Modelling the Rheological Behaviour of Enzyme Clarified Lime (*Citrus aurantifolia* L.) Juice Concentrate

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Abstract

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The rheological behaviour of enzyme clarified Lime (*Citrus aurontifolia* L.) juice was studied as a function of the total soluble solid (TSS) content (7.3–55.7°Brix), corresponding water activity (a_w) (0.985–0.831) at different temperatures (20–80°C) using co-axial controlled stress rheometer. The rheological parameter shear stress was measured up to the shear rate of 600 s^{-1}. The investigation showed that the enzyme clarified lime juice and its concentrate behaved like a Newtonian fluid with the viscosity (η) being in the range 3.964 to 50.290 mPa s depending upon the concentration and temperature used. The temperature dependency on the viscosity of lime juice was described by Arrhenius equation ($r > 0.99$) and the activation energy (E_a) of viscous flow was in the range 4.151 to 26.050 kJ/mol depending upon the total soluble solids content. The effect of total soluble solid content on the flow activation energy was described by exponential type equation ($r > 0.98$) and that of water activity was described by both the power law and exponential equations ($r > 0.99$). The effect of total soluble solid content on the viscosity of lime juice followed the second order exponential equation ($r > 0.99$) at the temperature used. The effect of water activity on the viscosity was described by both the power law and exponential type relationship ($r > 0.97$). The equations relating to the combined effect of temperature and total soluble solids content/water activity on the viscosity of enzyme clarified lime juice were established.

Keywords: combined effect; power law model; exponential model; rheology; viscosity; Arrhenius equation; activation energy

The processing and preservation of fruit juices by thermal processing such as heat sterilisation, evaporation, and pasteurisation is favoured for longer periods of storage. The processing of juice involves several unit operations, where the juice properties such as viscosity, soluble solid content, nature of soluble solids, and temperature vary during processing. The flow properties and the behaviour of the processed juice products are important in determining the power requirement for pumping, sizing the pipes design of the processing equipment such as heat exchangers, mixing, filling etc. (Telis-Romero *et al.* 1999; Kimball *et al.* 2004). The fruit juice processing and subsequent liquid properties are much important besides the rheological behaviour such as viscosity which arises from the flow and deformation of matter. This plays an important role in such processing as plant design, flow processes, quality control, and stability. The information on the viscosity of fruit juices as influenced by the concentration and temperature is of particular importance in the design and operation of several processing equipments (Krokida *et al.* 2001; Nindo *et al.* 2005).

The rheological behaviour of fruit juices in the original and depectinated forms is important in understanding the pumping and flow requirements in fruit juice processing industries including aseptic processing. The relationship between shear stress and shear rate was described by Ostwald-De-Waele model or the power law equation

$$\sigma = K\,\gamma^n \quad (1)$$

where:
σ – shear stress (Pa)
K – consistence index (Pa·s^n)
γ – shear rate (s^{-1})
n – flow behaviour index (–)

If the fluid is Newtonian in nature, $n = 1$ and hence K becomes viscosity η (Pa·s) of the fluid.

Enzymic clarification is one of the most important techniques to enhance qualitative and quantitative characteristics of juice. The effects of the enzyme pectinase, incubation time, and temperature on rheological characteristics of mango pulp was studied. It was found that enzyme treated mango pulp behaved like a pseudoplastic liquid and all variables had significant effects on rheological parameters of mango pulp (Bhattacharya & Rastogi 1998). Several authors studied the effect of pectinase on physicochemical characteristics of fruit juice clarification and reported that all the variables had a significant effect on the viscosity of juices (Rai *et al.* 2004; Lee *et al.* 2006; Sin *et al.* 2006; Abdullah *et al.* 2007). Ahmed and Ramaswamy (2004) studied the effects of temperature, total soluble solid content, α-amylase concentration, and pH on rheological characteristics of papaya puree using the response surface methodology. Several investigators reported that clarified and depectinated juices and their concentrates exhibit Newtonian flow behaviour (Ibarz *et al.* 1987, 1992a,b; Cepeda & Villaran 1999; Juszczak & Fortuna 2004). Several authors used Newtonian equation for describing rheological behaviour of food products such as Pomegranate juice (Altan & Maskan 2005), Pekmez (Kaya & Balibagli 2002), Liquorice extract (Maskan 1999), however, certain juices with a low pulp content and soluble solid content less than 30°Brix also behave like a Newtonian liquid (Krokida *et al.* 2001) described as:

$$\sigma = \eta\,\gamma \quad (2)$$

where:
σ – shear stress (Pa)
η – coefficient of viscosity (Pa·s)
γ – shear rate (s^{-1})

