INTERNATIONAL
Agrophysics
www.international-agrophysics.org

Int. Agrophys., 2021, 35, 31-40
doi: 10.31545/intagr/131801

Extraction of *Ziziphus lotus* fruit syrups: effect of enzymatic extraction and temperature on their rheological and chemical properties**

Touka Letaief[1,2,3]*, *Jamel Mejri*[1], *Sandrine Ressureição*[3], *Manef Abderrabba*[1], *and Rui Costa*[3]

[1]Laboratory of Materials Molecules and Applications, IPEST, BP 51, 2070 La Marsa, Tunisia
[2]National Agronomic Institute of Tunisia, University of Carthage, Tunisia
[3]Research Centre for Natural Resources, Environment and Society (CERNAS), College of Agriculture of the Polytechnic Institute of Coimbra, Bencanta, 3045-601 Coimbra, Portugal

Received October 21, 2020; accepted December 18, 2020

A b s t r a c t. Fruit syrups are attracting increasing interest in the food industry. *Ziziphus lotus* fruit syrups were elaborated through the traditional and enzymatic methods with 30, 50 and 70° Brix. A chemical analysis revealed that *Ziziphus lotus* fruit powder and syrups present a potential source of energy through their relatively higher content of carbohydrates. Rheological oscillatory tests showed that syrups of 30°Brix demonstrate a viscous type of behaviour, the 70°Brix syrups possess an elastic behaviour, while the 50°Brix syrups present a mixed behaviour over the temperature range of 20 to 80°C. These syrups did not demonstrate any thixotropy or time dependence of viscosity. The complex viscosity was described successfully with a mathematical model that incorporates both independent variables, with an Arrhenius-type dependence on temperature, with an activation energy of 21.94 kJ mol^{-1} for the whole Brix range. The flow behaviour evaluation of the 30 and 50°Brix showed that these are shear-thinning fluids, tending to Newtonian fluids at higher temperatures. The dynamic viscosity was well described by the power law and the dependence of its parameters on temperature was adequately described by a Turian approach. The syrups of *Ziziphus lotus* fruit demonstrated a potential for further beneficial research with a view to obtaining a commercial food product.

K e y w o r d s: *Ziziphus lotus* L., syrup, shear-thinning, rheology, enzymatic extraction

INTRODUCTION

Ziziphus lotus (*Z. lotus*) is a deciduous shrub belonging to the family of Rhamnaceae (Abdoul-Azize, 2016). This plant is common throughout Tunisia and is known locally as "Sedra". It has tasty fruit called "Nbeg" which are consumed raw (Hammi *et al*., 2015) 2-diphenyl-1-picrylhydrazyl radical scavenging activity and phosphomolybdenum assay. The optimum operating conditions for extraction were as follows: ethanol concentration, 50%; extraction time, 25 min; extraction temperature, 63°C and ratio of solvent to solid, 67 mL g^{-1}. Under these conditions, the obtained extract exhibited a high content of phenolic compounds (40.782 mg gallic acid equivalents g^{-1} dry matter. The varied composition of the fruit gives it a high nutritional value. In fact, the fruit pulp is rich in sugars, fibres, vitamin A, vitamin C, fatty acids, mineral matter, tannins and antioxidant compounds (Abdoul-Azize, 2016). In regions where this species is abundant, the fruit pulp is dried, processed into flour and incorporated in certain homemade pastry products (Bahrasemani Koohestani *et al*., 2019). Recent studies have made use of this fruit pulp as a functional ingredient for sponge cake preparation (Najjaa *et al*., 2020) and for juice formulation (Benidir *et al*., 2020). The transformation of this fruit pulp into other energetic products, notably syrup, is of interest for the development of new food products and alternatives for increasing the added value of this fruit.

Syrups are prepared from the pulps of other fruits, like date and carob, and are gaining increasing interest due to their richness in nutrients and bioactive compounds which contributes to their health benefits as confirmed by research (Dhaouadi *et al*., 2014; Taleb *et al*., 2016). These syrups can also be used as a natural sweetening agent in food product formulation (Borchani *et al*., 2019). Syrups are always

*Corresponding author e-mail: touka.letaief@gmail.com
**This work was supported by Foundation for Science and Technology for its support under UIDB/00681/2020 (2020-2024).

prepared according to the traditional method, in brief, this consists of mixing the fruit and water, heating the mixture, filtering and then boiling the juice obtained to the desired degree Brix (Dhaouadi *et al*., 2014). However, for further industrial application, it is useful to integrate an enzymatic treatment into the syrup manufacturing process. In fact, the enzymes may improve both the yield and the quality of the fruit juice and, as a consequence, affect the properties of the final product such as viscosity (Bahramian *et al*., 2011).

The viscosity and related rheological properties of fruit products are of high importance in the food field (Sengül *et al*., 2007). Their assessment will indicate the usefulness of the syrup to the consumer and on production lines, as a fluid-like material or as a solid-like material. These properties may be defined through the measurement of applied force and deformation over time (Tabilo-Munizaga and Barbosa-Cánovas, 2005).

In this context, the first study to elaborate the characteristics of *Z. lotus* fruit syrup is described in this article. The syrups which were obtained using both traditional and enzymatic methods were subjected to chemical and rheological characterizations.

MATERIALS AND METHODS

The ripe fruit of *Z. lotus* were harvested during August 2018 from the village of Oudhref-Gabes situated in southern Tunisia, then stored under dry conditions for further use. The fruit was manually pitted and crushed in a lab grinder. The extraction process followed two independent procedures.

Traditional extraction (TE) consisted of macerating a quantity of the obtained fruit powder for 30 min in water at a ratio of 1:4 (w/v). Next, the mixture was heated in an oil bath with a controlled temperature of 90°C. After 30 min of boiling, the mixture was filtered through a cloth and then centrifuged at 2907 g for 15 min (Rotanta 460R, Germany). The collected juice, with 17°Brix, was concentrated using a heating plate until the desired °Brix (30, 50 and 70) was reached. The three syrups were stored in glass jars at 4°C until they were required for analysis.

