Evaluation of Nutritional and Physical Properties of Watermelon Juice during the Thermal Processing by Using Alumina Nano-fluid in a Shell and Tube Heat Exchanger

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ABSTRACT

Background and Objectives: Thermal processing is an effective method in preventing microbial spoilage but high heat transfer in a long time process that leads to quality loss and increased energy consumption. Also it is important to consider sensitive nature of food products during the thermal processing. Due to the nano-fluids' unique thermo–physical properties compared with the conventional fluids (steam and hot water), their use in various industries to enhance the efficiency of equipment and energy optimization has increased.

Materials and Methods: The effects of alumina–water nano-fluids (0, 2, and 4% concentrations) on some nutritional properties (lycopene and vitamin C content), and some physical properties (color, pH and TSS) of watermelon juice treated by high temperature–short time (75, 80, and 85°C for 15, 30, and 45 seconds) in a shell and tube heat exchanger were evaluated.

Results: In compared with water, process time reduced by 24.88% and 51.63% for 2% and 4% nano-fluids, respectively. It had a significant effect on improving the properties of watermelon juice (P<0.05). Under the treatment conditions (75°C and 15s), with 0, 2, and 4% nano-fluids, 81.15, 84.81, and 91.28% of lycopene and 61.11, 63.70 and 67.04% of vitamin C were maintained, respectively. ΔE* values for the fruit juices processed with 0, 2 and 4% nano-fluids were 3.26, 2.21 and 1.14, respectively. Also pH and TSS changed in the range of 5.58–5.82 and 9.00–9.40%, respectively.

Conclusions: The results showed that qualitative and nutritional properties of watermelon juices processed with nano-fluids in terms of lycopene and vitamin C retention, and color were, respectively, 9.89, 6.18 and 50.38% better than the samples processed with water.

Keywords: Color, Heat exchanger, Lycopene, Nano-fluids, Vitamin C, Watermelon juice

Introduction

Fruit juices are usually pasteurized by heating with batch or continuous method in food industry. This thermal process may be done before or after packaging the product in the container. In batch pasteurization, specific amounts of the product are processed in steel jacketed vessels. These cases may be used both for heating (by vapor or hot water) and for cooling (by cold water). The continuous pasteurization is done by passing the juices through heat exchangers (including preheating, heating, holding and cooling stages). Pasteurization by high temperature and short time (HTST) is the usual method being used in the thermal treatment of juices currently. In this treatment, the usual temperature and time are 76.6–87.7°C and 25–30 seconds, respectively (1).

Although thermal processing is effective in preventing the microbial spoilage of juices but
transferring lots of energy in a long time to the products with heat sensitive features or components, beside the biochemical and nutritional changes and developing inappropriate reactions and final product’s quality loss, causes more energy usage (2). Nowadays, consumers’ demand for foods with long shelf life, high quality and appropriate price has increased. As a result, to answer this demand, food industry producers are in search of improving thermal processing methods and technologies that decrease damages of fresh, nutritious, and healthy foods (3).

Watermelon (Citrus lanatus) contains 93% water, 6.4% carbohydrate, 590 IU vitamin A and 8.1 mg in 100 g vitamin C. Lycopene carotenoid is watermelon’s red color’s factor and a strong antioxidant (4). Having 2.3–7.2 mg lycopene in each kg, watermelon is a rich source of this composition and an appropriate alternative for tomato products. Lycopene in watermelon is 40% more than in ripe red tomatoes (which are not processed), and is more bioavailable in fresh watermelon than in fresh tomato (5). Watermelon also contains vitamin C, which is an essential ingredient for collagen synthesis and also protecting the body against oxidative damages (6).

Consumers’ demand for functional foods caused processing watermelon juice derivatives. This product is supplier of antioxidants, vitamins and other nutritive composites and, beside the excellent organoleptic and nutritional properties, provides useful nutrients for health (7). According to low acidity and micro-organisms’ good growth conditions, watermelon juice must be pasteurized before consumption. The color is one the first properties, which affects the consumers’ decision while buying, so juices are packaging in transparent bottles (8). But thermal pasteurization may affect the juices’ color and appearance inappropriately by destruction of pigments. Also vitamin C, which is heat-sensitive, would be decreased. Nano-fluids replacement with usual thermal fluids (vapor or hot water) may be a good solution for solving these issues.

