Evaluation of Rheological, Textural and Thermal Properties of Quinoa (*Chenopodium Quinoa* Willd) Based Breakfast Puree

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Abstract: This study was conducted to determine the rheological, thermal, textural and color properties of quinoa based breakfast puree possessing high nutritional value and composed of mainly non-dairy milk (soy milk) which could be an alternative to conventional gluten-containing dairy breakfast meals. The rheological properties were evaluated under steady and dynamic shear conditions. The steady shear test was carried out at 27 °C using a rotational type of viscometer. Quinoa puree showed pseudo plastic non-Newtonian and time-independent flow behavior. Rheological data was modeled by using Power and Herschel Buckley Models (R^2>0.99). Dynamic shear properties were determined by applying sweep test using a rheometer. G' (elastic modulus) was reported to be greater than G'' (viscous modulus) exhibiting elastic behavior. Specific Heat (C_p) of quinoa puree was determined endothermically using Differential Scanning Calorimeter (DSC). The sample thermogram showed no glass transition point. But the melting point appeared at elevated temperature (above 120 °C). Textural properties of the puree in terms of consistency, cohesiveness and firmness confirmed its viscoelastic nature. Water activity was about 0.97 and the color was reasonably light and brownish.

Keywords: Quinoa puree, Rheological properties, Differential scanning calorimetry (DSC), Textural properties.

1. INTRODUCTION

Quinoa (*Chenopodium quinoa* Willd) botanically considered as pseudo-cereal or pseudo-grain is a native of South America and grows in the Andean mountains [1-3]. It is within the genus *Chenopodium* used as a cereal-like grain, but is not a grass [4]. It is reported that quinoa is an important source of minerals and vitamins, and also bioactive polyphenols [3]. The unique nature of quinoa is responsible for its comparative complete nutrients profile [5-7]. Quinoa has high protein content (approx.15%) and good amino acids balance [3, 5]. These nutritional properties of quinoa make it almost imperative to expand its utilization in new product development. The utilization of quinoa; like every other protein-containing starch based cereals, will be influenced by its functional and rheological properties. These include solubility, water-holding capacity (WHC), gelling, swelling and foaming properties, slurry consistency and viscosity [3, 8].

In formulation of starch-containing breakfast cereal puree/puree, one of the important factors influencing the quality of the product is the degree of gelatinization [9]. Gelatinization is an energy-absorbing endothermic process that can be monitored through Differential Scanning calorimetry (DSC) and has been used for the study of similar products [10]. This process involves disruption of the molecular order within starch granules when heated in the presence of water and subsequent loss of crystalline structure and birefringence, transition in thermal profile, increased granule swelling and viscosity [11-14].

It is generally accepted that viscosity increases until a certain point when starch-based food is heated in water due to starch granule-water interaction [8]. Depending on the nature of the food material, processing conditions and water-starch ratio, this viscosity influences elastic *(G'),* viscous (*G''*) and complex modulus (*G**) of the puree [15]. In a highly elastic protein-containing cereal such as wheat, starch is able to form a continuous network of particles together with the macromolecular network of hydrated protein [16]. However, quinoa protein is mainly globulin and does not possess the requisites to confer large viscoelastic capacities on its slurry [17]. A lower peak viscosity and positive setback are associated with harder textural pasty food products, while a higher peak viscosity and breakdown and also lower setback are associated with a sticky texture as observed by Gayin *et al*. [18] in cooked rice. This phenomenon is expected to be the behavior of quinoa puree.

The high protein content of quinoa has increased research focus on distribution of its nutrients [1], application as gluten-free bread supplements for celiac disease patients [19] and development of new products [20]. However, there are no published research

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investigating the breakfast puree formulation from the blend of quinoa, non-dairy milk and fruit cuts. The aim of this study is to investigate the textural, rheological and thermal properties of a creamy breakfast puree using the traditional recipe of a popular breakfast beverage in South America. For this purpose, quinoa puree is formulated from a blend of cooked whole quinoa, non-dairy milk and apple cuts and the formulated product were investigated.

