A Survey on the Centrifugal Freeze Concentration Method For Mulberry Molasses

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Abstract. Centrifugal freeze concentration is a new technique to obtain the concentrated solution from liquid foods in food industry, which is a method for recovering a food solute from a solution based on the separation of pure ice crystals from a freeze concentrated aqueous phase. The aim of this study was to investigate the concentration of mulberry molasses by the centrifugation freeze concentration method. For this purpose, the mulberry molasses (73.2 ^{o}Bx) was diluted to different total soluble dry matter contents (20, 25, 30, 35, 40, and 45 ^{o}Bx) and the method of freeze concentration assisted by centrifugation was applied. The concentrated solution which was obtained after the removal of formed ice by filtration was frozen again at same conditions and same processes were repeated (cycle). The percentage of concentrate, efficiency of concentration and recovered solute values were calculated for each cycle. According to the results of the successive three cycles, the amount of remaining solutions after the removal of ice content decreased and in contrary to increase in total soluble solid content, the concentration efficiency decreased. The percentage of concentrate changed between 79.4% and 94.8% and the recovered solute values reached to 0.80 and 0.93 kg/kg.

INTRODUCTION

Molasses (Pekmez), a kind of fruit juice concentrate, is a traditional Turkish food made of different fruits such as grape, mulberry, carob, watermelon, apricot, prune, fig, apple and sugar beet (Tosun and Ustun, 2003; Batu, 2005; Karababa and Işıklı, 2005; Liyana-Pathirana et al., 2006). Pekmez is a naturally nutritious food with total soluble solid content of 50–80% (Arıcı et al., 2004), high amounts of sugar, minerals and organic acids (Sengul et al., 2005; Yoğurtçu and Kamışlı, 2006).

Freeze concentration is a method for concentrating a food solute in a solution based on the separation of pure ice crystals to from a freeze-concentrated solution (Petzold et al., 2012). In this method water is removed at low temperatures preserving the quality of the original materials (Miyawaki et al., 2005). These foods can be kept without spoiling for a long time or it's ready for subsequent processing steps such as drying (Dinçer and Topuz, 2009).

One of the main unit operations in the food industry is the concentration of aqueous solutions. Generally, three techniques are used for concentration of food. These are evaporation, reverse osmosis and freeze concentration. As compared to evaporation and membrane technology: freeze concentration has some significant potential advantages for producing a concentrate with high quality because the process occurs at low temperatures where no vapor/liquid interface exists resulting in no loss of volatiles, the flavor and quality of freeze-concentrated products are exceptionally high, especially relative to their evaporated counterparts. These benefits make freeze concentration particularly suitable for the concentration of some products, such as fruit juices, coffee and tea extracts, and aroma extracts (Morison and Hartel, 2007).

Freezing is an important stage of this method and three techniques are used for the growth of ice crystals. These are suspension freeze concentration, film freeze concentration (progressive or falling film freeze concentration) and block freeze concentration (Aider et al., 2009; Sanchez et al., 2011). A typical installation for suspension freeze concentration consists of scraped surface heat exchangers to generate ice nuclei, recrystallisers, to increase ice growth and a system for separation of the ice from the liquid, usually by wash columns, operated at elevated pressures. (Van Weelden, 1994; Lee and Lee, 1998). Film freeze concentration is based on film crystallisation, which consists of the formation of a single crystal that grows layer by layer from the solution to be concentrated. In this process the fluid to be concentrated flows down over a chilled surface, which causes the crystallization of ice and the further growth of the ice crystals on the surface (Sanchez et al., 2009). The separation of ice and concentrated solution occurs because the ice adheres to the surface, while the concentrated liquid flows down along the surface. In block freeze concentration, also known as freeze–thaw concentration, the solution to be concentrated is completely frozen and then partially thawed to recover a fraction of liquid with a higher concentration (Aider et al., 2009; Nakagawa et al., 2010). Block freeze concentration consists of three stages: freezing, thawing and separation of the concentrated liquid fraction (Moreno et al., 2013). Additionally, the process can be repeated in successive cycles to increase the concentration index (Aider and Ounis, 2012). Assisted techniques improve the efficiency of processing for block freeze concentration. These techniques are the application of ultrasound, ice nucleation agents, vacuum, and centrifugation (Petzold and Aguilera, 2013). In a study of Petzold et al. (2012), the suction was generated by connecting a vacuum pump to the bottom of the frozen sample at ambient temperature and under vacuum in the freeze concentration of sucrose solutions. Watanabe and Arai (1994) have studied the application ice nucleation activity to freeze concentration. Centrifugation is a type of separation where the force of gravity is largely replaced by a higher driving force, through the application of centrifugal force (Toledo, 2007). An alternative for separating the concentrated solution from the ice fraction is the use of centrifugation. Centrifugation has been proposed by Petzold et al. (2015) in frozen blueberry and pineapple juices. In this study, frozen samples transferred to a centrifuge operated at 20°C for 10 min at 4600 rpm to force the separation of solutes from the frozen samples. This technique has high values of total soluble solid content, recovered solute and percentage of concentrate after the third cycles for both juices, values close to 0.74 kg solute per 1 kg initial solute, and reaching approximately 60% of the percentage of concentrate. In the study of Petzold and Aguilera (2012), sucrose solutions were transferred to a centrifuge operated at 20˚C for 15 min different centrifugation speeds (800, 1600 and 2400 RCF). Sucrose solutions reached approximately 0.73 kg of sucrose obtained per 1 kg of initial sucrose at 1600 RCF of centrifugation speed, independent of initial concentration of sucrose (5 to 20 wt.%) and freezing procedure (radial or undirectional freezing).The aim of this study is to investigate the concentration of mulberry molasses by the block freeze concentration method applied by centrifugal separation.

