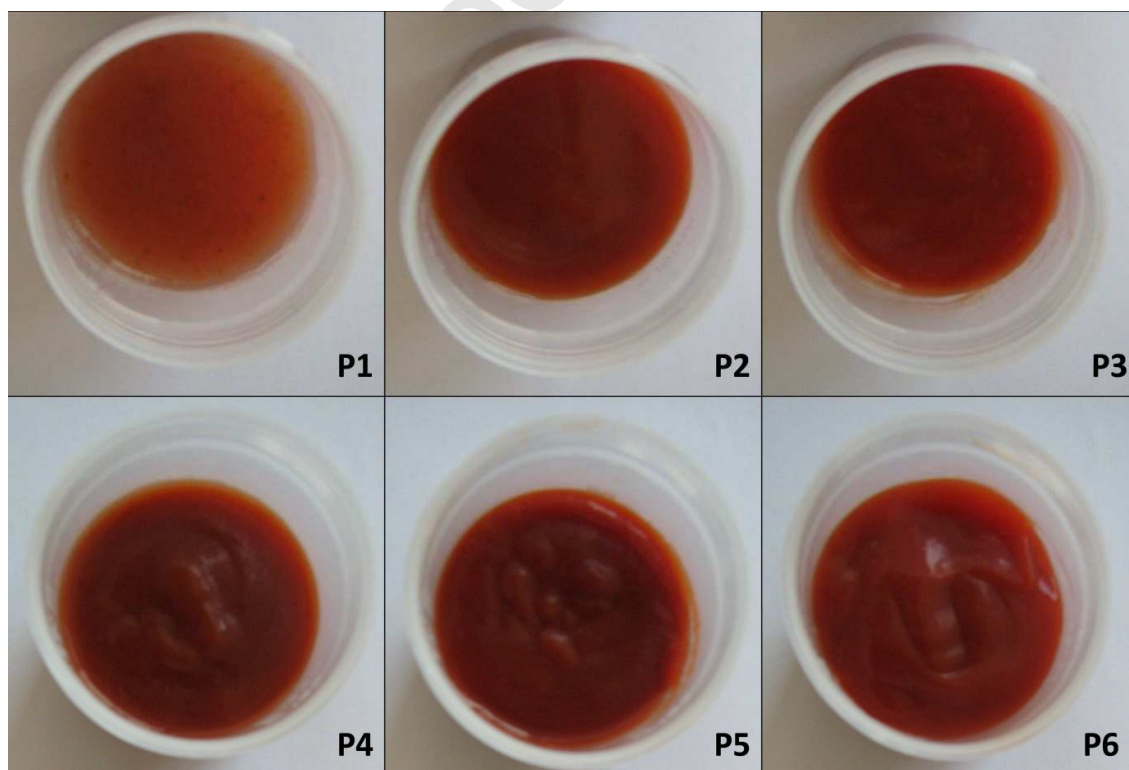


Fig. 2. Tomato ketchup with increased content of natural fibres (P1) and commercial ketchups (P2-P6)

The combination of chosen raw materials and technological process provides low cost tomato product with added value, since according to Regulation EC No 1924 (2006) on nutrition and health claims made on foods, a food can be referred to as a “source of fibre” or “containing fibre”, provided that the product contains more than 3 g/100 g or 1.5 g/100 kcal of dietary fibre. Obtained value added tomato ketchup (3.18 g/100 g and 3.88 g/100 kcal) was compared with commercial ketchups from Serbian market in order to explore its similarity with product already present at the market (Fig. 2).

Physico-chemical properties

Physico-chemical properties of tomato pomace, raw slurry (step 1) and pasteurized ketchup (step 6) are presented in Table 2.

The moisture level decreased during processing from $\approx 90\%$ to $\approx 78\%$, which is almost the same value obtained for commercial ketchups (67.42-79.02%). When the content of total soluble solids reached 15 ± 1 °Brix, seeds were separated. Total sugar content in ketchup with increased fibre content was 17.26%, similarly to commercial ketchups (12-18%), while final pH values and titratable acidity indicated lower acidity in comparison with commercial ketchups produced in Germany and Egypt (Sharoba et al., 2005). Value added ketchup had a pH value lower than 4.0, which is generally considered as a threshold for product stability (Rajchl et al., 2010), and further addition of acids to satisfy the demands of other markets is also possible. It should also be pointed out that value added ketchup had a lower sodium content and energy value than defined in USDA National Nutrient Database for Standard Reference, indicating that the obtained product could be further improved in these directions. Generally, these slight differences in content of basic nutrients between ketchups could be attributed to different formulation of ketchup with increased content of fibres in comparison to commercial ketchups.

Table 2 Change of basic physico-chemical properties during ketchup processing

| Sample | Moisture (%) | Sodium (mg/kg) | TSS (°Brix) | pH | Total acids (as citric acid %) | Total sugars (%) | Dietary fibre (%) | Cellulose (%) | Energy value per 100 g (kcal) |
|---------------|--------------|----------------|-------------|-----------|--------------------------------|------------------|-------------------|---------------|-------------------------------|
| Tomato pomace | 85.45±0.99 | 523±33 | - | 3.91±0.01 | 0.44±0.00 | 4.31±0.00 | 9.31±0.11 | 2.02±0.01 | - |
| Step 1 | 90.89±0.25 | 282±29 | 8.25±0.07 | 4.06±0.00 | 0.35±0.00 | 7.12±0.35 | - | - | - |
| Step 6 | 78.29±0.11 | 7052±212 | 20.45±0.13 | 3.85±0.00 | 0.87±0.00 | 17.26±0.35 | 3.18±0.04 | 0.11±0.01 | 82 |

* step 1 – raw slurry, step 6 – pasteurized ketchup

Results are expressed as mean±standard deviation ($n = 3$).