2. MATERIALS AND METHODS

2.1. Quinoa Puree Formulation and Processing

Quinoa grains, unsweetened soya milk, fresh apple, brown sugar, cinnamon and vanilla extract were purchased from a local market in Izmir, Turkey. The recipe was composed of 1 cup of white quinoa grains, 4 cups of drinking water, 4 cups of unsweetened soya milk, 4 middle sized red apples (peeled, cored and quartered), 4 table spoon soft brown sugar, 1 tea spoon ground cinnamon, and 2 tea spoon vanilla extract [21]. Quinoa grains placed in a cooking pan were boiled in water at 300 ^{o}C for 20 min using a hotplate (Stuart, UC152D, UK). The temperature was reduced to 100 ^{o}C and allowed to simmer for 15 min until the grain became tender after which it was drained completely and returned back to the cooking pan. 4 cups of unsweetened soya milk, 4 mid-sized red apples (peeled, cored and quartered), 4 table spoon soft brown sugar, and 1 tea spoon ground cinnamon were added and simmering continued at mild temperature (100 ^{o}C) for 10 min in order to prevent enzymatic browning of the apple, as well as facilitate effective integration of other ingredients. The mixture was transferred into a home-type blender (Arcelik, K1260, Turkey) and blended with addition 2 tea-spoon vanilla extract, until the puree became smooth. The mixture can be served warm or cold.

2.2. Texture Analysis

Texture profile of the samples were measured by a texture analyzer (TA-XT plus Texture Analyzer, Stable Micro System, UK) using back Extrusion Cell (A/BE) with 35 mm disc and extension bar of 5 kg load The applied cell speed of head and compression was 1 mm/min and 75%, respectively. These parameters were selected according to products having similar texture in the literature [22-24]. All the measurements were carried out at room temperature (20 °C). Samples were tested in triplicate. In order to reveal textural characteristics of the product firmness, consistency, and cohesiveness were determined. Simply, these parameters were calculated according to force-time curve obtained from texture analyzer. Firmness was the value of maximum force (peak) at certain point while consistency was the area of the curve until this point [23, 24]. Moreover, cohesiveness was the maximum negative force observed in the force-time curve [23].

2.3. Steady Shear Test

Steady shear test was applied to quinoa puree samples using a rotational viscometer (Haake Viscotester 550, Thermo Scientific, USA) equipped withFL-100 star shape middle sized spindle. The viscosity and shear stress of samples were measured at increasing shear rates (0-60 s^{-1}) for 300 s and at increasing and decreasing shear rates (0-60; 60-0 s^{-1}) for 600 s. Samples were tested in triplicate. Plots were generated by drawing collected data against shear rates and time in order to investigate the flow behavior and time dependency of samples. Rheological data was modeled by using Power and Herschel Buckley Models as shown in Eq. 1 and 2, respectively [25].

Power Law Model

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

τ: Shear stress (pa), k: consistency index (pa.s^{n}), n: flow behavior index (n=1 Newtonian, n<1 shear thinning)

Herschel-Buckley Models

$$\tau - \tau_o = K_H \dot{\gamma}^{nH} \quad (2)$$

τ: Shear stress (pa), τ_o: yield stress, K_H: consistency index (pa.s^{n}), n_H: flow behavior index (n < 1 shear thinning)

2.4. Dynamic Shear Test

Rheological tests (Stress sweep test) of Quinoa puree were carried out using a rheometer (Rheometer AR 2000-exTA, Thermal Instrument, USA) equipped with thermo-controller and a computer control system. Cone and plate geometry (Spindle: 25mm diameter, Angle 6^{0} and Gap size: 168 µm) was used in measurements. Samples were tested in triplicate.

The quinoa puree samples were pre-sheared at 1000 s^{-1} for 1min. The linear viscoelastic range of quinoa puree was pre-determined by stress sweep tests. The spectra of dynamic shear test data was

plotted and LVR (Linear Viscoelastic Region) was determined over a stress range of 0.08-10Pa at constant frequency 4.64 Hz. 50 data points were obtained and elastic modulus (G'), viscous modulus (G'') and complex modulus (G^*) were obtained to determine the rheological properties of the sample. *G'* is high for elastic materials while *G"* is high for viscous materials. G^* represents the total resistance of the sample to a deformation applied on it. In other word G^* is the combination of G' and G''. A fluid is considered viscous if $G'=0$ and $G''=G^*$, elastic if $G'=G^*$ and $G''=0$ or viscoelastic if $G'\neq 0$ and $G''\neq 0$ [26].