Thermal conductivity coefficient of usual fluids is much less than metals and metal oxides. For example, copper and alumina’s (Al₂O₃) thermal conductivity coefficient are, respectively, 700 and 60 times more than water’s. Thus, fluids containing suspended metal or metal oxide solid particles would have better thermal properties (9). Choi (1995) called nano powder’s suspension in fluids as nano-fluids for the first time, and proposed their prominent features (10). Nano-fluid refers to a stable two-phase composition of base fluid and nano-particle (at least in a less than 100 nano-meter dimension).

Up to now, no studies have been done about the effect of adding nano-particles to usual thermal fluids in order to process the fruit juices. So, this research aims to introduce a new technology in food thermal processing systems, improve the efficiency of heat transferring in shell and tube heat exchangers with the help of nano-fluids, and economize energy consumption of pasteurization by reducing processing time and maintaining product quality (lycopene and vitamin C content, total soluble solid (TSS), pH, and total microbial count of watermelon juice).

Materials and Methods

Intelligent thermal system and simulating it in computer: This system contains a shell and tube heat exchanger, two separate reservoirs, one for liquid food, and the other one equipped with a 1kw heater for heating the fluid (water or nano-fluid) and loop current tubes for transferring the fluids from the reservoir to the heat exchanger. All the components are made with 316L stainless steel, and are insulated with aluminum foam in order to reduce heat dissipation. Required power to dominate pressure drop is supplied by two 0.55kw steel centrifugal pumps (3 ph. induction motor, Western Electric, Australia). Beside this, control, return and drain valves are embedded in suitable places. Heater performance, and nano-fluid and liquid foods’ temperature are controlled by Thermocouples. Heat exchanging of crossing fluid through 13 tubes with liquid food crossing through shell is done completely distinct and countercurrent. Fluids’ current rate control is done by computer with two N700E vector invertors (Hyundai heavy industries co. LTD, Korea). For studying the fluid’s thermal changes, pt100 temperature sensors were installed in suitable places. In the designed circuit, the heater relays, electric-pumps, invertors and pt100 sensors were attached to the micro-controller inputs, and were connected to the monitoring system through USB port. Sending commands to the system was done by Visual Studio 2010 software; data receiving and drawing temperature–time diagrams were done online and automatically by the Microsoft Excel 2010 every 10 seconds (Figure 1) (11).
Nano-fluid preparation: Alumina nano-particles with 99% purity (US research nano-materials, Inc.) were dispersed in deionized distilled water with different volume concentrations of 0, 2 and 4% W/V. Then it was stirred completely for an hour with 1500 rpm in order to ensure nano-fluid’s stability. No sedimentation was seen in the produced nano-fluid after 24 hours.

Preparing the product: All glassware and knives were autoclaved at 121°C for 45mins. Other equipments were sterilized by hypochlorite before using. Fresh watermelons (Citrus lanatus) were purchased from a local market (Gorgan, Iran) and stored in a cool and dark place. Watermelon rinds were washed with pure ethanol before juice extraction. The watermelons were cut into two parts, and the flesh was scooped out and cut into small cubes. The cubes were placed in a juice processor (Hamilton model No. FH–145). The extracted juice was filtered with six layers of cheese cloth (VWR, West Chester, PA). The filtered juice was placed in autoclaved screw–top glass bottles, processed immediately with HTST method (76.6–87.7°C, 25–30 seconds), and then put inside ice bath (12).

Physicochemical properties measurement: Treated juices were analyzed for lycopene using the Fish et al. method (2002) (5). 5 mL 95% ethanol, 5 mL 0.05% (w/v) Butylated hydroxytoluene (BHT) in acetone, 10 mL hexane and approximately 0.6 g of watermelon juice was added to each dark colored bottle. After 15 min of shaking, 3 mL of deionized water were added to each bottle, and the bottles were shaken again for 5 min. The bottles were kept out at room temperature for 5 minutes before analysis. The upper hexane layer of each sample was analyzed at 503 nm wavelength using a spectrophotometer (Jenway spectrophotometer model No. 7305). Hexane was used as a blank. Lycopene content was calculated using the equation (1):

\[
\text{Lycopene (mg/kg juice)} = \frac{A_{503} \times 31.2}{\text{g juice}}
\]  