The enzymatic extraction (EE) process was based on testing the effect of the two enzymes, pectinase and cellulase. With reference to the method of Abbès *et al*. (2011), with some modifications, the fruit powder and the distilled water were mixed in a ratio of 1:4 (w/v). At pH 5, 833.5 nKat of pectinase 100 g^{-1} and 1.38 nKat of cellulase 100 g^{-1} were added to the mixture. The homogenous assortment obtained was heated in a thermo-controlled oil bath at 50°C for a period of 120 min. Then, the temperature was increased to 90°C in order to inactivate the enzymes. After filtration through a cloth, the obtained filtrate was centrifuged at 2907 g for 15 min. Three syrups with different °Brix values (30, 50 and 70) were obtained after the concentration of the juice by heating. The samples were stored in glass jars at 4°C until the tests were conducted.

The moisture content was evaluated according to the Association of Official Analytical Chemists methods AOAC 925.45 (AOAC, 1995). In brief, approximately 2 g of sample was packed into dried capsules and placed in an oven at 60ºC under a pressure of ≤50 mm Hg until a constant weight was obtained, after that, the capsules were cooled in a desiccator and weighed. The ash content was estimated with reference to (AOAC 900.2); the previously dried samples were placed in a muffle furnace at 550ºC for 2 h. In order to determine the crude protein level, the Kjeldahl method was used (AOAC 945.23) with a factor of 6.25. The crude fibre was analysed according to AOAC 962.09 and the crude fat level was determined using the Soxhlet apparatus referring to the AOAC 948.22 method.

The CIELAB coordinates (L*, a*, b*) of the syrups were read using a handheld Minolta CR 200 Chroma-Meter with an illuminator C. L* defines the lightness ranging from 0 (pure black) to 100 (diffuse white), a* and b* are the two channels for colour, where the a* axis extends from green (-a*) to red (+a*) and the b* axis extends from blue (-b*) to yellow (+b*).

Rheological analyses of the syrups were carried out using a Thermo Fisher Scientific HAAKE RheoStress 6000 rheometer controlled by HAAKE RheoWin Software version 1.3. Two measuring geometries were used: CC25 DIN Ti and P35 Ti L.

CC25 DIN Ti is a coaxial cylinder with a 32 mm diameter used for the liquid-like samples. Its titanium rotor has a length of 60 mm, an angle of 60° and a radius of 12.5 mm, the cap has an internal radius of 13.6 mm, the volume of the sample is 16.1 mL and there is a gap of 1.7 mm.

P35 Ti L is a plate-plate system with a diameter of 60 mm (17.5 mm is the radius of the cone and 18 mm is the radius of the measuring plate). This geometric system was used to analyse all of the samples.

With the plate-plate system, the oscillatory time sweep test was conducted in the controlled-stress (CS) mode with a shear stress of 10 Pa situated in the linear viscoelastic range at a frequency of 5Hz. The duration of the test was 600 s and the temperature was fixed at 20°C. In the same conditions, the oscillatory temperature ramp was performed in the range from 20 to 80°C, with the temperature increasing at a rate of 0.1°C s^{-1} and the measurements being performed each 30 s.

With the coaxial cylinder, the flow behaviours of liquid-like samples were determined using the CS/CR-rotation ramp test at a constant temperature. The applied shear rate was automatically controlled at an increasing order from 0 to 100 Hz over a period of 600 s. The effect of temperature was tested in independent tests at 20, 40, 60 and 80°C.

At a temperature of 20°C and only for the samples with 30 and 50°Brix, the test described above was followed by a CS/CR-rotation step test. The increase in the shear rate was followed by the maintenance of a constant value of 100 s^{-1} for 150 s and, finally, a decrease from 100 to 0 s^{-1} for 600 s.

These rheological measurements were completed in triplicate.

The oscillation tests allow for the elastic and viscous components to be obtained according to Mezger (2006):

$$G^* = G' + iG'', \tag{1}$$

where: G^* is the complex shear modulus (Pa), G' is the storage modulus (Pa), G'' is the viscous modulus (Pa), with $i = \sqrt{-1}$. The complex shear modulus is obtained using the Pythagoras theorem:

$$G^{*2} = G'^2 + iG''^2. \tag{2}$$

The ratio G''/G' allows one to determine if the material behaves as a solid, as a fluid or has an intermediate (viscous elastic) behaviour. This is more clearly seen with the loss angle (δ):

$$\delta = arctan\left(\frac{G''}{G'}\right), \tag{3}$$

where: δ is equal to 90° when the material is an ideal fluid and is equal to 0° when it is an ideal solid.

The complex viscosity is obtained from the complex shear modulus:

$$|\eta^*| = |G^*|/\omega, \tag{4}$$

where: η^* is the complex viscosity (Pa s) and ω (s^{-1}) is the rotation frequency.

The effect of temperature on the complex viscosity of the syrups was analysed using the Arrhenius equation (Rao *et al*., 1984):

$$\eta^* = \eta^*_\infty e^{\frac{Ea}{RT}}, \tag{5}$$

where: η^*_∞ is the complex viscosity at infinite temperature (Pa s), Ea is the activation energy (J mol^{-1}), R is the molar gas constant (J mol^{-1} K), and T is temperature (K).

The effect of the concentration of solids on the complex viscosity of the syrups was analysed using the following exponential relationship (Rao *et al*., 1984):

$$\eta^* = \eta^*_S e^{cC}, \tag{6}$$

where: η^*_S is the complex viscosity of the pure solvent (Pa s), c is the constant related to the solids content ($\%^{-1}$; m m^{-1}), and C is the solids content (%; m m^{-1}).

Equations (5) and (6) may be combined to deliver Eq. (7):

$$\eta^* = \eta^*_{S,\infty} e^{cC} e^{\frac{Ea}{RT}}, \tag{7}$$

where: $\eta^*_{S,\infty}$ is the complex viscosity of the pure solvent at infinite temperature (Pa s).