The dietary fibre content determined mathematically in the final product would be 4.19%; however, it is 3.18% due to seed separation. Value added ketchup had a more than ten times higher content of total dietary fibre than those defined in USDA National Nutrient

Database for Standard Reference. Regarding certain types of dietary fibres, it should be noted that cellulose is almost completely removed during the production process. Due to their significance for rheological properties and product stability, change of content of individual pectic substances during production was investigated (Fig. 3). During processing, content of total pectic substances increased with evaporation time and decreased after the step of seed separation (Fig. 3, Step 4). Further evaporation also increased total pectic content (Fig. 3, Steps 5 and 6). In comparison with commercial ketchups produced by standard production process, which contained about 3.5-4% of total pectic substances (Anthon et al., 2008), the produced value added ketchup contained about ten times less concentration (Fig. 3).

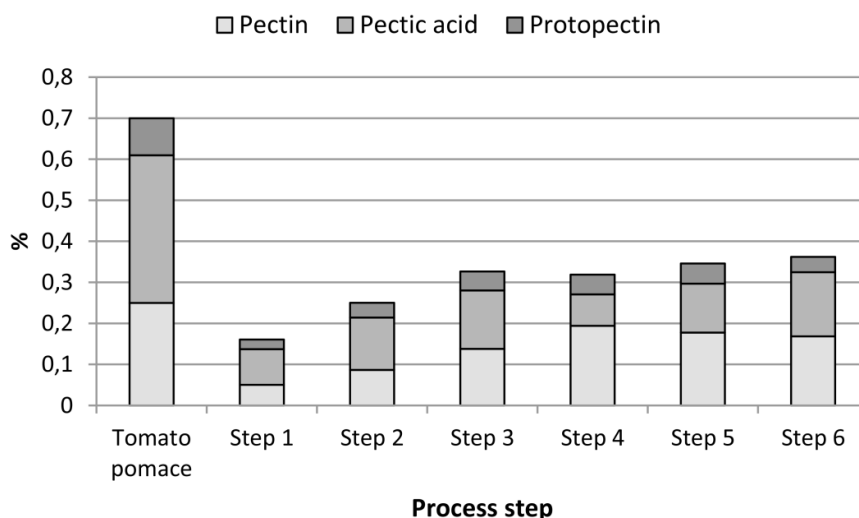


Fig. 3. Change of content of individual pectic substances during production (step 1 – raw slurry, step 2 – semi-concentrated slurry before salt addition, step 3 – concentrated slurry, step 4 - raw ketchup, step 5 – concentrated ketchup, step 6 (P1) – pasteurized ketchup)

Considering individual pectic substances, tomato pomace contained more pectic acids than pectin (methylated polygalacturonic acid) (Fig. 3). During processing, this ratio is changed in favour of pectin. Rapid decrease of pectic acid content between steps 3 and 4 could be explained by its lower solubility in water and therefore its retention on the sieve during seed separation (Fig. 3, Step 4). Further simultaneous increase of pectic acid content and decrease of pectin content might be explained by pectin hydrolysis by polygalacturonase (PG) and pectin methylesterase (PME) which could occur at lower temperatures used in this process (Anthon et al., 2002). Protopectin content increased during processing with increase of dry matter content, but dropped after pasteurization, possibly due to its degradation at higher temperatures (Cámara Hurtado et al., 2002). The enzymes were deactivated by pasteurization, which therefore provided both rheological and microbiological stability

during storage (Potter 2013). Although total fibre content was increased, the amount of gelling substances, i.e. pectic substances was too low for obtaining the desirable consistency defined as Bostwick value of 9 cm/30 s by the industrial producer of frozen pizza, so the gums were added.

Rheological properties

The influence of processing conditions on the flow behaviour of value added ketchup was also examined (Fig. 4) and the properties of final product (step 6 = P1) were compared to commercially available ketchups (P2-P6).