(1)

Where31.2 refers to the molar extinction coefficient. Lycopene retention calculated using equation (2):

\[
\text{Retention (\%)} = \frac{\text{mg lycopene/kg juice after treatment}}{\text{mg lycopene/kg juice before treatment}} \times 100
\]  

(2)

Acid ascorbic (Vitamin C) amount (mg in 100 g) was determined by indophenol method (13). The titrant was prepared with 50 mg of 2, 6-dichloroindophenol Na salt and 42 mg of sodium bicarbonate in 50 mL of water. The solution was diluted to 200 mL with distilled water. The extracting
solution was prepared with 15 g of metaphosphoric acid and 40 mL of acetic acid, and then diluted to 500 mL with distilled water. The solutions were stored in amber bottles at 4°C. A 100 mL of watermelon juice was added to 100 mL of the extracting solution. The solution was then titrated with the titrant until the solution turned bright pink for at least 5s. Vitamin C retention was calculated using equation (3):

\[
\text{Retention (\%)} = \frac{\text{mg ascorbic acid/100 mL juice after treatment}}{\text{mg ascorbic acid/100 mL juice before treatment}} \times 100
\]

The samples were analyzed for \(L^*\) (brightness), \(a^*\) (red–green) and \(b^*\) (yellow–blue) color parameters using separation method in Photoshop CS5 version 12 for watermelon juice picture taken by a Samsung 13 megapixel digital camera. Total color difference, i.e. \(\Delta E^*\) (a parameter that quantifies the overall color difference of a given sample compared to a reference sample) was calculated using equation (3) (14):

\[
\Delta E^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{0.5}
\]

\(\Delta L^* = (L^*_1 - L^*_0)\) \hspace{1cm} (5)

\(\Delta a^* = (a^*_1 - a^*_0)\) \hspace{1cm} (6)

\(\Delta b^* = (b^*_1 - b^*_0)\) \hspace{1cm} (7)

Where, subscript ‘0’ depicts the color value for the reference sample (untreated sample), and subscript ‘1’ depicts the color value for the sample being analyzed.

The pH of the sample was measured at 25°C, using a WTW GmbH pH meter Germany. Total soluble solid (TSS) content measurement of the juice samples was measured by a digital refractometer (CETI, ABBE refractometer Belgium) at 25°C and expressed in °Brix.

**Results**

**Effect of using alumina nano-fluid on thermal processing time:** In the system equipped to shell and tube heat exchanger, watermelon juice was processed at 75, 80, and 85°C for 15, 30, and 45s by alumina–water nano-fluid at concentrations of 0, 2, and 4%. By increasing the concentration of nano-fluid, time reduction was more intuitive. For example, by using 4% nano-fluid as heat transfer medium, the time reduced by 51.63% in comparison with water (Figure 2).

**Figure 2:** Temperature changes and time reduction during the thermal processing of watermelon juice by 2% and 4% alumina nano-fluid compared with water
Based on the results of previous studies, heat transfer coefficient of 2 and 4% nano-fluids increased to 8 and 13%, respectively, in comparison with water (15). This is because of high thermal conductivity of nano-particles, so that in 85°C, the thermal conductivity of 2 and 4% nano-fluids increased to 6.69 and 12.75%, respectively, in comparison with water. Also, by increasing the temperature from 27°C (environment temperature) to 85°C (processing temperature), the thermal conductivity of nano-fluids increased around by 9.66%. Reducing the process time in addition to energy saving improves the nutritional and physical properties of the product. Immediate drop of temperature in water curve at t=25 min may also occur due to the opening door of the tank by the operator to control the water level.

**Effect of thermal processing with alumina nano-fluid on watermelon juice’s lycopene:** Lycopene content of watermelon juice was reduced by increasing the temperature and processing time (16). Lycopene retention (%) of the juices processed with nano-fluid was significantly higher than that of the juices processed with water \((P<0.05)\). So that lycopene retention of the juice by processing with water at 75°C and 15s was 81.15%, while for this defined operation condition, with the help of 2 and 4% nano-fluid, it was 84.81 and 91.28%, respectively (Figure 3). This is due to the high thermal conductivity of nano-fluids, and therefore, reducing the total processing time.