MATERIALS AND METHODS

Materials

Mulberry molasses (73.2 ˚Brix, SEREL Inc.) were obtained from a local market in Izmir, Turkey. Diluted samples with the total soluble solid contents of 20, 25, 30, 35, 40, and 45 ˚Brix (˚Bx) were prepared for the experiments by mixing with water.

Methods

Freezing and centrifugation

Diluted mulberry molasses (25g) were placed into plastic centrifugal tubes (internal diameter D=3cm) were frozen in a static freezer at -20˚C for 12 hours. Then, the frozen samples were removed from the freezer (Vestel SVC-145, Turkey) and rapidly transferred to a centrifuge (Nüve NF800, Turkey) operated at 4100 rpm for 15 min at room condition. After centrifugation, the concentrated solution (solute) was collected, and the remaining frozen core (ice fraction) was thawed so that the total soluble solids content was determined in both fractions. The total soluble solids content of separated ice fraction (C_i) and total soluble solid content of concentrated sample (C_c) were analyzed at ambient temperature with a refractometer (HANNA HI 96801 Digital Refractometer, USA). The concentrated solution which was obtained the after removal of formed ice by filtration was frozen again at same conditions and same processes were repeated three times (cycle).

Modelling of Rheological Behaviour

Rheological properties of diluted and concentrated of mulberry molasses samples were measured by Brookfield Viscometer (Model LVDV-II pro, Brookfield Engineering Laboratories, USA) at 25 ˚C . Shear stress- shear rate data were obtained from experimental measurements. Data was fitted to 4 different rheological models (Newtonian, Bingham, Power Law, Herschel-Bulkley) (Rao, 2014) by using IBM SPSS Statistics Package (vers. 20).

Newtonian Model: $\sigma = \eta \dot{\gamma}$ (5)

Power Law Model: $\sigma = k(\dot{\gamma})^n$ (6)

Bingham Model: $\sigma - \sigma_0 = k\dot{\gamma}$ (7)

Herschel-Bulkley Model:

$$\sigma - \sigma_0 = k(\dot{\gamma})^n \quad (8)$$

where σ is shear stress (Pa), $\dot{\gamma}$ is shear rate (1/sec), σ_0 is yield stress (Pa), n is flow behaviour index, k is consistency coefficient (Pa.s ^{n}).

Calculations

The calculated values of thawing fraction (f) (Nakagawa et al., 2010, Miyawaki et al., 2012), percentage of concentrate (PC,%), efficiency (E, %), and recovered solute (Y, kg solute/kg initial solute) were calculated as defined in the references (Nakagawa et al., 2010, Petzold et al., 2013).

Freeze concentration is a method for concentrating a food solute in a solution based on the separation of ice crystals to from a freeze-concentrated solution. Block freeze concentration consists of freezing, thawing and separation stages. The concentrated phase is melting more quickly than ice phase, therefore, concentrated phase is separated from the ice phase. Freeze concentration occurs at low temperatures where no vapor/liquid interface exists resulting in no loss of volatiles, therefore, the flavor and quality is higher than evaporation.

Fig. 1 shows the total soluble solid content (^{o}Bx) values of concentrated molasses at each cycle. A general increase in total soluble solid content (^{o}Bx) was observed by increasing the number of cycles. The highest increase was seen in the initial total soluble solid content of 20 ^{o}Bx sample and reached to 41.4 ^{o}Bx after the third cycle. On the contrary, the increase in initial total soluble solid content (^{o}Bx) leads to a decrease in total soluble solid content of the later cycles since the water in the sample decreases and by increasing the number of cycles, water in the frozen sample also decreases. Generally by increasing the number of cycles, total soluble solid content of ice fraction (^{o}Bx) increased. According to Petzold et al. (2015), by increasing the number of cycles, total soluble solid content (^{o}Bx) in the concentrated fraction and the separated ice fraction increased. Fig. 2 shows the calculated thawing fraction values at each cycle. The thawing fraction was used to follow the development of process with increasing the number of cycles, thawing fraction also increased. The highest thawing fraction was observed at the total soluble solid content of 40°Bx.