The production of citrus fruits has been increasing mainly due to the extended cultivation of citrus fruits in countries like USA, Brazil, Spain, Iran, India etc. because of the temperate and dry climatic conditions. Citrus fruits are classified as acid fruits; their soluble solids are mainly composed of organic acids and sugars. Citrus fruits contain a host of active phytochemicals and there are more than hundred bioactive compounds contained in citrus fruits. They also contain complex mixtures of flavonoid compounds, which include flavanone and flavones. Citrus fruits are among the most prominent cancer-preventing agents. Flavonoids possess a wide range of biological activities, such as the inhibition of key enzymes in mitochondrial respiration, protection against coronary heart diseases, and exhibit also anti-inflammatory, antioxidative, anticytotoxic, antitumor, and antimicrobial activities (Harborne & Williams 2000).

Lime juice is used for the preparation of several beverages such as ready to serve (RTS), carbonated and non-carbonated, squash, cordials, and other lime juice based drinks with sugar-flavouring agents. Lime juice is concentrated and stored in frozen conditions mainly for use as the base material for the preparation of lemonade. Lime cordial is prepared using clarified lime juice to an extent of 25%, TSS 30° Brix, acidity not more than 3.5%, and preservative, that has refreshing tartness and a highly distinctive flavour. Lime-barley water was prepared from lime squash by the addition of barley starch. Enzyme hydrolysis of lemon juice was carried out using commercial pectinase enzyme while the reduction in the particle size due to enzyme was reported (Carvalho *et al.* 2006). Rheological information on juice and its concentrate is necessary to design the processing equipment and process control of several unit operations. This is very useful for up scaling the process and commercialisation of the lime juice products. The present investigation was carried out to study the effects of total soluble solid concentration/water activity and temperature on the rheological behaviour of lime (*Citrus aurantifolia* L.) juice, and to model the rheological characteristics.

MATERIAL AND METHODS

Raw material. Fresh lime (*Citrus aurontifolia* L.) fruits at optimal maturity, with uniform size and shape and no visible infections were procured from local market of Mysore, India. The fruits were thoroughly washed with water and halved with a sharp stainless steel knife. The juice was extracted using stainless steel hand-held juice squeezer and filtered through a stainless steel sieve. It was then pasteurised in a water bath for 2 min at a temperature of 85°C to inactivate the enzymes and cooled to room temperature by ice cold water. The enzyme based clarification was carried out using a commercial enzyme, pectinex ultra SPL (Novozyme, Bagsvaerd, Denmark). The concentration of the enzyme used was 0.2% and it was incubated at 45°C for 4 h in a constant temperature water bath. The enzyme was heat-inactivated by placing the juice in a water bath maintained at 90°C for 2 min and the juice was then immediately cooled in ice cold water. The juice was subsequently centrifuged at 15 000 rpm using a continuous centrifuge (CEPA, Lahr/Baden, Germany), and the clarified lime juice was subjected to concentration by vacuum evaporation.

Juice concentration. Lime juice was concentrated by vacuum evaporation technique using laboratory rotary vacuum evaporator (Model Laborata 4001; Heidolph, Kelheim, Germany) with reduced pressure. It was concentrated to different concentration levels and subjected to rheological measurements.

Total soluble solids. The total soluble solids content was determined using digital hand-held refractometer (Atago Co., Ltd., Tokyo, Japan) and the total soluble solid content as °Brix.

pH. A digital pH meter was used to measure the pH of lime juice (Cyber Scan, Bangalore, India) at 25°C.

Density. The density of lime juice was measured using the pycnometer at 25°C and was expressed as g/ml.

Chemical composition. The total solids content of the juice was estimated by vacuum oven method. The ash content of the juice was measured gravimetrically by drying the juice in hot air oven in a silica crucible and placing it in a muffle furnace at 550°C for 16 hours. The ash content was calculated by the difference in weight and expressed in %. Acidity was determined by the titration method with standard 0.01N NaOH solution using phenolphthalein as indicator and expressed as % citric acid. Ascorbic acid content in the juice was determined by the titration method using 2,6-dichloro-phenol. Indo-phenol dye as indicator and expressed as mg/100 ml of juice (Ranganna 1986).