**Effect of thermal processing with alumina nano-fluid on the watermelon juice’s vitamin C content:** Vitamin C content can be used as an indicator of freshness for fruits and vegetables in terms of other nutrients. When vitamin C of a fruit juice is well retained, other nutrients may also be well retained (17). It is well-known that vitamin C is very sensitive to heat treatment. Marfil et al. (2008) reported that treatment temperature is directly related to degradation. In order to maintaining of vitamin C, thermal processing should be done in the shortest time and lowest temperature (17). Accordingly, nano-fluids replacement with water, in order to reduce processing time, was effective significantly \((P<0.05)\). So that for processing with water at 75°C and 15s, vitamin C retention was 61.11%, while this percentage, for this defined operation condition with help of 2 and 4% nano-fluid, was 63.70 and 67.40%, respectively (Figure 4). As can be seen in Figure 4, there is a small difference in vitamin C retention percentage of the juices treated with 2% and 4% nano-fluids at 85°C. Also it is probably due to the extreme sensitivity of vitamin C, which is quickly destroyed at high temperatures.

**Effect of thermal processing with alumina nano-fluid on the color of watermelon juice:** In CIELAB (CIE L*a*b* color space) system, \(L^*\) represents the difference between whiteness \((L^*=100)\) and blackness \((L^*=0)\), “\(a^*\)” shows difference between green color \((-a^*)\) and red \((+a^*)\), and “\(b^*\)” shows the difference between blue color \((-b^*)\) and yellow \((+b^*)\) (18).
results obtained from data related to the effect of process time and temperature on colorimetric parameters showed that $a^*$ is reduced and $b^*$ is increased gradually. For raw juice, $L^*$ was 57.24, which was decreased to 54.32 for the juice processed with water at 85°C and 45s ($P<0.05$). A lower $L^*$ value in the pasteurized juice may be attributed to the common darkening of pasteurized juice. While decreasing of this parameter for processing with 2 and 4% nano-fluids under this defined operation condition was 55.28 and 56.03; therefore, $L^*$ did not have any significant decrease ($P>0.05$). Nano-fluid treatment was more efficient than pasteurization with water in retaining the original $L^*$ values.

Value of $a^*$, which refers to the redness of the juice relating to the lycopene content, reduced from 2.18 for raw juice to 0.88 for juices processed with water at 85°C and 45s significantly ($P<0.05$). This parameter for processing with 2 and 4% nano-fluids under this defined operation condition was 1.27 and 1.63, respectively, so that $a^*$ reduction was not significant ($P>0.05$). Hence, by reducing the time of thermal process exposure with the help of nano-fluids, the watermelon juice’s redness was maintained better.

Also thermal processing changed $b^*$ values of watermelon juice, so that $b^*$ increased significantly from 0.12 for raw juice to 2.06 for juices processed with water at 85°C and 45s, ($P<0.05$). These values for processing with 2 and 4% nano-fluids in this defined operation condition were 1.79 and 1.54, respectively. As shown in Figure 5, by increasing the thermal processing temperature and time, the value of $\Delta E^*$ increases ($P<0.05$). The most total color difference ($\Delta E^*$), which determines the difference between processed juice color and raw juice color, with the amount of 3.26, was related to thermal processing with water at 85°C and 45s, while this parameter for processing with 2 and 4% nano-fluids in this defined operation condition got 2.21 and 1.14, respectively. Increasing the value of $\Delta E^*$ is along with the darkening of color. Watermelon color changes due to enzymatic browning (poly phenolase activity in oxygen presence). Because of applying heat, enzyme deactivation and bleeding is very poor, and ascorbic acid degradation leads to producing brown pigments more through anaerobic ways. So, thermal processing prevents enzymatic browning of watermelon juice in the long run (19).