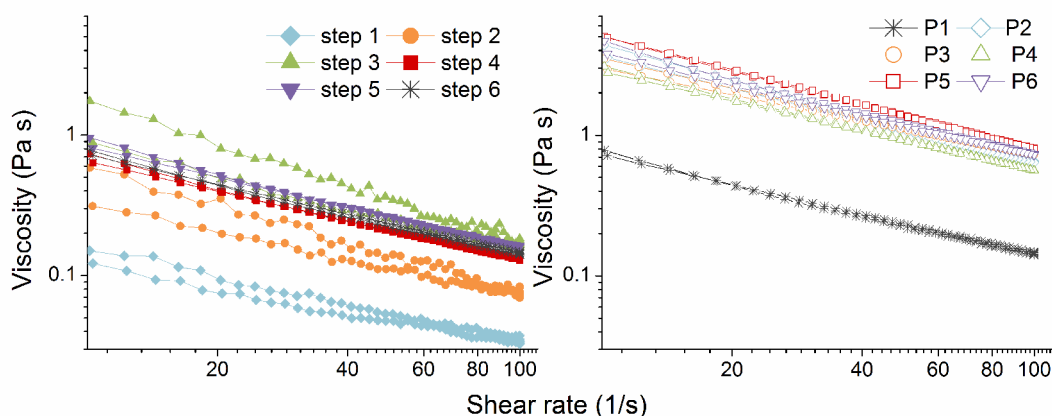


Fig. 4. Viscosity vs. shear rate of different ketchup processing steps (step 1 – raw slurry, step 2 – semi-concentrated slurry before salt addition, step 3 – concentrated slurry, step 4 – raw ketchup, step 5 – concentrated ketchup, step 6 (P1) – pasteurized ketchup (value added ketchup) and comparison with commercial products (P2-P6)

Overall, the examined tomato ketchups exhibited thixotropic behaviour over the whole range of shear rate studied ($0\text{--}100\text{ s}^{-1}$). These results were in agreement with other authors who also reported shear thinning and thixotropic behaviour in tomato products (Tiziani and Vodovotz, 2005). The flow curves were fitted with the power law model by calculating the consistency coefficient and flow behaviour index (Table 3), since this model turned out to be best fitted to the experimental shear stress–shear rate data ($r > 0.97$).

During mixing and heating (steps 1-3) the consistency increased (indicating that samples became more viscous), whereas the flow behaviour index decreased (indicating the samples became more shear-thinning). The apparent viscosity of the samples reported at a fixed shear rate (100 s^{-1}) increased with increasing processing time, with a step increase occurring between 30 and 45 minutes of processing.

The viscosity increase was influenced by total solid content increase during processing (Table 2) as a function of juice dehydration/concentration. Viscosity dependence of ketchup on pulp or total solids content and naturally occurring pectic substances was already noticed by Sanchez et al. (2002) and Koocheki et al. (2009). The sample, which was heated and mixed for 45 minutes, was also characterized by the highest value of the thixotropic loop

area, an indicator of structural destruction of the system. During mixing and heating, shear forces led to decrease in pulp, seed and peel particles sizes which yields a larger interfacial area and stronger interparticle interactions resulting in increased viscosity and thixotropy. Moreover, processing conditions changed particles shape from spheroidal to elongated leading to greater resistance to flow, as reported by Sanchez et al. (2002).

Table 3 Changes in flow curve parameters during ketchup processing and comparison with commercial products*

| Sample | Yield stress, τ_0 (Pa) | Apparent viscosity at 100 s^{-1} (Pa s) | Hysteresis loop area, S (Pa/s) | Consistency index, K (Pa s^n) | Flow behaviour index, n (-) | Coefficient of correlation, r |
|-------------|-----------------------------|---|----------------------------------|--|-------------------------------|---------------------------------|
| Step 1 | n.d. | 0.033±0.002 | 23.33±1.72 | 0.402±0.014 | 0.452±0.012 | 0.9937 |
| Step 2 | 2.24±0.01 | 0.077±0.004 | 134.05±17.04 | 1.385±0.129 | 0.370±0.039 | 0.9861 |
| Step 3 | 3.54±0.42 | 0.198±0.016 | 483.65±56.50 | 6.170±0.759 | 0.224±0.002 | 0.9709 |
| Step 4 | 4.35±0.13 | 0.130±0.001 | 25.60±0.06 | 3.192±0.017 | 0.302±0.003 | 0.9993 |
| Step 5 | 4.81±0.08 | 0.157±0.005 | 24.56±2.18 | 3.877±0.323 | 0.303±0.010 | 0.9994 |
| Step 6 (P1) | 4.29±0.10 | 0.137±0.008 | 0 | 3.387±0.263 | 0.307±0.003 | 0.9995 |
| P2 | 20.59±0.62 | 0.646±0.006 | 449.65±41.93 | 20.285±0.120 | 0.247±0.000 | 0.9996 |
| P3 | 11.36±0.45 | 0.735±0.008 | 316.45±14.64 | 11.955±0.191 | 0.390±0.001 | 0.9999 |
| P4 | 14.46±1.43 | 0.556±0.008 | 121.50±15.13 | 14.425±0.219 | 0.293±0.007 | 0.9993 |
| P5 | 46.36±1.05 | 0.803±0.006 | 0 | 31.110±0.636 | 0.204±0.005 | 0.9960 |
| P6 | 49.82±0.65 | 0.741±0.008 | 326.80±63.64 | 20.415±0.530 | 0.273±0.003 | 0.9952 |

* step 1 – raw slurry, step 2 – semi-concentrated slurry before salt addition, step 3 – concentrated slurry, step 4 – raw ketchup, step 5 – concentrated ketchup, step 6 (P1) – pasteurized ketchup (value added ketchup), P2-P6 – commercial ketchups

Results are expressed as mean±standard deviation ($n = 3$).