For predominantly viscous (liquid-like) syrups, flow curves were determined with the following analysis of the results. The power-law model was used to describe the flow behaviour:

$$\eta = K\dot{\gamma}^{n-1}, \tag{8}$$

where η is the dynamic viscosity (Pa s), K is the consistency index (Pa s^n) and n is the flow behaviour index that is equal to 1 for Newtonian fluids, higher than 1 for shear-thickening fluids and smaller than 1 for shear-thinning fluids (Mezger, 2006).

The consistency index and the flow behaviour indexes were tested against a Turian approach (Ramaswamy and Marcotte, 2005) to verify the type of dependence with temperature:

$$K = K_0 e^{-kT}, \tag{9}$$

$$n = n_0 + mT, \tag{10}$$

where: K_0, k, n_0 and m are the Turian parameters.

The results are presented in terms of means ± standard deviation of three replicates. One-way and two-way ANOVA were used to compare the means. The significant difference is considered when $p < 0.05$. SPSS Statistics 25 software (IBM, USA) was used to perform these statistical analyses.

Table Curve 2D and Table Curve 3D (Systat Software Inc., USA) were used to fit 2D and 3D data. The fitting quality of each model was assessed using the coefficient of determination (R^2):

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y-\hat{y})^2}{\sum_{i=1}^{n}(y-\bar{y})^2}. \tag{11}$$

RESULTS AND DISCUSSION

The chemical compositions of the pulp powder and the syrups prepared using the traditional method and the enzymatic method are given in Table 1.The pulp powder is characterized by a low moisture level of 14.93% which may explain the hard consistency of the pulp and its ability to be preserved for a long time. This fruit reveals low contents in term of ash (2.78% d.m.), protein (3.33% d.m.), fibre (5.35% d.m.) and fat (0.39% d.m.). These values are in accordance with those obtained by Abdeddaim *et al.* (2014) analysing the same species, *Z. lotus*. The ash and fibre contents were respectively 3.2 and 4.84% d.m., with a lower value for the protein content (1.18% d.m.) and higher value for the fat content (0.79% d.m.). The energy value of 1636.36 kJ 100 g^{-1} reflects the high energetic intake of this fruit. The rich composition of dry matter which mainly consisted of carbohydrates, suggests that this fruit can be valorized in the production of valuable products such as syrup.

The transformation of the fruit powder into a syrup significantly affected the chemical composition ($p < 0.05$). An increase in the level of carbohydrate was observed coupled with a decrease in the ash and protein contents. The amount of fat in the unprocessed fruit was very low, therefore, it was not detected in all of the syrups. Also, the syrup preparation affected the fibre content as it was not detected in

Table 1. Chemical compositions of *Z. lotus* fruit and its derivatives syrups

Components	Pulp powder	Syrups with traditional extraction			Syrups with enzymatic extraction		
Total soluble solids (°Brix)	–	30	50	70	30	50	70
Moisture (g 100 g^{-1}, w.b.)	14.39 ± 0.38[a]	69.34 ± 0.14[b]	50.68 ± 0.01[c]	32.54 ± 0.05[d]	70.9 ± 0.01[b]	51.92 ± 0.18[c]	29.43 ± 0.59[d]
Ash*	2.78 ± 0.04[a]	2.47 ± 0.09[b]	2.68 ± 0.08[b]	2.52 ± 0.04[b]	2.38 ± 0.11[c]	2.14 ± 0.08[c]	2.52 ± 0.08[c]
Crude protein*	3.33 ± 0.14[a]	2.16 ± 0.29[b]	2.05 ± 0.04[b]	2.06 ± 0.07[b]	2.16 ± 0.5[b]	2.12 ± 0.02[b]	2.19 ± 0.18[b]
Crude fibre*	5.35 ± 0.35	ND	ND	ND	ND	ND	ND
Crude fat*	0.39 ± 0.06	ND	ND	ND	ND	ND	ND
Total carbohydrates*	93.49 ± 0.16[a]	95.37 ± 0.39[b]	95.27 ± 0.04[c]	95.42 ± 0.04[d]	95.46 ± 0.64[b]	94.55 ± 0.15[c]	95.29 ± 0.09[d]
Energy (kJ 100 g^{-1})	1636.36 ± 0.46	1633.36 ± 0.38	1629.81 ± 0.32	1632.54 ± 0.14	1634.81 ± 0.45	1638.96 ± 0.31	1632.5 ± 0.33

*Grams per 100 g of dry material, ND – not detected. Average values in the same row, with different indexes are significantly different ($p < 0.05$).

all of the transformed samples. The enzymatic treatment did not have a noticeable effect on the compositions of the syrups compared to the traditional extraction methods. The compositions of *Z. lotus* syrups indicate their ability to be used in the food industry as a substitute for chemical ingredients.

The CIELAB coordinates of the *Z. lotus* syrups prepared using both traditional and enzymatic extraction methods are given in Table 2. The values of L*, a* and b* are significantly ($p < 0.05$) affected by the total degree Brix. Samples presenting a lower degree Brix tend to have a red (higher a*) and yellow (higher b*) tinge and present higher lightness values (L*). No effect of the enzyme treatment on the colour parameters was observed.

The study of the rheological behaviour of these syrups provides a partial explanation for their physical properties and outlines the factors affecting their behaviour for the purposes of future industrial exploitation and consumer use. The characterization of its liquid-like or solid-like state behaviour at different temperatures is essential for the determination of how its properties may be usefully manipulated.

The complex shear modulus (G) varies from 2.6 Pa obtained at the highest temperature and lower Brix (80°C/30°Brix) value treated with the enzyme, to 459.8 Pa obtained at the lowest temperature and higher Brix (20°C/70ºBrix) value, this result was obtained using the traditional extraction method, measured at 5 Hz (Table 3). These values are in the range of very soft gel structures (5-10 Pa, like salad dressings) to viscoelastic gels (50 to 5 000 Pa, like creams and food pastes) according to Mezger (2006). Values with similar orders of magnitude were also found in syrups. Date syrups presented values of the order of 10^5 Pa at 20°C to 10^1 Pa at 80°C (Abbès *et al*., 2015). Honey also presented values in this range at 20°C for frequencies between 10^{-3} to 1 Hz (Schellart, 2011) 5 and 10% by weight and between 10^2 and 10^3 Pa at 30 Hz (Bakier, 2016).