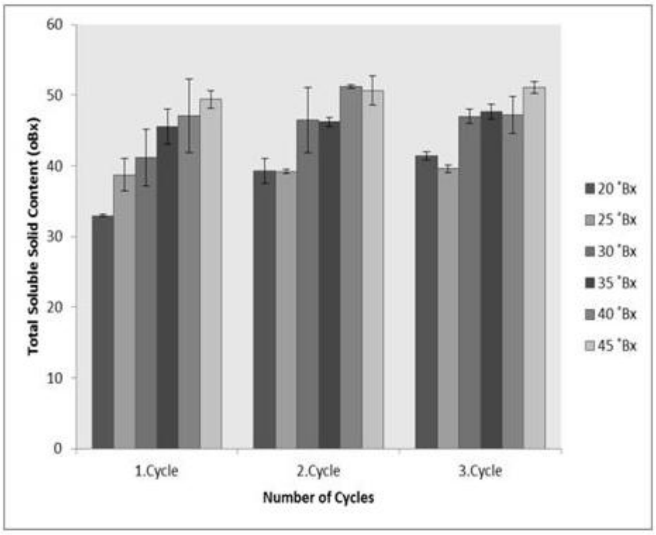

Figure 1
The total soluble solid content of concentrated molasses

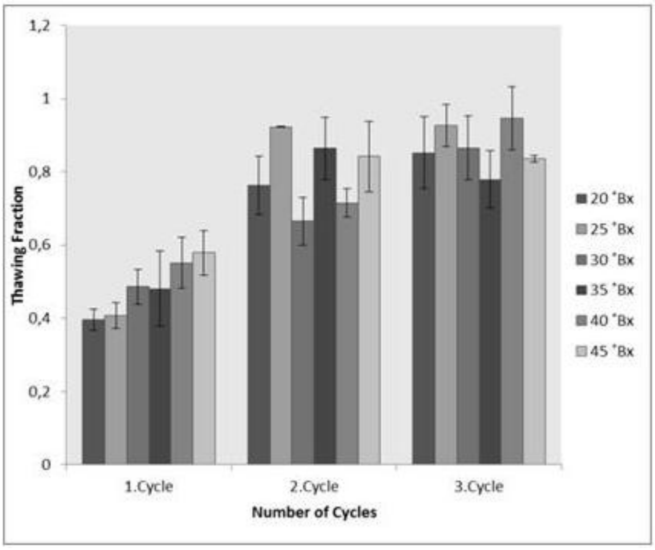

Figure 2
The thawing fraction for each cycle

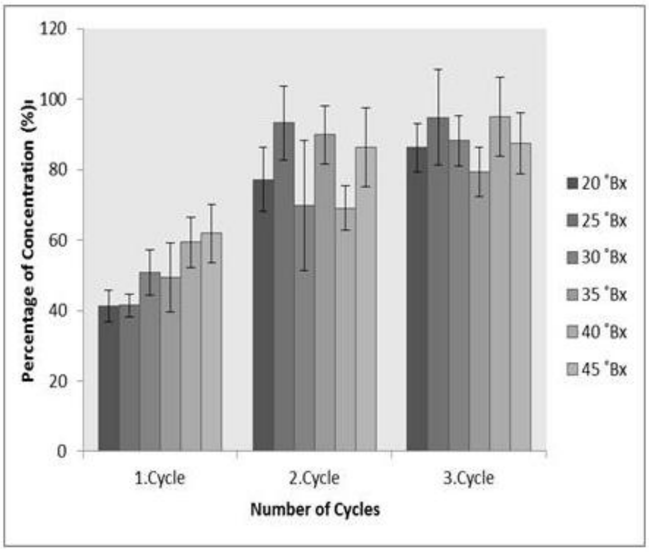

Figure 3
The percentage of concentrate for each cycle

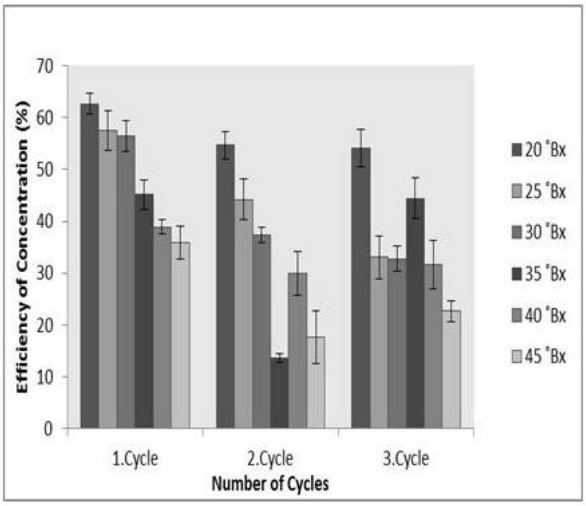

Figure 4
The efficiency of concentration for each cycle

Fig. 3 shows the percentage of concentrate at each cycle. As the number of cycle increases, percentage of concentrate increased. At end of the third cycle, the percentage of concentrate changed between 79.4% and 94.8%. At the research of Petzold et al. (2015), the percentage of concentrate increased for blueberry and pineapple juices at each cycle and reached to 60 % for the blueberry juice and 61% for the pineapple juice. Fig. 4 shows the efficiency of concentration at each cycle. As the number of cycles increased, the efficiency of concentration decreased. The efficiency of concentration was found to be at the highest at 20 °Bx.

Fig. 5 shows the recovered solute (expressed as kg solute/kg initial solute) at each cycle. As a general trend, the amount of recovered solute increased after each cycle. At the end of the third cycle, the recovered solute values ranged between 0.80 and 0.93 kg solute/kg initial solute. The recovered solute values of 0.67 to 0.74 kg/kg for blueberry and 0.48 to 0.73 kg/kg for pineapple juice was reported by Petzold et al., 2015.