Further processing involved seed separation (step 4), an operation during which aggregates and interactions between seeds and other particles were disrupted. This resulted in transition from a highly thixotropic to an almost shear thinning behaviour as well as decrease in system viscosity although total solid contents slightly increased. Repeated evaporation, which followed seed separation (step 5), influenced the increase in sample consistency and viscosity due to an increase in total soluble solids content. Product pasteurization resulted in a slight decrease in sample consistency and viscosity (step 6) in comparison to those observed in step 5, although rise in temperature led to a significant increase in total soluble solids content. Previous investigations of xanthan gum and guar gum mixtures showed that there is a rapid decrease of viscosity at higher temperatures (Xue and Sethi, 2012). In addition, at lower temperature xanthan gum molecules exist as a double helix, but it is converted into disordered coil at higher temperature (Renou et al., 2013; Xu et al., 2013). Namely, the semi-solid behaviour of ketchup is not only influenced by the content and type of dispersed and soluble material, but it is the result of a complex interaction between the pulp, soluble pectin, added hydrocolloids, soluble solids, organic acids and the high volume concentration of particles (Sharoba et al., 2005).

Yield stress measurements showed that this system parameter (the stress required to initiate flow of the material) was dominated by the content of total solids, as well as the interaction among the pectin, added hydrocolloids, soluble solids, organic acids and particles during processing.

Changes in storage (G') and loss (G'') modulus with temperature, during ketchup processing are presented in Fig. 5.

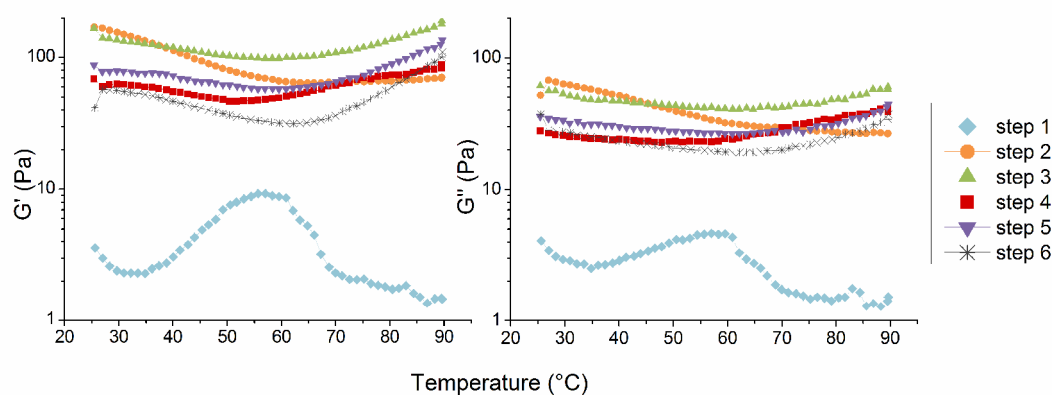


Fig. 5. Changes in system viscoelasticity with temperature in different ketchup processing steps (step 1 – raw slurry, step 2 – semi-concentrated slurry before salt addition, step 3 – concentrated slurry, step 4 - raw ketchup, step 5 – concentrated ketchup, step 6 – pasteurized ketchup)

Concerning the produced tomato ketchup prepared in this study, the highest elastic modulus (G' value) was achieved in the sample heated and mixed for 45 minutes, at 60 °C. The elastic modulus increased along with the increase in the content of total solids as water content was reduced during processing. This is the consequence of seed separation after 45 min of evaporation which significantly disrupted the structure and removed a large portion of insoluble particles. Insoluble fiber fraction increased the viscosity of ketchup by its water-holding capacity although it does not participate in the formation of the gel structure (Javanmard and Endan, 2010).

The changes in the elastic modulus, determined using dynamic oscillation tests, were in accordance with those of viscosity and consistency ~~followed by flow curve measurements~~. The mechanical spectra recorded for the raw formulation (step 1), ~~which reflected the whole processing scheme~~, has also pointed out that the most dominant elastic properties could be expected at the temperature of 60 °C, while further temperature increase will yield less elastic systems.

In comparison to commercial ketchups, tomato ketchup prepared in this study from tomato processing industry by-products, was characterized by lower viscosity and yield stress values. It is necessary to highlight that consistency, and therefore the viscosity of ketchup described in this paper, was adjusted according to the demands of producers of frozen pizza

from Italy. For the purpose of the standard manufacturing process in industrial conditions on the existing equipment, it was necessary to adjust the consistency of ketchup to 9 cm/30 s as by Bostwick consistometer. This consistency caused that the viscosity of the produced ketchup corresponded to the one characteristic for tomato sauce, which in the case of independent marketing had to be packed in jars. However, the correction of the production process in the direction of dry matter increase or the correction of the formulation in the direction of hydrocolloid content increase could provide a viscosity of the final product as typical for the ketchup packed in tubes.