2.5. Thermal Properties

Thermal properties of raw quinoa samples and quinoa puree were determined by differential scanning calorimeter (DSC Model Q10, TA Instrument, USA). 6.8 mg dry raw quinoa samples and 6.5 mg quinoa puree samples were prepared. Samples were placed in a hermetically sealed pan and scanned at different heating rates (in dry nitrogen atmosphere at a gas flow of about 50 mL·min^{-1}). Onset temperature was 5 °C and samples were heated up to 120 °C with 10 °C/min heating rate. Same measurement was performed without any sample and results were considered as blank. *Cp* was calculated according to Eq. 3 given below [27].

$$C_p = Q \times 60/r \times M \quad (3)$$

where

C_p= specific heat (J/g °C)

Q= sample heat flow (J/s)

r= scanning rate (°C/min)

M= sample weight (g)

2.6. Color and Water Activity (aw)

A colorimeter (chromometer type CR-400, Minolta Sensing, Osaka, Japan) was used to determine the quinoa color. Equipment calibration was done with the aid of air and a small droplet of quinoa puree (≈20 mL) was placed on the measuring head of the instrument. Three readings were taken at three different positions in the measurement screen in terms of L*, a*, and b* color coordinates.

Water activity (aw) of both dried quinoa and puree were measured by Hygrolab C1 bench top apparatus (Rotronic, Swiss) at room temperature.

3. RESULTS AND DISCUSSION

3.1. Color and Water Activity

The color characteristics of the Quinoa puree was measured using Hunter CIE color scale and the results presented in Table **1**. The puree appeared reasonably light as the value of L* is above 50 [28]. Jan *et al*. [29] attributed colour changes of quinoa starch to the presence of carotene and phenolic compounds similarly indicated in Mir *et al*. [30] as well. High cooking temperature during product formulation in conjuction with the mentioned compounds including other ingredients could be responsible for low L* and negative a*. The greyish-brown colour of the cooked quinoa is due more to non-enzymatic browning such as caramelization and maillard reactions rather than enzymatic changes [31]. Because the puree is obtained at elevated temperature (>150 °C) which is too high for oxidative enzymes to survive. However, the presence of soy-milk may facilitate non-enzymatic browning reaction between protein and starch (Maillard browning reaction) as observed by Delgado-Andrade *et al*. [32].

Water is affecting food safety, stability, quality and physical properties, in which its state in a solution or within solid food matrix is expressed by the activity coefficient (a_w) [33]. Table **1** showed *aw* of both raw (dry) quinoa and cooked quinoa puree. The influence of water in quinoa puree is pronounced by the changes in viscosity and consistency [33]. The water activity of quinoa puree is about 0.97, *i.e*. it has high content of unbounded free water which is facilitating an increase in dissolution of the solid content. The influence of the dissolved solid (quinoa) affected the flow behavior of puree. This flow behavior is due to interaction between quinoa macromolecules and water molecules. The larger the macromolecules the lower are the rate at which intermolecular interactions affect the mobility of

Table 1: Color and Water Activity (aw) Parameter of Quinoa Puree

Parameters	Average
L*	68.99±0.13
a*	-1.29±0.08
b*	15.03±0.05
aw (Quinoa)	0.49±0.01
aw (Quinoa paste)	0.97±0.00

n=2 and ± indicates standard deviation.

solvent (water) in the macromolecules [33]. The same explanation applies to the specific moisture content required for phase transition of material at a given temperature. At small increment in the critical water content and/or water activity, the structure could be collapsed or crystallization may occur [34].

3.2. Rheological Properties

3.2.1. Steady Shear Test

Rheological measurement of Quinoa puree exhibited non-Newtonian shear thinning (pseudo plastic) behavior (the apparent viscosity decreased as the shear rate increased) indicating the alignment of the components of the puree with the flow as shown in Figure **1**. Rheological data collected over the shear rate range of 0-60 s^{-1} were modelled using Power Law and Herschel-Buckley Model. The main difference between these two models is that Herschel-Buckley Model possesses a yield term (τ_o) while Power Law does not. However, consistency and flow behavior index are common for both model as shown in Eq. 1 and 2 [25]. In order to determine the yield stress, τ_o, shear stress at the wall τ_W, is plotted with respect to shear rate at the wall γ_W and τ_o is extrapolated as shown in the Figure **2**. Table **2** shows the comparision between the parameters of the two models. The consistency coefficient (K, $Pa.s^n$) given in natural log and flow behavior indices (n) obtained from the Power Law and Herschel-Buckley Model as shown in Figure **2a** and **2b**, are 2.79, 2.83 and 0.48, 0.49,respectively. In the light of these, generated error values for the two models are similar but Herschel-Buckley fitted slightly better than Power Law with higher R^2.