Table 2. CIELAB coordinates (L*, a*, b*) of *Z. lotus* syrups

CIELAB coordinates	Syrups with traditional extraction			Syrups with enzymatic extraction		
	30	50	70	30	50	70
L*	29.00 ± 0.00[a]	25.70 ± 0.00[b]	24.87 ± 0.20[c]	29.23 ± 0.05[a]	25.70 ± 0.10[b]	24.97 ± 0.11[c]
a*	7.50 ± 0.40[a]	6.30 ± 0.28[b]	4.23 ± 0.28[c]	7.40 ± 0.10[d]	6.55 ± 0.07[e]	4.10 ± 0.14[f]
b*	4.85 ± 0.21[a]	1.10 ± 0.14[b]	-0.40 ± 0.00[c]	5.20 ± 0.28[a]	1.90 ± 0.17[b]	-1.60 ± 0.14[c]

Explanations as in Table 1.

Table 3. Complex shear modulus (Pa) of *Z. lotus* syrups

T (°C)	Syrups with traditional extraction (°Brix)			Syrups with enzymatic extraction (°Brix)		
	30	50	70	30	50	70
20	12.7 ± 0.4[a]	72.2 ± 3.3[b]	459.8 ± 9.8[c]	10.8 ± 0.2[d]	42.6 ± 0.5[e]	436.4 ± 27.2[f]
40	8.9 ± 0.1[a]	51.6 ± 1.1[b]	348.2 ± 11.6[c]	7.7 ± 0.2[d]	44.5 ± 0.3[e]	312.0 ± 19.7[f]
60	5.0 ± 0.1[a]	28.5 ± 0.3[b]	200.8 ± 6.2[c]	4.3 ± 0.1[d]	30.5 ± 0.1[e]	171.3 ± 8.6[f]
80	3.0 ± 0.0[a]	16.9 ± 0.1[b]	124.8 ± 3.1[c]	2.6 ± 0.1[d]	9.4 ± 0.1[e]	113.0 ± 5.7[f]

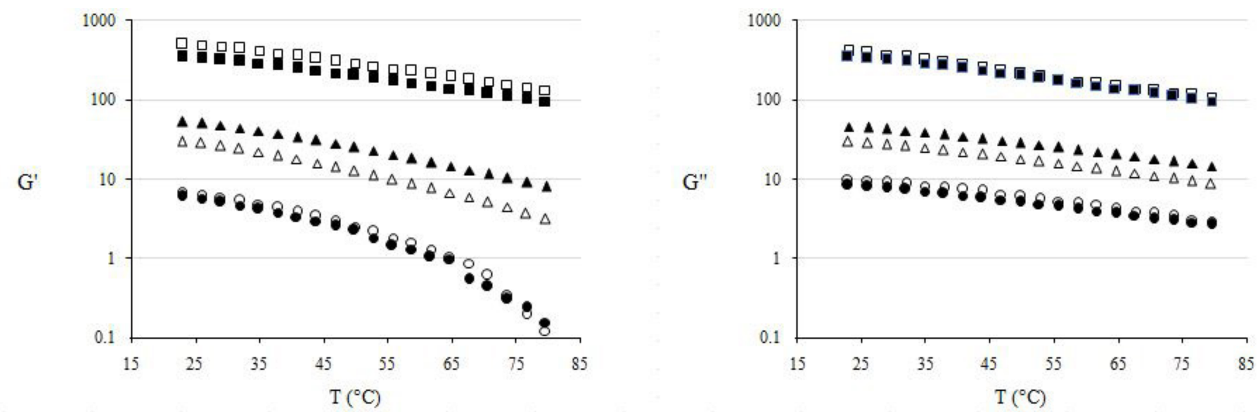

Fig. 1. *G*' and *G*'' modulus dependence on temperature, degree Brix of the syrup with and without enzyme treatment (●30°C, ○30°C enzyme, ▲50°C, Δ 50°C enzyme, ■70°C, □70°C enzyme).

The complex shear modulus decreased with the rise in temperature and increased at the higher degree Brix (Table 3), thereby reflecting the syrup states that exhibit a more viscous liquid state at a higher temperature and lower degree Brix. The enzymatic treatment also affected ($p < 0.05$) the values of G, they decreased. In fact, the enzymes pectinase and cellulase ensure the cleavage of the pectin and cellulose polymers and hence promote the prevalence of the viscous state. A decrease in G^* is related to a decrease in the complex viscosity. It has already been observed that the enzymatic tretament of other syrups and fruit juices decreases their viscosity (Al-Hooti *et al*., 2002) which is native to the Mediterranean region and originated in the Arabian Gulf area, is now becoming an important commercial crop in Kuwait. Because of the tremendous efforts of the Public Authority for Agriculture and Fisheries Resources, date palm cultivation has developed quickly in Kuwait during the last decade. These newly planted date fruit trees, as well as tissue culture plants being produced and distributed by KISR, would start bearing fruit in a few years. It may not then be possible to consume all the fresh date fruit locally and, subsequently, newer avenues for turning this surplus fruit into value-added products will become a necessity and a commercially viable venture. Technology was developed on a laboratory scale for the production of date syrup from tamer fruits of two commercial varieties, Birhi and Safri, for further use in food products. Both the varieties were found to be high in total sugar contents (about 88%).