Colour properties

Different colour parameters were measured during production of ketchup with increased fibre content in order to determine whether the chosen technological process lead to significant loss of red colour. The hue angle showed a trend of transition from red colour – raw slurry to orange red colour – pasteurized ketchup (Fig. 6.a). Similarly, Barreiro et al. (1997) observed increase in hue angle caused by thermal degradation of tomato double concentrate. Furthermore, total colour change (ΔE), which indicates the degree of colour difference between two samples, was calculated for production steps 2-6 in relation to the process step 1 (raw slurry). The obtained values were: 1.72 (step 2), 2.88 (step 3), 2.43 (step 4), 1.76 (step 5), and 3.56 (step 6). The greatest total colour change was observed after the pasteurization (step 6), which could be explained by thermal degradation of carotenoids, the Maillard reaction, and oxidation of ascorbic acid (Barreiro et al., 1997). This was the only sample whose colour difference in comparison with the raw slurry was obvious to the human eye. However, since this difference was not pronounced (only slightly higher than 3), it was decided not to add colour enhancers to the formulation. The colour of the commercial samples used in sensory evaluation was also measured in order to compare their values with produced value added ketchup (Figure 6b).

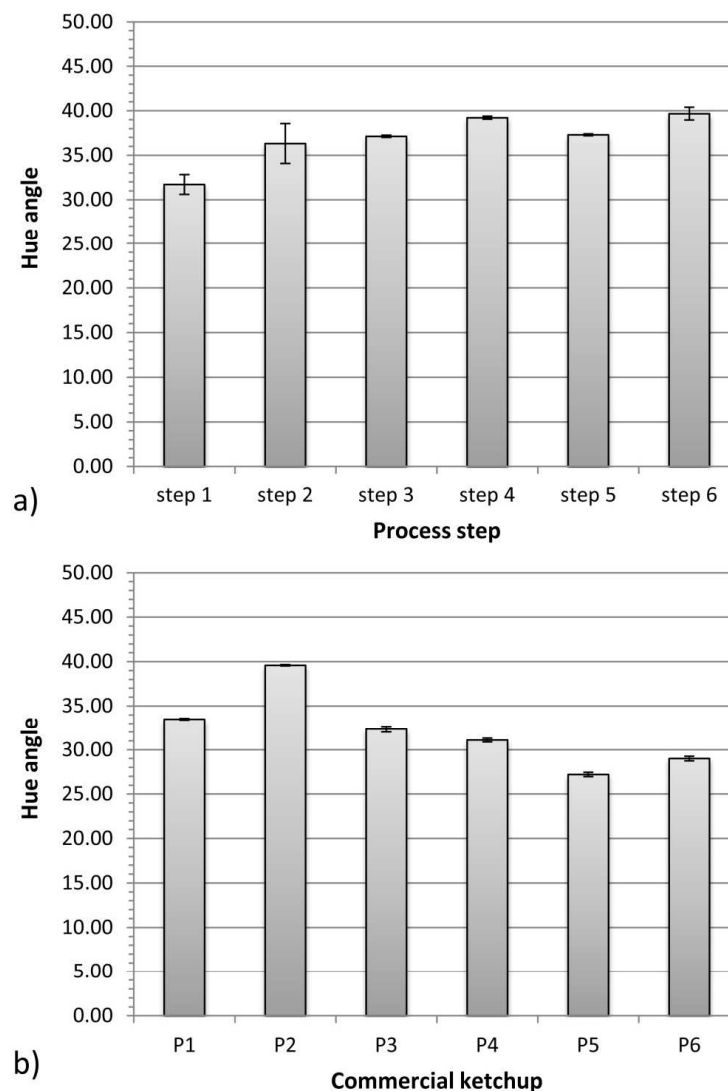


Fig. 6a,b. Change of hue angle values during production of tomato ketchup with increased content of natural fibres (step 1 – raw slurry, step 2 – semi-concentrated slurry before salt addition, step 3 – concentrated slurry, step 4 - raw ketchup, step 5 – concentrated ketchup, step 6 (P1) – pasteurized ketchup) (a); comparison of P1 hue angle value with commercial products (P2-P6) (b)

Sensory properties

The list of descriptors with definitions is given in Table 4. The relationship between the selected sensory attributes and evaluated ketchup samples were visualized by loading and score plots (Fig. 7.a,b). The first two principal components explained 85.07% of the total variability. The plots show that the chosen sensory descriptors enabled a clear discrimination between ketchup samples wherein those that described fresh tomato odour and flavour have been found most influential for such neat separation of our sample (P1). On the other hand, colour and highly expressed spicy flavour and odour have been most important descriptors for discrimination among commercially available ketchup samples.

Table 4 Sensory descriptors and definitions in the sensory analysis of the tomato ketchup samples

| Descriptor | | Definition |
|------------|----------------------|---|
| Colour | Intensity of redness | Evaluation of the red colour intensity. |
| Texture | Viscosity | Degree of resistance to flow. Evaluated by the rate of flow of liquid when sample is poured from a spoon. |
| Taste | Salty | Basic taste produced by a sodium chloride perceived on the tongue. |
| | Sour | Basic taste produced by acid that is perceived on the tongue. |
| | Sweet | Basic taste produced by sugars and sweeteners perceived on the tongue. |
| | Aftertaste | Taste lingering in the mouth after the ketchup was tested. |
| Flavour | Spicy | Aromatics associated with a variety of spices such as basil, pepper, cinnamon, thyme, etc. |
| | Tomato | Aromatics associated with fresh tomato. |
| Odour | Spicy | Odours associated with various spices evaluated by smelling. |
| | Tomato | Odours associated with fresh tomato evaluated by smelling. |

The sample having the most noticeable spicy odour is P2 (due to the presence of cinnamon), while the sample with the most intense red colour was P5. This is in accordance with instrumentally measured hue angle values, which was the lowest for this sample indicating more prominent red hue (Fig. 6b). Since the aim was to closely match the sensory properties of standard raw material used in ketchup production (tomato concentrate) without resemblance to tomato waste, the obtained results are encouraging in terms of the applied technological process because the obtained product possesses sensory properties more similar to fresh or slightly processed tomato. It should be taken into account that consumers' preference of a certain product is susceptible to the influence of ethnicity, socioeconomic status, education, dietary habits, gender and age (Claybon and Barringer, 2002; Devine et al., 1999). Therefore tomato ketchup with increased content of natural fibres is suitable for sensory and rheological adjusting to meet demands of different markets. This means that it could be modified in order to be more viscous, red or spicy according to preference of consumers from certain markets.