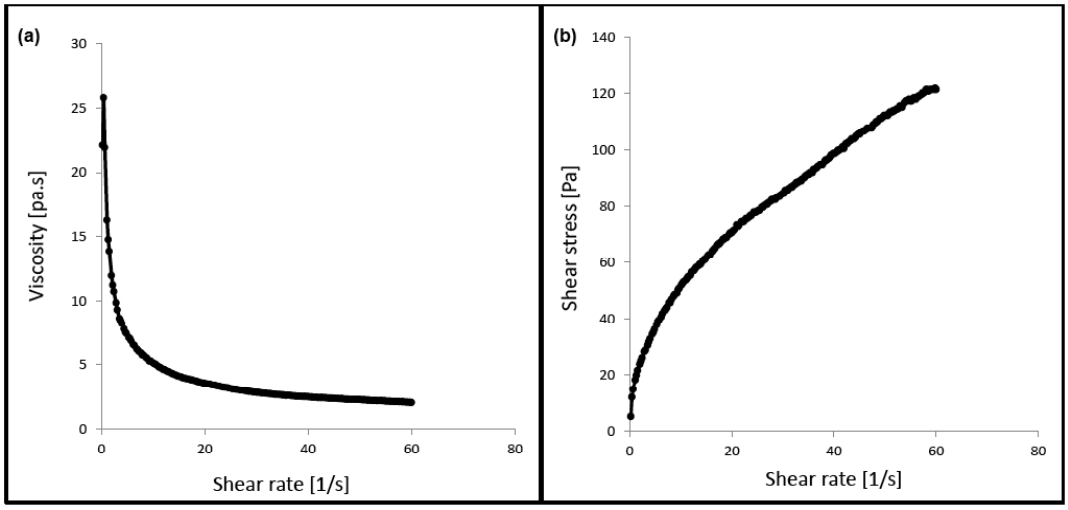

Figure 1: Non-Newtonian pseudoplastic behavior of quinoa puree, (**a**) viscosity vs shear rate and (**b**) shear stress vs shear rate.

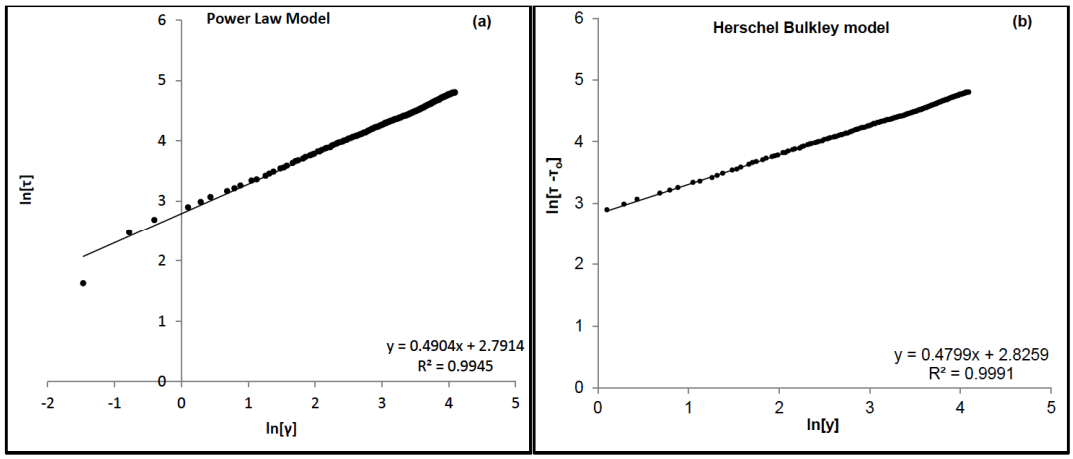

Figure 2: (**a**) Power Law and (**b**) Herschel-Buckley model for quinoa puree.

Table 2: Comparision between Models Parameters

Models	Power Law Model	Herschel Bulkley Model
RMSE stress	1.18	1.04
RMSE strain	1.03	1.01
R^2	0.99	1.00
n	0.48	0.49
K (pa.sn)	1.23	1.20

RMSE: root mean square error.