The loss and storage modulus (*G''* and *G'*) of all of the syrups decreased with temperature in the range studied of 20 to 80°C, as shown in Fig. 1. This is an expected result since at higher temperatures the mobility of the molecules is higher (Katsuta and Kinsella, 1990). No abrupt change in both moduli was observed, which is an indication that no phase change occurred within the studied temperature range. Both moduli presented a decrease with temperature that was close to linearity, except for *G'* (the elastic component) of the 30°Brix samples, which decreases more as the temperature rises, tending towards a more viscous (liquid-like) behaviour. This may be observed more clearly in Fig. 2, where the loss angle delta (Eq. (3)) of the syrups is shown for the temperature range studied. The 30°Brix syrup always has a more viscous behaviour (> 45°) over the entire temperature range, for the samples treated with and without enzyme. Syrups of 50°Brix presented mixed properties: more elastic (solid-like) at 20°C for the samples treated or not treated with enzyme, but increasingly viscous up to 80°C. The elastic behaviour is observed over the whole temperature range studied for the 70°Brix syrups (< 45°). This must be due to the lower content of water molecules, the solvent molecules that constitute the

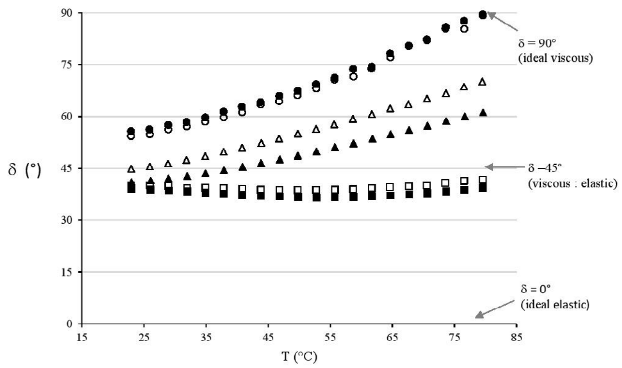

Fig. 2. Phase shift dependence on temperature and degree Brix of the syrup, with and without enzyme treatment. Explanations as in Fig. 1.

flow medium to these syrups and are thus responsible for the magnitude of its flow properties. As explained by Ben Thabet *et al.* (2009) rheological, thermal, sensory properties and by its antioxidant activity. Syrups from date palm sap have a good nutritional value marked by high amounts of sugars (58-75 g 100 g^{-1} fresh matter basis, the interaction between the water molecules and the other molecules affected the molecular movement in the sample.

Glucose syrups and honey presented a viscous behaviour at 20°C (Schellart, 2011) as well as date syrups with 80°Brix (Abbès *et al*., 2015). The difference between the behaviour of *Z. lotus* and the abovementioned products may be the additional fibre and protein that these syrups contain. Honey is composed of solids (77-88%) of which close to 95% are sugars (Machado De-Melo *et al*., 2018). *Z. lotus* contains between 95.94 and 97.03% carbohydrates, of which, according to Abdeddaim *et al*. (2014), no more than 86% are sugars. The fibre and protein these *Z. lotus* syrups contain may explain their more elastic behaviour at low water contents (70°Brix), with these polymers contributing to a more solid structure rather than forming a fluid typical of high sugar content solutions.

The activation energy is the energy required to resist against the frictional forces and thus set the molecules in motion, thereby reflecting the effect of temperature change on the viscosity values (Makhlouf-Gafsi *et al*., 2016). In this work, the Arrhenius model parameters were estimated using Eq. (5), with an R^2 value higher than 0.99, and with activation energies varying between 21.6 and 24.6 kJ mol^{-1}, for the studied ranges of temperature, for each set of degree Brix and enzyme treatment (data not shown).Overall these values are less than half the ones of date syrups that presented activation energies ranging from 48.9 to 75.2 kJ mol^{-1} (Abbès *et al*., 2015). This divergence with the activation energy of *Z. lotus* syrups may be due to the different origin and the composition of the raw material affecting the chemical structure of the obtained syrups and thereby influencing the activation energy (Makhlouf-Gafsi *et al*., 2016). As discussed previously, *Z. lotus* syrups contain more fibre and protein than date syrups and it may be the case that temperature has a lower effect on the viscosity of solutions of these molecules than on sugar solutions. Barreto *et al*. (2003) temperature and plasticizer content. The shear stress-shear rate plot showed typical Newtonian behaviour in all of the studied systems. The effect of temperature on the viscosity was described by the Arrhenius equation, where the activation energy values obtained varied from 7.5 to 12.1 kJ mol^{-1} as the concentration changed from 10.5 to 13.0% (w/w and Cepeda and Collado (2014) reported, for protein-rich and fibre-rich products respectively, activation energies lower than 12.3 kJ/mol and (Mossel *et al.,* 2000) blue top iron bark, gum top, heath, narrow leafed iron bark, stringy bark, tea tree, yapunyah and yellow box reported activation energies of sugar-rich solutions (honey) in the range of 60-120 kJ mol^{-1}.

Although the variation of the mean between the samples is relatively low, the activation energy is affected by the extraction method and the degree Brix. However, these effects are related to the solids content of these syrups, with the viscosity following an exponential trend according to Eq. (6). These findings are in accordance with the results of Borchani *et al*. (2019) and Abbès *et al*. (2015) who confirmed that enzymatic treatment enhances the activation energy, though no relationship with the solids content was established. Nevertheless, Chetana *et al.* (2004) also observed the same influence of solids content in polydextrose and maltodextrin solutions.

The complex viscosity of *Z. lotus* syrups was thus shown to decrease exponentially both with the inverse of temperature and with solids content. This combined effect may be approached with a 3D model according to Eq. (7), assuming one value of activation energy for the entire degree Brix range and for both extraction methods, despite this simplification, the method allowed for the generation of output data with a good prediction accuracy, confirmed by a high R^2 and small errors of model parameters (Table 4, Fig. 3).

Table 4. Complex viscosity as a function of temperature and solids content: parameters and its errors of fitting Eq. (7)

$\eta^*_{s,\infty}$ (Pa s^{-1})	***c*** × 10^6($\%^{-1}$)	*Ea* (kJ mol^{-1})	R^2
0.100 ± 0.001	2.337 ± 0.512	21.94 ± 0.58	0.984

Within the ranges studied, the solids content affects the complex viscosity more than the temperature by an order of magnitude of 10, as illustrated in Fig. 3. When the solids content is decreased from 70.57 to 29.10%, at the same temperature, the viscosity can increase by 40 to 60 times, while the temperature can only increase the viscosity from 4 to 8 times when it is increased from 20 to 80°C, at different solid contents.