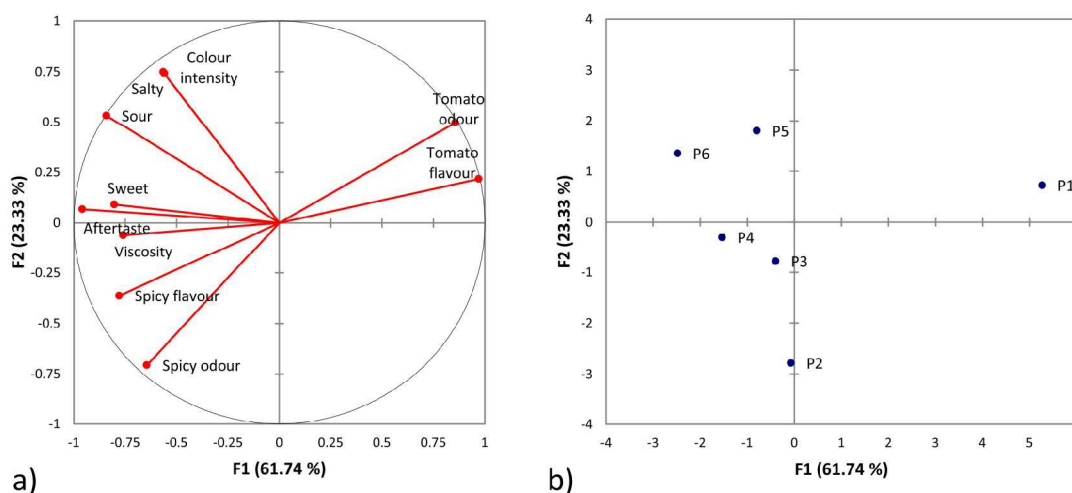


Fig. 7a,b. Loading (a) and score (b) plots of the first two principal components; P1 – value added ketchup, P2-P6 – commercial ketchups

Conclusion

Fresh tomato pomace was upgraded into a value added product – of tomato ketchup with increased content of natural fibres using standard processing equipment. The value added ketchup contained 3.18 g/100 g of total dietary fibre and therefore could be labelled as a “source of fibre”. Although the rheological properties of the ketchup with increased fibre content depend mostly on total solids and insoluble particles content, they remained in the limits of standard tomato products. The results of sensory analysis indicate that tomato odour and flavour were the most important for clear separation of the value added ketchup. The obtained results are encouraging in terms of the applied technological process since it resulted in a product with sensory properties more similar to fresh or slightly processed tomato. Flavour, viscosity and colour of ketchup with increased fibre content could be modified to meet the demands of consumers from different markets.

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References:

- AACC (2000). Approved methods of the American Association of Cereal Chemists (10th ed.). St. Paul, MN, USA.
- Agribusiness handbook (2009). Fruit and vegetable processing, FAO, Rome, Italy.
- Alam, K., Ahmed, M., Akter, S., Islam, N., & Eun, J-B. (2009). Effect of Carboxymethylcellulose and Starch as Thickening Agents on the Quality of Tomato Ketchup. *Pakistan Journal of Nutrition*, 8, 1144-1149.
- Albanese, D., Adiletta, A., D’Acunto, M., Cinquanta, L., & Di Matteo, M. (2014). Tomato peel drying and carotenoids stability of the extracts. *International Journal of Food Science and Technology*, 49, 2458–2463.
- Alvarado, A., Pacheco-Delahaye, E., & Hevia, P. (2001). Value of a tomato byproduct as a source of dietary fiber in rats. *Plant Foods for Human Nutrition*, 56, 335–348.
- Anthon, G. E., Sekine, Y., Watanabe, N., & Barrett, D. M. (2002). Thermal inactivation of pectin methylesterase, polygalacturonase, and peroxidase in tomato juice. *Journal of Agricultural and Food Chemistry*, 50, 6153-6159.