The consistency coefficients obtained from the two models are reasonably high compared to what is obtainable in literature for similar product. Nindo *et al*. [35] modelled blueberry puree with Power Law over the shear rate of 0-100 s^{-1} and observed a consistency of 0.62 $Pa.s^n$. The higher consistency value obtained from quinoa puree is a similar attribute of oat cereals starch [11]. Rheological behavior of suspensions depends on temperature, shear rate and time of shearing [36]. A decrease in the viscosity of quinoa puree was observed as the shear time and rate increased. However, viscosity remained constant when shearing continued above 300 s and shear rate above 60 s^{-1} (data not shown).

Time dependency of the flow was investigated by checking the hysteresis loop and employing the shear stress decay method as indicated by Alvarez and Canet [9]. The results were shown in Figure **3**. The hysteresis loop formed by plotting the shear stress against ascending and descending shear rates for a complete cycle. The difference between the two curves is known as hysteresis and the loop area designates the threshold for the amount of energy required to have a thixotropic break down in the puree structure which becomes irrecoverable [37, 38, 9]. Small hysteresis is observed and the degree of heterogeneity of the puree appeared very low compared to other suspension/ slurry such as infant foods [9]. The absence of hysteresis between the curves indicates time-independency of the flow behavior of puree samples (Figure **3**).

3.2.2. Dynamic Shear Test

The result from oscillation sweep test of quinoa puree is shown in Figure **4**. A sinusoidal shear strain function was applied to the sample to investigate its elastic, viscous or viscoelastic properties. A similar trend was observed both in Elastic modulus (G') and complex modulus (G^*). However, variation of viscous modulus (G'') as a function of stress was not pronounced. As stated by Chung and McClements [39], gel and solid pasty food products (like quinoa) has a dynamic shear modulus G^* which contains elastic (G') (storage modulus) and a viscous component G'' (loss modulus) at the same time, further confirming viscoelastic nature of these products. Therefore, the loss modulus (G'') component of quinoa puree is low compared to elastic modulus (G'). $G'>G''$ at early state indicated that quinoa puree is well structured at the initial oscillatory stress but become relatively viscous as stress increases. However, there is no visual difference observed between loss, elastic and complex moduli at oscillatory stress above 8.0Pa.s on the curve according to Figure **4**.

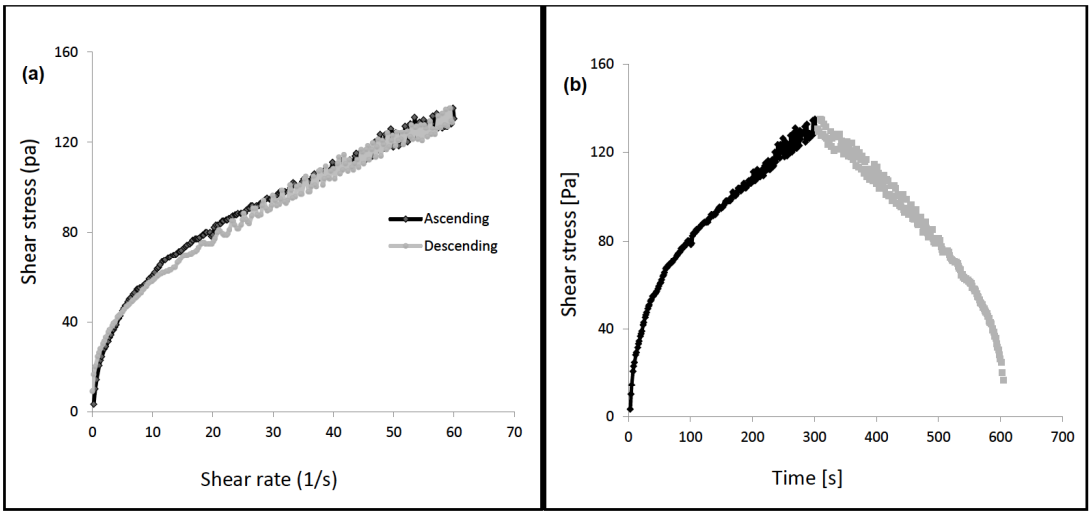

Figure 3: Time independent flow behavior of quinoa puree (**a**) Hysteresis and (**b**) Up-down loop.