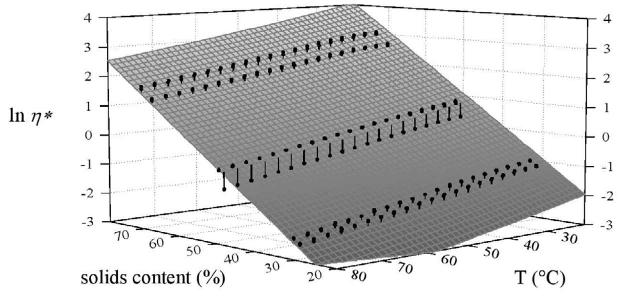

Fig. 3. Natural logarithm of complex viscosity variation according to temperature and solids content.

The flow curves of 30 and 50°Brix syrups prepared using traditional and enzymatic methods, obtained at 20, 40, 60 and 80°C, are shown in Fig. 4. For all of the temperatures and treatments examined, the syrups exhibited non-Newtonian behaviour. The shear stress rose with the increase in shear rate thereby reflecting shear-thinning (pseudoplastic) behaviour, translating into a dynamic viscosity decrease with the increasing shear rate. Date syrup evaluated at a temperature range from 20 to 80°C, also presented shear-thinning behaviour, which may be attributed to the effect of high temperature on overcoming the molecular resistance to flow by the disentanglement of long-chain branching (Gabsi *et al*., 2013). Despite the increase in temperature to 80°C, the syrups retained their non-Newtonian behaviour thereby demonstrating their stability independently of temperature variation. Syrups prepared with maltodextrin or polydextrose also presented shear-thinning behaviour, for a temperature range between 25 and 80ºC and with a solids content between 35 and 65% (m/m) (Chetana *et al*., 2004), while syrups prepared with sorbitol and sucrose presented a Newtonian behaviour. This may explain the behaviour of our syrups which contain a portion of long polysaccharides though most of the composition of the solids are expected to be sugars, as discussed previously.

Additionally, a test to evaluate the degree of thixotropy was performed. The shear rate was increased to 100 s^{-1}, the rate was maintained for 150 s, and then decreased to zero. The ascendant and descendant flow curves overlap (data not shown), presenting no hysteresis, which is an indicator of the absence of thixotropy. Also, these properties were shown to be time independent since the viscosity does not change after rest and at a constant shear rate (data not shown).

The samples with higher degree Brix demonstrated higher response values in the measured shear stress, which ranged from 0 to around 30 Pa and from 0 to around 140 Pa, respectively, for the 30 and 50°Brix samples. Thus, the rise in total soluble solids increased the viscosity, as in the oscillatory tests, which may be explained by the higher water content for the 30°Brix samples. Similar results were described for other liquid products like maple syrups and date syrups (Ngadi and Yu, 2004; Gabsi *et al*., 2013).

Enzymatic treatment also had an effect on the dynamic viscosity, which may be explained by the lower solids content of these samples, as discussed above with regard to complex viscosity. The samples that were treated with enzymes, at the same temperature and with a lower solids content, presented lower values of shear stress thereby reflecting a lower viscosity. A similar observation was reported in studies by Borchani *et al*. (2019) for pear syrup and Abbès *et al*. (2015) for date syrup. The enzyme promoted pectin degradation and as a consequence increased the free water content by reducing the water-holding capacity (Abbès *et al*., 2015) and additionally resulted in the presence of smaller molecules characterized by a greater degree of mobility.

The flow curves were fitted successfully (R^2 close to 1) with the power law model adequately defining the flow behaviour of these liquid samples. The consistency and

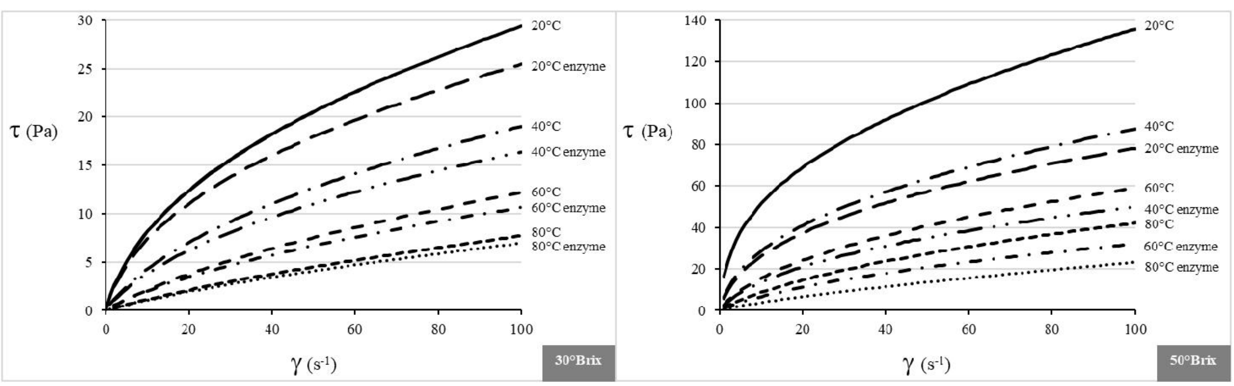

Fig. 4. Flow curves of syrups at 30 and 50°Brix with and without enzyme treatment at temperatures of 20, 40, 60 and 80°C.

Table 5. Consistency and flow behaviour indexes for syrups of 30 and 50°Brix

Brix	Treatment	T (°C)	K (Pa s^n)	N	R^2
30	normal	20	1.973 ± 0.011	0.597 ± 0.001	0.983
		40	0.797 ± 0.029	0.703 ± 0.009	0.962
		60	0.335 ± 0.012	0.791 ± 0.010	0.951
		80	0.144 ± 0.005	0.869 ± 0.008	0.940
	enzyme	20	1.854 ± 0.013	0.578 ± 0.002	0.988
		40	0.744 ± 0.027	0.687 ± 0.006	0.964
		60	0.334 ± 0.011	0.762 ± 0.007	0.966
		80	0.145 ± 0.016	0.850 ± 0.001	0.953
50	normal	20	17.960 ± 0.014	0.440 ± 0.000	0.998
		40	8.246 ± 0.131	0.527 ± 0.006	0.992
		60	3.583 ± 0.067	0.627 ± 0.006	0.979
		80	1.865 ± 0.004	0.695 ± 0.007	0.983
	enzyme	20	7.792 ± 0.099	0.513 ± 0.006	0.991
		40	3.077 ± 0.092	0.623 ± 0.012	0.975
		60	1.172 ± 0.045	0.743 ± 0.006	0.953
		80	0.604 ± 0.033	0.810 ± 0.000	0.977