Water activity. The water activity of lime juice at different concentrations was measured using digital water activity meter at 25°C (Aqua Lab, model 3T E; Decogon Devices, Pullman, USA)

Colour measurement. The colour parameters of the clarified lime juice were measured using Hunter color meter (Mini scan XE plus, model 45/0-S; Hunter Laboratory Inc., Reston, USA). The measurements were carried out at 10° observation, D65 illuminant source, and expressed as L^*, a^*, and b^* values in Hunter scale. L^* refers to lightness, $-a^*$ refers to greenness, and $-b^*$ refers to blueness.

Rheological measurements. The rheological measurements were carried out using MCR100 controlled stress rheometer (Paar Physica, Anton Paar, GmbH, Ostfildern, Germany) equipped with coaxial cylinders (CC 27), the radii ratio of coaxial cylinders being 1.08477. The rheometer is equipped with an electric temperature controlled peltier system (TEZ-15P-C) to control the experimental temperature, and to maintain constant temperature a circulating water bath was used (Viscotherm VT-2; Paar Physica, Anton Paar GmbH, Ostfildern, Germany). The rheological parameter shear stress (Pa) was measured linearly increasing up to a shear rate of 600 s^{-1} with 10 min time duration, collected were 30 shear stress-shear rate data points and analysed using universal Software US 200 (Physica Anton Paar GmbH, Ostfildern, Germany).The rheological measurements were carried out at temperatures of 20, 35, 50, 65, and 80°C. All the measurements were carried out in triplicate and a fresh sample was used in each measurement.

Statistical analysis. The experimental results, data analysis, and the different mathematical models were fitted using statistical software (Statistica 7.0; Statsoft Inc., Tulsa, USA). The fitting and estimates were calculated at $P \leq 0.05$ significance level using the method of least square approximation.

RESULTS AND DISCUSSIONS

Physico-chemical characteristics

The physico-chemical characteristics of the enzyme clarified lime (*Citrus aurontifolia* L.) juice are reported in Table 1. The total soluble solids content was 7.3°Brix and pH 2.426 which were lower than those of Bearss seedless (*Citrus latifolia* L.) juice, which may be due to variations in the variety and maturity level. The acidity of the

Table 1. Physico-chemical characteristics of enzyme clarified lime juice

Parameter	Quantity
Total soluble solids (°Brix)	7.30 ± 0.00
pH	2.426 ± 0.005
Density (g/ml)	1.027 ± 0.0007
Total solids (%)	7.843 ± 0.0012
Acidity (% as citric acid)	7.165 ± 0.063
Ash (%)	0.259 ± 0.010
Ascorbic acid (mg/100 ml)	7.07 ± 0.08
Colour values	
Hunter L^*	10.33 ± 0.035
Hunter a^*	–0.696 ± 0.070
Hunter b^*	–0.960 ± 0.055

Mean ± SD (n = 3)

clarified lime juice was 7.165% while that of Bearss seedless lime juice was in the range 6.33–6.86%. Ascorbic acid content of the clarified lime juice was about 7.07 mg/100 ml which is much lower compared to that of Bearss seedless lime juice, and the density of juice was marginally lower because of the lower quantity of solids content compared to that of seedless lime juice. The ash content of the clarified juice was 0.259% which was markedly lower as compared to that of seedless lime juice and may have been due to the clarification process (Ziena 2000). Ascorbic acid content of the lime juice was markedly lower than those of other citrus fruits because of thermal degradation of ascorbic acid (Wang *et al.* 2007). The hunter colour values were lower which indicates a significant clarification of lime juice by pectinase enzyme.

Flow behaviour

Figure 1 shows the typical rheogram of the enzyme clarified lime juice which revealed that there was a linear increase in shear stress with respect to the increase in shear rate, passes through origin, with viscosity-shear rate curve almost parallel to x-axis which indicated that the flow was Newtonian in nature. The magnitude of the viscosity values of the enzyme clarified lime juice was estimated using Newtonian model (Eq. 2) and was in the range 3.964 to 50.290 mPa·s depending upon the concentration and temperature studied as reported in Table 2. The results showed that the temperature