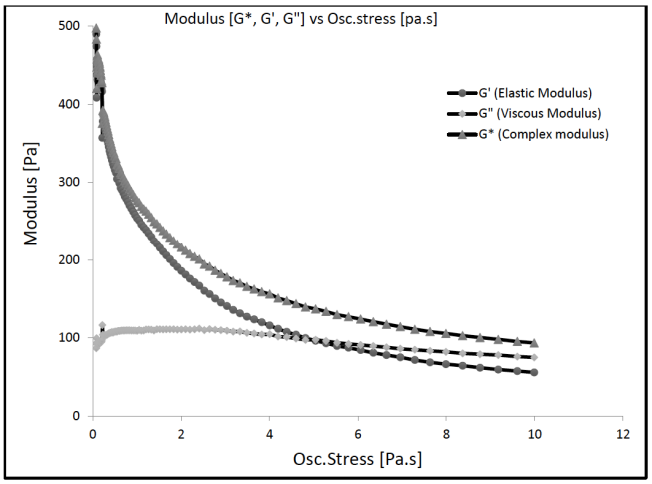

Figure 4: Loss, Elastic and Complex Moduli [Pa] vs Osc stress [Pa.s] of quinoa puree.

3.3. Textural Properties

Table **3** shows some parameters obtained from the texture profile analysis of quinoa puree. Textural characteristics of porridge, slurry or puree is basically determined by the relative proportional ratio between the meal and water used in it preparation as indicated by Onyango [40]. Quinoa puree firmness (hardness) is found as 442.01 Pa·s. Depending on the preference of consumers, thick or thin quinoa puree can be obtained by adjusting solid to liquid ratio. The average consistency of Quinoa puree was measured as 12.64 N·s. Consistency of porridge was found with in 5.58 N·s to 34.04 N·s and it could be regarded as relatively viscous puree [40]. Also, the maximum negative force is taken as an indication of consistency/resistance that is referred to as cohesiveness. The more the negative value, the more cohesive is the sample [41]. Quinoa puree work of cohesion can be influenced by varying the processing parameters.

Table 3: Textural Properties of Quinoa Puree

Sample	Firmness (Pa)	Consistency (N.s)	Cohesiveness (N.s)
quinoa	442.01±14.82	12.64±0.52	-1.84±0.17

n=3 and ± means standard deviation.

3.4. Thermal Properties (DSC Analysis)

DSC analysis revealed the structural differences between raw and cooked quinoa and the results were presented in the heat flow thermograms (Figure **5a**). Raw quinoa did not exhibit a clear melting point. The melting started at temperature above 80 °C and not completed at120°C. The glass transition point, *i.e*. T_g, is not observed. Moreover similar observation was obtained for quinoa puree (Figure **5b**). There was no T_g point but more clear melting point about 100 ^oC was observed in the thermogram. Water acts as a plasticizer that facilitates the transformation of amorphous food materials from their glassy state into rubbery state [42]. Cuq and Icard-Vernière [42] observed no significant difference in the endothermic peak even at 20 g water/100g dry matter. This fact may explain the closeness in melting point of raw and processed quinoa. The Specific Heat C_p (J/g ^oC) of raw and cooked quinoa were compared in Figure **5c** and **5d**. The specific heat of Quinoa puree was found to be 1.77, 7.52, and 13.27 J/g ^oC at 30, 50, and 70 ^oC, respectively (R^2=0.45) On the other hand the specific heat of raw sample was measured as 1.67, 2.09, and 2.51 J/g °C at the same temperatures (R^2=0.87). Comparing increase rate of the C_p of cooked and raw dry quinoa samples, there was a progressive increase in C_p of quinoa puree between 20 ^oC and 100 ^oC, whereas dry sample showed a much higher C_p increase at temperature above 70 ^oC. This may be due to the reduction in water molecule as a result of evaporation at 100 ^oC in processed sample. As a result, reducing the number of effective solvent molecules are responsible from a decrease in the thermal conductivity and subsequently a decrease in the specific heat capacity [43]. However, the dependency of thermal properties to temperature, food composition and moisture content are also responsible for the difference in C_p of processed and raw quinoa [43, 44].