Table 6. Turian parameters applied to consistency and flow behaviour indexes for syrups of 30 and 50°Brix

°Brix	Treatment	K_0 (Pa s^n)	$k\times10^2$ (°C^{-1})	R^2	n_0	$m\times10^3$ (°C^{-1})	R^2
30	normal	4.816 ± 0.125	4.468 ± 0.049	0.999	0.514±0.013	4.521 ± 0.230	0.995
	enzyme	4.455 ± 0.250	4.399 ± 0.109	0.999	0.496±0.013	4.464 ± 0.230	0.995
50	normal	39.291 ± 1.572	3.915 ± 0.073	0.999	0.356±0.012	4.325 ± 0.219	0.995
	enzyme	19.511 ± 1.171	4.599 ± 0.117	0.999	0.420±0.022	5.055 ± 0.406	0.987

flow indexes are presented in Table 5 and the results of the Turian approach to studying its dependence on temperature are presented in Table 6.

The consistency constant *K* decreased exponentially with temperature (Eq. (9)) as a result of the higher mobility of the molecules, mirroring the decrease in viscosity. The warming process leads to an increase in molecular thermal energy and the distance between molecules, as explained by (Makhlouf-Gafsi *et al*., 2016), decreasing friction and resulting in a viscosity decrease. For 30°Brix, *K* is similar for enzyme treated samples and non-enzyme treated samples and varied between 0.144 Pa s^n at 80°C and 1.97 Pa s^n at 20°C. For 50°Brix, *K* varied between 0.604 Pa s^n at 80°C and 7.79 Pa s^n at 20°C for enzyme treated samples, while it was twice as high for the traditional extraction samples.

The flow index presents the opposite trend of that of the consistency index, it increases with the rise in temperature and decreases with a higher solids content. Once again, the enzymatic treatment only had an effect on the 50°Brix samples leading to an increase in the *n* index from 0.44 to 0.695 and from 0.513 to 0.81 with respect to the normal and enzymatic extraction samples. For all of the samples studied, the flow index is close to 1, the index of a Newtonian fluid, since at higher shear rates the polymer chains in shear-thinning fluids tend to align with the flow and this decreases the resistance of the fluid to the flow (Mezger, 2006). The Turian approach is fully confirmed with the index *n* showing a linear dependence with temperature (Eq. (10), Table 6).

CONCLUSIONS

1. Fruit syrups of *Z. lotus* were successfully obtained and characterized. A chemical analysis showed that these syrups can be used as a source of energy.

2. The rheological measurements for the studied concentrations within the temperature range 20-80°C showed that the 30°Brix samples displayed a viscous behaviour, thereby creating the potential for consumer use or enabling them to be pumped in a manufacturing environment, while the 70°Brix samples presented a predominantly elastic behaviour, resulting in a syrup which is difficult to manipulate. These syrups did not demonstrate thixotropy or any time dependence of viscosity.

3. The complex viscosity of the samples decreased with temperature and with decreasing solids content, they were described successfully with a mathematical model that incorporates both independent variables, with an Arrhenius-type dependence on temperature. The influence of enzyme treatment on viscosity occurs through its influence on the solids content.

4. The flow behaviour evaluation proved that the 30 and 50°Brix are shear-thinning fluids, tending to Newtonian fluids at higher temperatures.

5. Dynamic viscosity has been well described by the power law and the dependence of these parameters on temperature was adequately described by a Turian approach.

Conflict of interest. The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

REFERENCES

Abbès F., Bouaziz M.A., Blecker C., Masmoudi M., Attia H., and Besbes S., 2011. Date syrup: Effect of hydrolytic enzymes (pectinase/cellulase) on physico-chemical characteristics, sensory and functional properties. LWT - Food Sci. Technol., 44(8), 1827-1834. https://doi.org/10.1016/j.lwt.2011.03.020

Abbès F., Masmoudi M., Kchaou W., Danthine S., Blecker C., Attia H., and Besbes S., 2015. Effect of enzymatic treatment on rheological properties, glass temperature transition and microstructure of date syrup. LWT - Food Sci. Technol., 60(1), 339-345. https://doi.org/10.1016/j.lwt.2014.08.027

Abdeddaim M., Lombarkia O., Bacha A., Fahloul D., Abdeddaim D., Farhat R., Saadoudi M., Noui Y., and Lekbir A., 2014. Biochemical characterization and nutritional properties of *Zizyphus lotus* L. fruits in Aures region, northeastern of Algeria. Annals Food Sci. Technol., 15(1), 75-81.

Abdoul-Azize S., 2016. Potential benefits of jujube (*Zizyphus lotus* L.) bioactive compounds for nutrition and health. J. Nutr. Metab., Article ID 2867470. https://doi.org/10.1155/2016/2867470

Al-Hooti S.N., Sidhu J.S., Al-Saqer J.M., and Al-Othman A., 2002. Chemical composition and quality of date syrup as affected by pectinase/cellulase enzyme treatment. Food Chem., 79(2), 215-220. https://doi.org/10.1016/S0308-8146(02)00134-6

AOAC, **1995.** Official Methods of Analysis (A. of O. A. Chemists (ed.)).

Bahramian S., Azin mehrdad, Chamani M., and Gerami A., 2011. Optimisation of enzymatic extraction of sugars from dates. Middle-East J. Scientific Res., 7(2), 211-216.