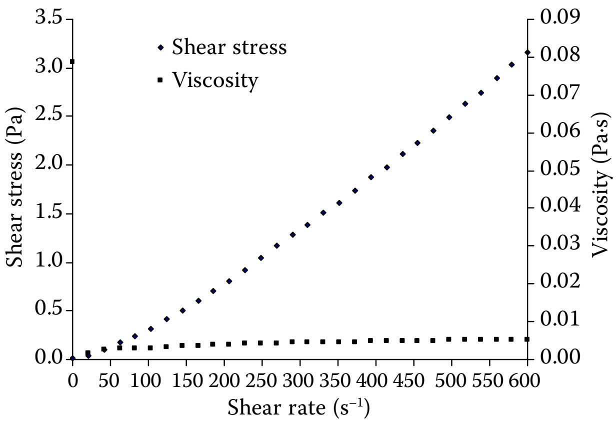

Figure 1.Typical rheogram of enzyme clarified lime juice at 16.8°Brix and temperature 50°C

and total soluble solids content or water activity had a significant effect on the lime juice viscosity. With the increase in soluble solids content, a significant ($P \leq 0.05$) increase in viscosity was observed while a significant ($P \leq 0.05$) decrease in viscosity was found with the increase in water activity of the enzyme clarified lime juice. The water activity of the juice was dependant on the solids content, nature of solute, and solute-solvent interactions. The viscosity of the enzyme clarified lime juice decreased significantly ($P \leq 0.05$) with the increase in temperature. The viscosity of juices strongly depends on inter-molecular forces between molecules and water-solute interactions, which result from the strength of hydrogen bonds and inter-molecular spacing as both are strongly affected by the temperature and concentration. In the case of the enzyme clarified lime juice, soluble solids (acids and sugars) content plays a vital role in the magnitude of viscosity. The increase in temperature significantly decreases the magnitude of viscosity because of the increase in thermal energy of the molecules which enhances the mobility of molecules and increases inter-molecular spacing (Steffe 1996; Rao 2007). Several authors have reported a similar type of results for different juices and other products such as cherry juice (Juszczak & Fortuna 2004), pineapple juice (Shamsudin *et al.* 2007), orange juice (Ibarz *et al.* 2009), pomegranate juice (Kaya & Sozer 2005), and liquorice extract (Maskan 1999).

Effect of temperature

The temperature has a major non-linear effect on the Newtonian viscosity. The effect of tem-

Table 2. Viscosity and activation energy (E_a) values of enzyme clarified lime juice at different soluble solids, water activity (a_w), and temperatures

TSS (°Brix)	a_w	Temperature (°C)	Viscosity (mPa·s)	R	Activation energy (E_a) (K J/mol)	r
		20	50.290 ± 0.006	0.9999		
		35	27.054 ± 0.005	0.9996		
55.7	0.831	50	17.458 ± 0.006	0.9993	26.050 ± 0.008	0.9940
		65	12.735 ± 0.006	0.9980		
		80	10.291 ± 0.005	0.9982		
		20	15.051 ± 0.009	0.9994		
		35	10.098 ± 0.010	0.9990		
44.8	0.900	50	8.185 ± 0.006	0.9885	12.158 ± 0.015	0.9976
		65	7.479 ± 0.006	0.9801		
		80	7.145 ± 0.006	0.9704		
		20	7.413 ± 0.008	0.9842		
		35	6.623 ± 0.003	0.9796		
30.5	0.948	50	6.013 ± 0.010	0.9823	5.070 ± 0.028	0.9969
		65	5.528 ± 0.008	0.9855		
		80	5.262 ± 0.006	0.9868		
		20	5.948 ± 0.006	0.9816		
		35	5.292 ± 0.004	0.9868		
16.8	0.975	50	4.877 ± 0.005	0.9894	4.656 ± 0.011	0.9950
		65	4.543 ± 0.005	0.9901		
		80	4.321 ± 0.004	0.9901		
		20	5.269 ± 0.005	0.9878		
		35	4.739 ± 0.006	0.9895		
7.3	0.985	50	4.389 ± 0.003	0.9905	4.151 ± 0.024	0.9933
		65	4.139 ± 0.004	0.9915		
		80	3.964 ± 0.005	0.9918		

Mean ± SD (n = 3)

perature on the viscosity of the enzyme clarified lime juice with different soluble solids contents or water activities was described using the Arrhenius equation:

$$\eta = \eta_\infty \mathrm{Exp}\,(E_a/RT) \qquad (3)$$

where:

η – viscosity (Pa·s)

η_∞ – material constant/pre-exponential coefficient/frequency factor (Pa·s)