- AOAC International (2000). Official Methods of Analysis of Association of Official Analytical Chemists, (17th ed.). Arlington, Virginia, USA.
- Bannwart, G. C. M-C., Bolini, H. M. A., Toledo, M. C-F., Kohn, A. P. C., & Cantanhede, G. C. (2008). Evaluation of Brazilian light ketchups II: quantitative descriptive and physicochemical analysis. *Ciência e Tecnologia de Alimentos*, 28, 107-115.
- Barreiro, J. A., Milano, M., & Sandoval, A. J. (1997). Kinetics of colour change of double concentrated tomato paste during thermal treatment. *Journal of Food Engineering*, 33, 359-371.
- Bayod, E., Månsson, P., Innings, F., Bergenståhl, B., & Tornberg, E. (2007). Low shear rheology of concentrated tomato products. Effect of particle size and time. *Food Biophysics*, 2, 146-157.
- Bayod, E., Willers, E. P., & Tornberg, E. (2008). Rheological and structural characterization of tomato paste and its influence on the quality of ketchup. *LWT-Food Science and Technology*, 41, 1289-1300.
- Belović, M., Pestorić, M., Mastilović J., & Kevrešan, Ž. (2012). Identification and selection of the descriptors for establishing a sensory profile of tomato by a multidimensional approach. *Food and Feed Research*, 39, 33-39.
- Cámara Hurtado, M., Greve, L. C., & Labavitch, J. M. (2002). Changes in cell wall pectins accompanying tomato (*Lycopersicon esculentum* Mill.) paste manufacture. *Journal of Agricultural and Food Chemistry*, 50, 273-278.
- Capanoglu, E., Beekwilder, J., Boyacioglu, D., Hall, R., & de Vos, R. (2008). Changes in Antioxidant and Metabolite Profiles during Production of Tomato Paste. *Journal of Agricultural and Food Chemistry*, 56, 964–973.
- Claybon, K. T., & Barringer, S. A. (2002). Consumer acceptability of color in processed tomato products by African-American, Latino and Prototypical consumers. *Journal of Food Quality*, 25, 487-498.
- Devine, C. M., Sobal, J., Bisogni, C. A., & Connors, M. (1999). Food Choices in Three Ethnic Groups: Interactions of Ideals, Identities, and Roles. *Journal of Nutrition Education*, 31, 86-93.
- Elleuch, M., Bedigian, D., Roiseux, O., Besbes, S., Blecker, C., & Attia, H. (2011). Dietary fibre and fibre-rich by-products of food processing: Characterisation, technological functionality and commercial applications: A review. *Food Chemistry*, 124, 411–421.
- EN 15505 CEN/TC 275 (2008). Foodstuffs - Determination of trace elements - Determination of sodium and magnesium by flame atomic absorption spectrometry (AAS) after microwave digestion. European Committee for Standardization, Brussels, Belgium.
- Englyst, H. N., & Hudson, G. F. (1996). The classification and measurement of dietary carbohydrates. *Food Chemistry*, 57, 15–21.

- Farahnaky, A., Abbasi, A., Jamalian, J., & Mesbahi, G. (2008). The use of tomato pulp powder as a thickening agent in the formulation of tomato ketchup. *Journal of Texture Studies*, *39*, 169–182.
- Francis, F. J., & Clydesdale, F. M. (1975). Food colourimetry: Theory and applications. Westport, Connecticut: The Avi Publishing Company, Inc.
- García Herrera, P., Sánchez-Mata, M. C., & Cámara, M. (2010). Nutritional characterization of tomato fiber as a useful ingredient for food industry. *Innovative Food Science and Emerging Technologies*, *11*, 707–711.
- Goñi, I., & Hervert-Hernández, D. (2011). By-Products from Plant Foods are Sources of Dietary Fibre and Antioxidants, Phytochemicals - Bioactivities and Impact on Health, Prof. Iraj Rasooli (Ed.), ISBN: 978-953- 307-424-5, InTech, Available from: <http://www.intechopen.com/books/phytochemicals-bioactivities-and-impacton-health/by-products-from-plant-foods-are-sources-of-dietary-fibre-and-antioxidants>
- Goodman, C. L., Fawcett, S., & Barringer, S. A. (2002). Flavor, Viscosity, and Color Analyses of Hot and Cold Break Tomato Juices. *Journal of food science*, *67*, 404-408.
- Hongsoongnern, P., & Chambers, E. (2008). A lexicon for texture and flavor characteristics of fresh and processed tomatoes. *Journal of Sensory Studies*, *23*, 583-599.
- ISO 8586 (2012). *Sensory analysis - General Guidelines for The Selection, Training and Monitoring of Selected Assessors and Expert Sensory Assessors*; International Organization for Standardization: Geneva, Switzerland.
- ISO 8589 (2007). *Sensory analysis — General guidance for the design of test rooms, AMENDMENT 1*; International Organization for Standardization: Geneva, Switzerland.
- Javanmard, M., & Endan, J. (2010). A Survey on Rheological Properties of Fruit Jams. *International Journal of Chemical Engineering and Applications*, *1*, 31-37.
- Johansson, L., Virkki, L., Maunu, S., Lehto, M., Ekholm, P., & Varo, P. (2000). Structural characterisation of water soluble β -glucan of oat bran. *Carbohydrate Research*, *42*, 143–148.
- Kalogeropoulos, N., Chiou, A., Pyriochou, V., Peristeraki, A., & Karathanos, V. T. (2012). Bioactive phytochemicals in industrial tomatoes and their processing byproducts. *LWT- Food Science and Technology*, *49*, 213-216.
- Koocheki, A., Ghandi, A., Razavi, S. M. A., Mortazavi, S. A., & Vasiljevic, T. (2009). The rheological properties of ketchup as a function of different hydrocolloids and temperature. *International Journal of Food Science and Technology*, *44*, 596–602.
- Laufenberg, G., Kunz, B., & Nystroem, M. (2003). Transformation of vegetable waste into value added products: (A) the upgrading concept; (B) practical implementations. *Bioresource Technology*, *87*, 167–198.