Bahrasemani Koohestani M., Sahari M.A., and Barzegar M., 2019. The effect of jujube powder incorporation on the chemical, rheological, and sensory properties of toffee. Food Sci. Nutrition, 7(2), 678-688. https://doi.org/10.1002/fsn3.912

Bakier S., 2016. Rheological properties of honey in a liquid and crystallized state. In Intech: Vol. i (Issue tourism). https://doi.org/http://dx.doi.org/10.5772/57353

Barreto P.L.M., Roeder J., Crespo J.S., Maciel G.R., Terenzi H., Pires A.T.N., and Soldi V., 2003. Effect of concentration, temperature and plasticizer content on rheological properties of sodium caseinate and sodium caseinate/sorbitol solutions and glass transition of their films. Food Chem., 82(3), 425-431. https://doi.org/10.1016/S0308-8146(03)00006-2

Ben Thabet I., Besbes S., Masmoudi M., Attia H., Deroanne C., and Blecker C., 2009. Compositional, physical, antioxidant and sensory characteristics of novel syrup from date palm (*Phoenix dactylifera* L.). Food Sci. Technol. Int., 15(6), 583-590. https://doi.org/10.1177/1082013209353079

Benidir M., El Massoudi S., El Ghadraoui L., Lazraq A., Benjelloun M., and Errachidi F., 2020. Study of Nutritional and organoleptic quality of formulated juices from jujube (*Ziziphus lotus* L.) and dates (*Phoenix dactylifera* L.) fruits. The Scientific World J., 9872185. https://doi.org/10.1155/2020/9872185

Borchani M., Masmoudi M., Ben Amira A., Abbès F., Yaich H., Besbes S., Blecker C., Garvin A., Ibarz A., and Attia H., 2019. Effect of enzymatic treatment and concentration method on chemical, rheological, microstructure and thermal properties of prickly pear syrup. Lwt, 113 (March), 108314. https://doi.org/10.1016/j.lwt.2019.108314

Cepeda E. and Collado I., 2014. Rheology of tomato and wheat dietary fibers in water and in suspensions of pimento purée. J. Food Eng., 134, 67-73. https://doi.org/10.1016/j.jfoodeng.2014.03.007

Chetana R., Krishnamurthy S., and Yella Reddy S.R., 2004. Rheological behavior of syrups containing sugar substitutes. European Food Res. Technol., 218(4), 345-348.

Dhaouadi K., Belkhir M., Akinocho I., Raboudi F., Pamies D., Barrajón E., Estevan C., and Fattouch S., 2014. Sucrose supplementation during traditional carob syrup processing affected its chemical characteristics and biological activities. LWT - Food Sci. Technol., 57(1), 1-8. https://doi.org/10.1016/j.lwt.2014.01.025

Gabsi K., Trigui M., Barrington S., Helal A.N., and Taherian A.R., 2013. Evaluation of rheological properties of date syrup. J. Food Eng., 117(1), 165-172. https://doi.org/10.1016/j.jfoodeng.2013.02.017

Hammi K.M., Jdey A., Abdelly C., Majdoub H., and Ksouri R., 2015. Optimization of ultrasound-assisted extraction of antioxidant compounds from Tunisian *Zizyphus lotus* fruits using response surface methodology. Food Chem., 184, 80-89. https://doi.org/10.1016/j.foodchem.2015.03.047

Katsuta K. and Kinsella J.E., 1990. Effects of temperature on viscoelastic properties and activation energies of whey protein gels. J. Food Sci., 55(5), 1296-1302. https://doi.org/10.1111/j.1365-2621.1990.tb03920.x

Machado De-Melo A.A., Almeida-Muradian L.B. de, Sancho M.T., and Pascual-Maté A., 2018. Composition and properties of *Apis mellifera* honey: A review. J. Apicultural Res., 57(1), 5-37. https://doi.org/10.1080/00218839.2017.1338444

Makhlouf-Gafsi I., Baklouti S., Mokni A., Danthine S., Attia H., Blecker C., Besbes S., and Masmoudi M., 2016. Effect of ultrafiltration process on physico-chemical, rheological, microstructure and thermal properties of syrups from male and female date palm saps. Food Chem., 203, 175-182. https://doi.org/10.1016/j.foodchem.2016.02.055

Mezger T.G., 2006. The Rheology Handbook. Elsevier Science Limited.

Mossel B., Bhandari B., D'Arcy B., and Caffin N., 2000. Use of an arrhenius model to predict rheological behaviour in some australian honeys. LWT – Food Sci. Technol., 33(8), 545-552. https://doi.org/10.1006/fstl.2000.0714

Najjaa H., Arfa A. Ben, Elfalleh W., Zouari N., and Neffati M., 2020. Jujube (*Zizyphus lotus* L.): Benefits and its effects on functional and sensory properties of sponge cake. PLoS ONE, 15(2), 1-14. https://doi.org/10.1371/journal.pone.0227996

Ngadi M.O. and Yu L.J., 2004. Rheological properties of Canadian maple syrup. Canadian Biosystems Engineering / Le Genie Des Biosystems Au Canada, 46, 15-18.

Ramaswamy H.S. and Marcotte M., 2005. Food Processing: Principles and Applications. CRC Press.

Rao M.A., Cooley H.J., and Vitali A.A., 1984. Flow properties of concentrated juices at low temperatures. Food Technol., 38(3), 113-119.

Schellart W.P., 2011. Rheology and density of glucose syrup and honey: Determining their suitability for usage in analogue and fluid dynamic models of geological processes. J. Structural Geology, 33(6), 1079-1088. https://doi.org/10.1016/j.jsg.2011.03.013

Sengül M., Ertugay M.F., Sengül M., and Yüksel Y., 2007. Rheological characteristics of carob pekmez. Int. J. Food Properties, 10(1), 39-46. https://doi.org/10.1080/10942910600627996

Tabilo-Munizaga G. and Barbosa-Cánovas G.V., 2005. Rheology for the food industry. J. Food Eng., 67(1-2), 147-156. https://doi.org/10.1016/j.jfoodeng.2004.05.062

Taleb H., Maddocks S.E., Morris R.K., and Kanekanian A.D., 2016. The antibacterial activity of date syrup polyphenols against *S. aureus* and *E. coli*. Frontiers in Microbiol., 7(FEB), 1-9. https://doi.org/10.3389/fmicb.2016.00198