E_a – flow activation energy (J/mol)

R – gas constant (J/mol K)

T – temperature (°K)

The energy of viscous flow activation was in the range 4.151 to 26.050 kJ/mol depending upon the soluble solids content of the enzyme clarified lime juice as given in Table 2. The flow activation energy (E_a) is defined as minimum energy required to overcome the energy barrier before the elementary flow can occur and the viscous flow occurs as a sequence of events which are shifts of particles in the direction of the shear force action from one equilibrium position to another overcoming a potential energy barrier whose height determines the free activation energy of the viscous flow. Higher activation energy values indicate a greater influence of temperature on the viscosity and flow activation energy values increase with the increase in soluble solids content of the samples indicating that higher energy was required to overcome the potential energy barrier at higher soluble solids content of juice. Therefore, the temperature has a greater effect on the sample with higher soluble solids contents. The magnitude of activation energy conformed to the values reported for other fluid foods (Juszczak & Fortuna 2004; Altan & Maskan 2005; Kaya & Sozer 2005; Ibarz *et al.* 2009; Juszczak *et al.* 2009; Vandresen *et al.* 2009).

Effects of soluble solid contents and water activity on activation energy

The activation energy for viscous flow of lime juice increased significantly ($P \leq 0.05$) with the increase in soluble solids content but decreased significantly ($P \leq 0.05$) with the increase in water activity, both trends being non-linear in nature. The variation of the activation energy with the concentration and water activity can be described by two models, namely the power law and exponential model, as:

$$E_a = a\,(C)^b \quad (4)$$

$$E_a = a\exp(bC) \quad (5)$$

$$E_a = a\,(a_w)^{b^*} \quad (6)$$

$$E_a = a\exp(b^+ \times a_w) \quad (7)$$

where:
E_a – activation energy (kJ/mol)
a – empirical constant (kJ/mol)
C – total soluble solids content (°Brix)
a_w – water activity (–)
b – constant ($Brix^{-1}$)
b^* – constant (–)

The exponential model ($r > 0.98$) was more effective in describing the influence of the soluble solids content on the flow activation energy of the enzyme clarified lime juice than the power law model ($r < 0.95$) as shown in Table 3, which indicated that the relationship between the flow activation energy and total soluble solid content was exponential in nature. A similar type of results was reported in the case of pomegranate juice (Kaya & Sozer 2005). The effect of water activity on the flow activation energy was described by both the power law and exponential relation ($r > 0.99$). The parameter b^* was negative which indicated that the increase in water activity leads to a decrease in the flow activation energy of the enzyme clarified lime juice. There was a similar finding in the case of orange juice (Ibarz *et al.* 1994).

Effect of total soluble solids content

The concentration of the soluble solids and insoluble solids has a strong non-linear effect on the viscosity of the Newtonian fluids. Several investigators have employed different models to investigate the effect of soluble solids content on the viscosity of different fluids (Ibarz *et al.* 2009, 1989) and the equations were:

Power law: $\eta = a\,(C)^b$ (8)

Exponential first order: $\eta = a\exp(bC)$ (9)

Exponential second order: $\eta = a\,\mathrm{wxp}(bC + cC^2)$ (10)

where:
η – viscosity (mPa·s)
a – constant (mPa·s)
b – constant ($Brix^{-1}$)
c – constant ($Brix^{-2}$)
C – total soluble solids content (°Brix)

The parameters of variation in the viscosity of the lime juice with soluble solids content by three models at different temperatures are shown in Table 4. The parameter b in the power law and exponential models decreased significantly ($P \leq 0.05$) with the increase in temperature. This indicates that at lower temperatures, the viscosity of the lime juice increases rapidly when the concentration increases, which could be due to a change in thermal energy of the molecules and inter-molecular spacing. The exponential second order model was better in describing the influence of total soluble solids content on the viscosity of the enzyme clarified lime juice at different temperatures ($r \geq 0.99$). The

Table 3. Effect of total soluble solid content and water activity on activation energy (E_a) of enzyme clarified lime juice

Model	a (K J/mol)	b ($Brix^{-1}$)(–)	r
$E_a = a\,(C)^b$	0.000476 ± 0.000001	2.706 ± 0.004	0.9500
$E_a = a\exp(bC)$	1.109 ± 0.005	0.0562 ± 0.0001	0.9803
$E_a = a\,(a_w)^{b^*}$	3.553 ± 0.054	−10.853 ± 0.013	0.9960
$E_a = a\exp(b^* a_w)$	521 586.1 ± 12 601.0	−11.942 ± 0.045	0.9964