**Figure 5:** The effect of different processing temperature and time on the retention percentage of watermelon juice's $\Delta E^*$ treated with water and 2 and 4% alumina nano-fluids

**Effect of thermal processing with alumina nano-fluid on watermelon juice’s pH and Brix:** It appeared that the treatments did not affect the pH of the juice ($P>0.05$); therefore, the overall quality of the juice might be preserved. The pH values for the treatments ranged from 5.58 to 5.82. Juice had slight changes in Brix index but the changes were not significant ($P>0.05$). The Brix values for the treatments ranged from 9.0 to 9.4. Thermal pasteurization did not affect the pH or the Brix of watermelon juice, indicating that the treatments minimized the biochemical reaction in the juice samples.

**Discussion**

**Thermal processing time:** The results showed that time and temperature had reverse effect, and nano-fluid concentration had direct effect on the nutritional and physical properties of the juice. The process time for different concentrations of nano-fluids, in comparison to water, reduced significantly. Therefore, juice was less exposed to high temperatures. In this way, nano-fluids' replacement with water had significant effect on maintaining the nutritional and physical properties of the watermelon juice.

**Lycopene content:** By increasing time and temperature of the process, the juice's lycopene content reduced, while the percentage of lycopene retention of the juices treated with nano-fluid compared to those treated with water was higher at an acceptable level. A significant reduction in tomatoes’ lycopene content under boiling process (100°C and 15 min) has been reported (21). But in another study, the
positive effect of tomato juice’s thermal processing (90°C and 1 min) on lycopene extraction was seen. Pasteurization provided more lycopene so that lycopene content of fresh tomato juice was 1024, and the pasteurized tomato juice was 2643 µg in 100cc (22). In order to maintain the vitamin C content, thermal processing should be done in the shortest time and the lowest temperature (17).

**Vitamin C content:** Under the same conditions of temperature and time, vitamin C retention of the juices treated with nano-fluid compared to those treated with water was higher. Paul & Gosh (2012) studied thermal processing effect in 70–90°C temperature range on the vitamin C content of pomegranate juice, and reported that vitamin C’s retention range was around 69% at 70°C (23). Effect of combination of heating and thermo–sonication treatment on thermal degradation of vitamin C in cress (*Nasturtium officinale*) in the temperature range of 82.5–92.5°C was studied by Rui et al. (2010). Thermal blanching time at 90°C (in order to reducing 90% of peroxidase activity) was 70s, which was around 14 times more than that of the thermo–sonication treatments (5s). This large time difference causes to maintain more vitamin C in thermo–sonication treatment (94%) rather to thermal blanching (29%) (24).

**Color:** The results showed that the pasteurized watermelon juice had a lower L* and b* values than the untreated juice. A lower L* value in the pasteurized juice was due to darkening during heating. Also, by reducing the time of thermal process exposure with the help of nano-fluids, the watermelon juice’s redness (a*) was maintained better. Cortes et al. (2008) showed that b* values of orange juice treated with thermal process (90°C and 20 s) were considerably higher than those of raw juice (25). According to Lee & Coates (2003), the b* and a* values of orange juice during thermal process (90°C and 30 s) increased and decreased, respectively (19). Total color differences (ΔE*) were greater with the juice pasteurized with water than with the nano-fluid treated juice. Due to reduction of total thermal processing time, the nano-fluid treated juice retained the original color better than the water–treated samples.

**pH and Brix:** Generally, pH and Brix did not change significantly. Similar results for orange–carrot juice treated with pulsed electric fields (PEF) were reported by Rivas et al. (2006) (26). Also Heinz et al. (2003) found that PEF–pasteurized apple juice did not show practical difference in pH.

**Conclusion:** Increasing the time and temperature of thermal processing affected the nutritional and physical properties of juices. In this way, by using water as a usual heating medium, the amount of lycopene and vitamin C, by exposure to heat during the process decreases gradually. Also the processing conditions led to the darkening of the juices. But overall, pH and TSS did not change significantly. The results obtained from this research showed that adding alumina nano-particles to water led to improvement in maintaining the nutritional and physical properties of the product. This is because of the unique thermal properties of nano-fluids, and especially their high thermal conductivity in comparison to usual thermal fluids (vapor and hot water). Use of nano-fluids has increased in different industries and everywhere where heat exchanging processes are essential in order to increase the efficiency of heat exchangers and energy optimization. Thus considering the sensitive nature of products during thermal processing is an important point in food industry. Use of nano-fluids, in addition to reducing the process time and thus energy saving, leads to improving the nutritional and physical properties of final products.

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