CONCLUSION

The present study was aimed to determine rheological, thermal and physicochemical characteristics of a novel breakfast puree formulated from a cooked mixture of whole quinoa, non-dairy milk and apple-cuts. It was visualized that the color of quinoa puree was slightly changed as cooking proceeded. This may have been as a result of non-enzymatic browning process, common to thermal treatment of food matrix having high amount of protein and carbohydrate like quinoa puree. Water activity (aw) of raw quinoa is low enough to have long shelf life. But puree has higher a_w compared to raw quinoa which affects the storability of this product.

The product possessed desirable textural qualities such as firmness, cohesiveness and consistency. Rheologically, quinoa puree lies between elastic and

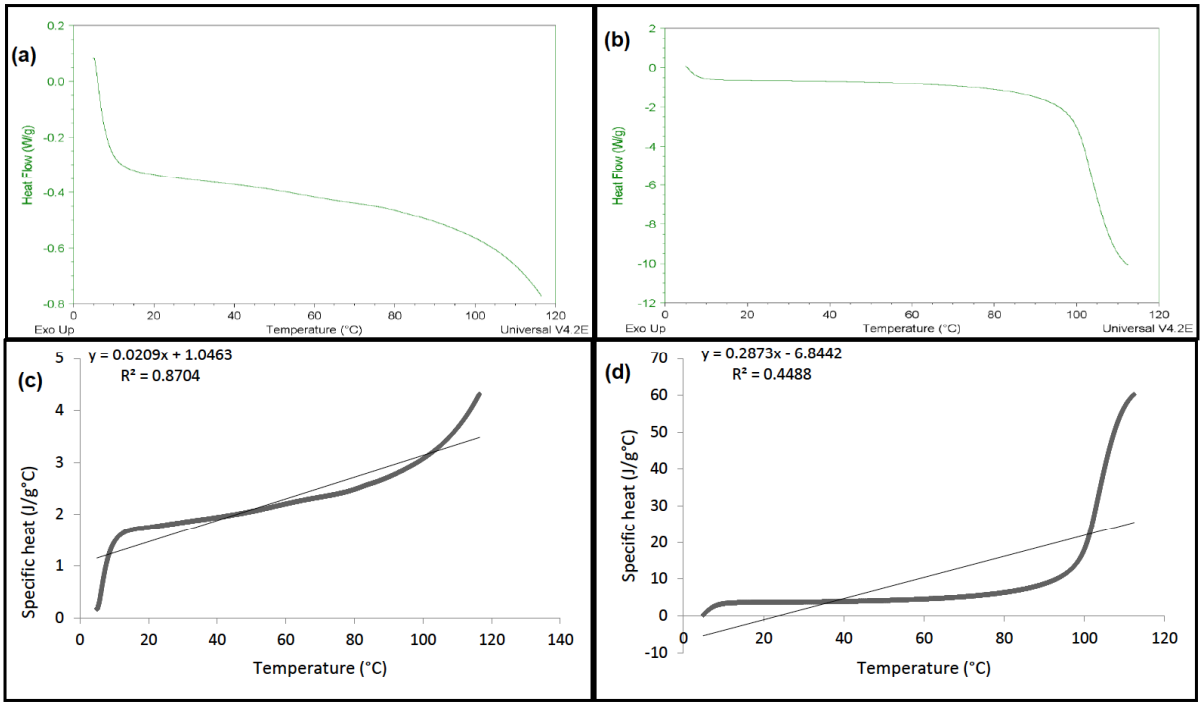

Figure 5: DSC Thermograms of raw (**a**) and cooked quinoa (**b**) and specific heat capacity (J/g ^{o}C) of raw (**c**) and cooked quinoa (**d**).

viscous (viscoelastic) and its flow behavior data were fitted well to Power and Herschel Bulkley non-Newtonian models. However, ability to quantify yield stress, better R^2 and lower RMSE makes Herschel Bulkley model more feasible and preferable for viscoelastic fluid like quinoa puree. No glass transition point was observed in the DSC thermogram of both quinoa puree and dry sample. The negative total heat flows observed in both thermograms may be due to melting or gelatinization especially in the wet sample. However, C_p of quinoa puree was higher than that of dry sample at relatively lower temperature, whereas the reverse was the case at elevated temperature (above 70 ^{o}C).

Nutritionally, this highly proteinous novel product could be a good replacement for gluten-containing breakfast products. This makes it appropriate for individual that are predisposed to celiac-disease. Also, its non-dairy constituent (soy milk) can increase its utilization among lactose-intolerance people.

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