Mean ± SD ($n = 3$); b ($Brix^{-1}$); b^* (–)

Table 4. Parameters of the (a) power law model, (b) exponential model and (c) second order exponential model relating total soluble solid content to viscosity of enzyme clarified lime juice at different temperatures

Temperature (°C)	a (mPa·s)	b (Brix^{-1})	c (Brix^{-2})	r
(a) Power law model: $\eta = a\,(C)^b$				
20	$3.44 \times 10^{-7} \pm 5.0 \times 10^{-9}$	4.674 ± 0.003		0.9700
35	$3.11 \times 10^{-4} \pm 1.0 \times 10^{-6}$	2.817 ± 0.002		0.9111
50	0.1210 ± 0.0004	1.197 ± 0.001		0.8632
65	0.5284 ± 0.0018	0.752 ± 0.001		0.8762
80	0.8668 ± 0.0020	0.584 ± 0.0007		0.9059
(b) Exponential 1st model: $\eta = a\exp(bC)$				
20	0.367 ± 0.001	0.0880 ± 0.0001		0.9808
35	1.169 ± 0.002	0.05543 ± 0.00002		0.9561
50	2.101 ± 0.001	0.03661 ± 0.00001		0.9470
65	2.645 ± 0.004	0.02699 ± 0.00003		0.9620
80	2.916 ± 0.001	0.02184 ± 0.00002		0.9815
(c) Exponential 2nd model: $\eta = a\exp(bC + cC^2)$				
20	8.180 ± 0.005	−0.05567 ± 0.00003	0.00158 ± 0.000001	0.9991
35	6.832 ± 0.010	−0.04387 ± 0.00009	0.001229 ± 0.000001	0.9961
50	5.590 ± 0.003	−0.02800 ± 0.00004	0.000866 ± 0.00000005	0.9940
65	4.595 ± 0.006	−0.01210 ± 0.0011	0.000549 ± 0.000002	0.9970
80	3.961 ± 0.008	−0.000898 ± 0.00005	0.000322 ± 0.000003	0.9997

Mean ± SD (n = 3)

parameters of second order exponential model are shown in Table 4c in which the parameters a and c of the model decreased and parameter b was found to increase significantly ($P \leq 0.05$) with the increase in total soluble solids content. This indicates that the viscosity of the lime juice was sensitive to temperature because the parameter c which relates the viscosity quadratically with the concentration was found to decrease with increased temperature. Therefore, the second order exponential model better describes the effect of soluble solids content on the viscosity of the lime juice at different temperatures.

Effect of water activity

The variation in the viscosity of the juice in relation to water activity was described by the power law as well as exponential type equations:

Power law: $\eta = a\,(a_w)^b$ (11)

Exponential model: $\eta = a\exp(b\,a_w)$ (12)

where:

η – viscosity (mPa·s)

a – constant (mPa·s)

b – constant (–)

a_w – water activity (–)

The parameters of the power law and exponential models were reported in Tables 5a and b, respectively. The results indicated that both models were suitable for describing the viscosity of the lime juice with specific water activity. The parameter b was negative which indicates that the viscosity would decrease with the increase in water activity as water activity mainly depends on the solids content in the juice. The magnitude of b decreased with the increase in temperature which indicated the effect of water activity on viscosity being markedly high at lower temperatures. A similar type of results was reported for other juices (Irbaz *et al.* 1989, 1992a,b).

Combined effect of temperature and total soluble solids content

From the engineering point of view, it is very useful and important to obtain a single equation

Table 5. Parameters of the (a) power law model and (b) exponential model relating water activity to viscosity of enzyme clarified lime juice at different temperatures

Temperature (°C)	a (mPa·s)	*b* (–)	*r*
(a) Power law model: $\eta = a\,(a_w)^b$			
20	3.532 ± 0.004	–14.331 ± 0.006	0.9991
35	3.567 ± 0.003	–10.897 ± 0.004	0.9970
50	3.715 ± 0.001	–8.305 ± 0.002	0.9969
65	3.822 ± 0.003	–6.494 ± 0.006	0.9997
80	3.378 ± 0.001	–5.338 ± 0.003	0.9960
(b) Exponential model: $\eta = a\exp(b\,a_w)$			
20	36 217 505.0 ± 203312.8	–16.236 ± 0.009	0.9985
35	713 713.8 ± 3168.9	–12.283 ± 0.032	0.9956
50	3 9085.7 ± 81.6	–9.299 ± 0.002	0.9953
65	5 253.0 ± 31.2	–7.252 ± 0.007	0.9993
80	1 469.6 ± 4.8	–5.969 ± 0.003	0.9977

Mean ± SD (n = 3)

describing the effect of both temperature and soluble solids content on the viscosity of the enzyme clarified lime juice. Several authors have used different equations to describe the combined effect of temperature and soluble solids content on the juice viscosity.