- Lenucci, M. S., Durante, M., Anna, M., Dalessandro, G., & Piro, G. (2013). Possible Use of the Carbohydrates Present in Tomato Pomace and in Byproducts of the Supercritical Carbon Dioxide Lycopene Extraction Process as Biomass for Bioethanol Production. *Journal of Agricultural and Food Chemistry*, *61*, 3683–3692.
- Meilgaard, M., Civille, G. V., & Carr, B. T. (2000). *Sensory evaluation techniques*. (Ed.3rd ed.). Boca Raton New York: CRC Press.
- Mert, B. (2012). Using high pressure microfluidization to improve physical properties and lycopene content of ketchup type products. *Journal of Food Engineering*, *109*, 579–587.
- Navarro-González, I., García-Valverde, V., García-Alonso, H., & Periago, M. J. (2011). Chemical profile, functional and antioxidant properties of tomato peel fiber. *Food Research International*, *44*, 1528–1535.
- O'Shea, N., Arendt, E. K., & Gallagher, E. (2012). Dietary fibre and phytochemical characteristics of fruit and vegetable by-products and their recent applications as novel ingredients in food products. *Innovative Food Science and Emerging Technologies*, *16*, 1–10.
- Potter, N. N. (2013). *Food Science*, fourth ed. Springer Science & Business Media, New York.
- Prasanna, V., Prabha, T. N., & Tharanathan, R. N. (2007). Fruit Ripening Phenomena-An Overview. *Critical Reviews in Food Science and Nutrition*, *47*, 1-19.
- Rajchl, A., Voldřich, M., Čížková, H., Hronová, M., Ševčík, R., Dobiáš, J., & Pivoňka, J. (2010). Stability of nutritionally important compounds and shelf life prediction of tomato ketchup. *Journal of Food Engineering*, *99*, 465-470.
- Regulation (EC) no 1924/2006 of the European Parliament and of the Council (2006) December 2006
- Regulation of methods of physical and chemical analysis for quality control of grain, milling and bakery products, pasta and quickly frozen dough (1988). *Official Gazette of SFRJ*, *74*. (in Serbian)
- Regulation of methods of sampling, physical and chemical analysis for quality control of fruit and vegetable products (1983). *Official Gazette of SFRJ*, *29*. (in Serbian)
- Renou, F., Petibon, O., Malhiac, C., & Grisel, M. (2013). Effect of xanthan structure on its interaction with locust bean gum: Toward prediction of rheological properties. *Food Hydrocolloids*, *32*, 331-340.
- Rodríguez, R., Jiménez, A., Fernández- Bolaños, J., Guillén, R., & Heredia, A. (2006). Dietary fibre from vegetable products as source of functional ingredients. *Trends in Food Science & Technology*, *17*, 3–15.
- Ruiz Celma, A., Vizcaíno Galán, A., Tapia Delgado, M., Cuadros Blázquez, F., González González, A., & Rubiales, F. (2009). Primeros resultados del secado solar de pieles-semillas del tomate industrial. I Congreso Tecnológico del Tomate para Industria. Badajoz, 12 a 13 de noviembre de 2009.

- Sanchez, M. C., Valencia, C., Gallegos, C., Ciruelos, A., & Latorre, A. (2002). Influence of processing on the rheological properties of tomato paste. *Journal of the Science of Food and Agriculture*, *82*, 990-997.
- Sarkar, A., & Kaul, P. (2014). Evaluation of tomato processing by-products: a comparative study in a pilot scale setup. *Journal of Food Process Engineering*, *37*, 299–307.
- Sharoba, A. M., Senge, B., El-Mansy, H. A., Bahlol, H. E., & Blochwitz, R. (2005). Chemical, sensory and rheological properties of some commercial German and Egyptian tomato ketchups. *European Food Research and Technology*, *220*, 142–151.
- Tiziani, S., & Vodovotz, Y. (2005). Rheological effects of soy protein addition to tomato juice. *Food Hydrocolloids*, *19*, 45-52.
- USDA National Nutrient Database for Standard Reference,
<http://ndb.nal.usda.gov/ndb/foods/show/3582?fgcd=&manu=&facet=&format=&count=&max=35&offset=&sort=&qlookup=ketchup>, accessed 31 July 2015
- Yangilar, F. (2013). The Application of Dietary Fibre in Food Industry: Structural Features, Effects on Health and Definition, Obtaining and Analysis of Dietary Fibre: A Review. *Journal of Food and Nutrition Research*, *1*, 13-23.
- Xu, Q., Xing, Y., Che, Z., Guan, T., Zhang L., Bai Y., & Gong L. (2013). Effect of chitosan coating and oil fumigation on the microbiological and quality safety of fresh-cut pear. *Journal of Food Safety*, *33*, 179–189.
- Xue, D., & Sethi, R. (2012). Viscoelastic gels of guar and xanthan gum mixtures provide long-term stabilization of iron micro- and nanoparticles. *Journal of nanoparticle research*, *14*, 1239-1253.