Power law model: $\eta = a\exp(E_a/RT) \times (C)^c$ (13)

Exponential 1st order: $\eta = a\,\mathrm{Exp}\,(E_a/RT + cC)$ (14)

Exponential 2nd order: $\eta = a\,\mathrm{Exp}\,(E_a/RT + cC + dC^2)$ (15)

where:

η – viscosity (mPa·s)
a – pre-exponential constant (mPa·s)
b – E_a/R
E_a – flow activation energy (J/mol)
R – universal gas constant (J/mol K)
T – absolute temperature (°K)
c – constant (Brix^{-1})
d – constant (Brix^{-2})
C – total soluble solids content (°Brix)

Table 6 showed that the exponential second order model was better in describing the combined effect of temperature and total soluble solids content on the viscosity of the enzyme clarified lime juice concentrate. The final equation which represents the combined effect of temperature and total soluble solids content on the viscosity of the enzyme clarified lime juice was given by:

$$\eta = 1.082 \times 10^{-3}\,\mathrm{Exp}\,(2685.89/T - 0.04654\,C + 0.001321\,C^2) \quad (r > 0.97)$$

where:

η – viscosity (mPa·s)
T – temperature (°K)
C – total soluble solids content in °Brix

The surface plot shows the combined effect of temperature and total soluble solids content on the viscosity of the enzyme clarified lime juice concentrate as given in Figure 2. The magnitude of viscosity depends on both the temperature

Table 6. Parameters of the different models relating to temperature and soluble solid concentration on viscosity of enzyme clarified lime juice

Model	Equation	*a* (mPa·s)	*b* = Ea/*R*	*c* (Brix^{-1})	*d* (Brix^{-2})	*r*
Power law	13	$3.109 \times 10^{-9} \pm 2.71 \times 10^{-11}$	2795.45 ± 0.76	3.453 ± 0.003	–	0.9230
Exponential– 1st order	14	$1.218 \times 10^{-4} \pm 2.0 \times 10^{-7}$	2707.19 ± 0.82	0.06439 ± 0.00003	–	0.9474
Exponential 2nd order	15	0.001082 ± 0.00003	2685.89 ± 0.93	–0.04654 ± 0.00005	0.001321 ± 0.000001	0.9743

Mean ± SD (n = 3)

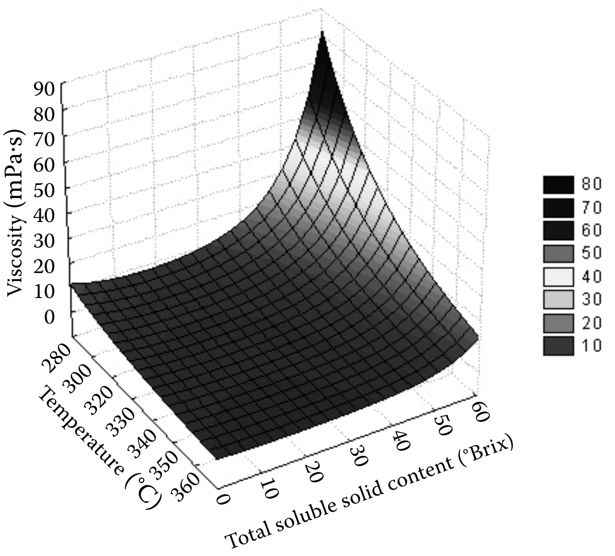

Figure 2. Surface plot for combined effect of temperature and total soluble solid content on viscosity of enzyme clarified lime juice

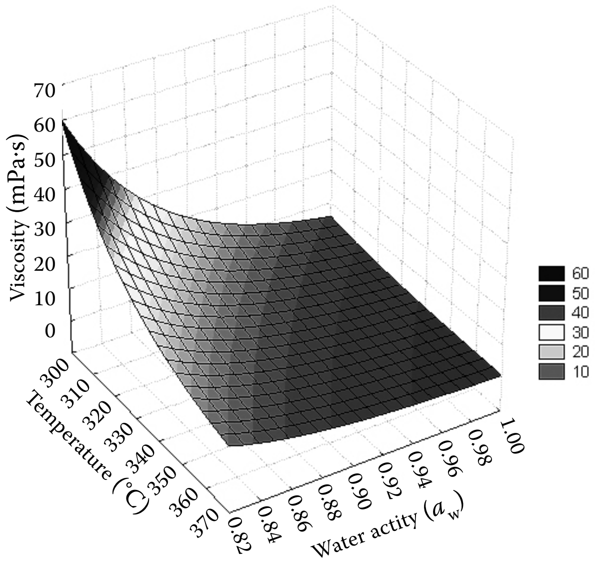

Figure 3. Surface plot for combined effect of temperature and water activity on viscosity of enzyme clarified lime juice

and total soluble solids content of the juice. At lower temperatures, the magnitude of viscosity rapidly increased with the soluble solids content and increased marginally at higher temperatures which was due to the increase in thermal energy of the molecules and the increase in intermolecular spacing at higher temperatures.

Combined effect of temperature and water activity

It is also very important to establish a combined single equation relating temperature and water activity to the viscosity of the lime juice concentrate. The two models were used to obtain a single equation for describing the combined effect of temperature and water activity on the lime juice viscosity. Generally, the power law and exponential type equation are used to describe the combined effect of temperature and water activity on the viscosity of juices.

Power law: $\eta = a \exp(E_a/RT) \times (a_w)^c$ (16)

Exponential model: $\eta = a \exp(E_a/RT + c\,a_w)$ (17)

where:

η – viscosity (mPa·s)
a – pre-exponential constant (m Pa s)
b – E_a/R
E_a – flow activation energy (J/mol)
R – universal gas constant
T – absolute temperature (°K)
a_w – water activity (–)
b – constant (–)

The parameters of the combined effect of temperature and water activity are given in Table 7. Both models were able to explain the combined effect of temperature and water activity on the enzyme clarified lime juice. The models coefficient c was negative, which indicated that the viscosity of the juice decreased with increasing water activity. The suggested models were:

$\eta = 5.46 \times 10^{-4}(a_w)^{-11.878} \exp(2684.45/T)$ ($r > 0.97$)

$\eta = 334.44 \times \exp(2683.89/T - 13.394\,a_w)$ ($r > 0.97$)

Table 7. Parameters of the different models relating to temperature and water activity on viscosity of enzyme clarified Lime juice

Model	Equation	a (mPa·s)	b = Ea/R	c (–)	r
Power law	16	0.000546 ± 0.000002	2684.45 ± 0.88	–11.878 ± 0.003	0.9747
Exponential	17	334.44 ± 1.93	2683.89 ± 0.87	–13.394 ± 0.004	0.9738

Mean ± SD (n = 3)

Figure 3 shows the surface plot for the combined effect of temperature and water activity on the viscosity of the enzyme clarified lime juice. The magnitude of viscosity increased rapidly at lower water activities whereas marginally at higher water activity levels, which indicated that both temperature and water activity had a significant effect on the viscosity of the enzyme clarified lime juice while at higher temperature the mobility of molecules was higher because of the increase in inter-molecular spacing.

CONCLUSIONS

The results of the present study indicated that enzyme clarified juice concentrate exhibited Newtonian properties with viscosity (η) in the range of 3.964 mPa to 50.290 mPa s strongly depending on the temperature and soluble solids content/water activity. The energy of activation (E_a) of viscous flow increased exponentially with the increase in total soluble solids content, whereas water activity was described by both the power law and exponential type equations. The effect of total soluble solids content on the viscosity of the lime juice was followed by second order exponential equation, whereas the effect of water activity on viscosity was described by both the power law and exponential type relationship. Mathematical models that were suitable for describing the rheological behaviour of the enzyme clarified lime juice in terms of temperature and soluble solids content/water activity are presented. From this study, it is possible to compute the viscosity of lime juice at various temperatures and soluble solids content/water activity levels. This information on the rheological behaviour of lime juice concentrate will be helpful in scaling up the process, optimum process design, the handling and storage for better quality lime juice products commercial applications.

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