Knowledge about the flow behavior of concentrated samples is pertinent to quality control, sensory evaluation and food processing and handling operations (transport, mixing, homogenization, sterilization, concentration) (Rao et al., 1984). The rheological properties of diluted (25, 35 and 45 ˚Bx) and freeze concentrated of mulberry molasses samples were measured (0-100 rpm, 18 spindle number) and R^2 and RMSE (Root-Mean-Square Error) values were calculated to determine the model describing the reological changes.

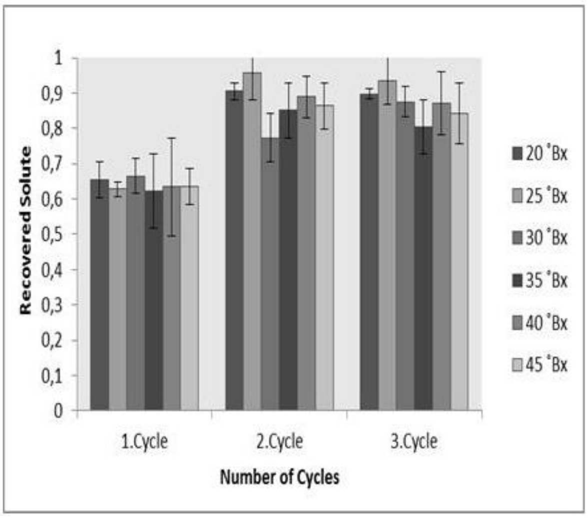

Figure 5
The recovered solute for each cycle

Table 1: (a., b., c., d., e., f.,): Statistical evaluation of the rheological model best fitting the experimental data of samples

a.

Models	Parameters	Inıtıal Concentration (˚Bx)	Initial	1.Cycle
Newtonian	η	25 ˚Bx	0.018±0.001	0.035±0.002
		35 ˚Bx	0.038±0.001	0.075±0.001
		45 ˚Bx	0.084±0.001	0.117±0.001
	R^2	25 ˚Bx	0.936	0.872
		35 ˚Bx	0.970	0.999
		45 ˚Bx	0.994	0.999
	RMSE	25 ˚Bx	0.217	0.453
		35 ˚Bx	0.281	0.278
		45 ˚Bx	0.273	0.278
Power Law	k	25 ˚Bx	0.002±0.001	0.198±0.054
		35 ˚Bx	0.020±0.008	0.093±0.019
		45 ˚Bx	0.057±0.009	0.098±0.007
	n	25 ˚Bx	1.457±0.099	0.623±0.061
		35 ˚Bx	1.141±0.090	0.953±0.044
		45 ˚Bx	1.084±0.033	1.038±0.016
	R^2	25 ˚Bx	0.985	0.967
		35 ˚Bx	0.977	0.992
		45 ˚Bx	0.997	0.999
	RMSE	25 ˚Bx	0.151	0.221
		35 ˚Bx	0.245	0.263
		45 ˚Bx	0.206	0.263

b.

Models	Parameters	Inıtıal Concentration (˚Bx)	2.Cycle	3.Cycle
Newtonian	η	25 ˚Bx	0.049±0.001	0.048±0.002
		35 ˚Bx	0.069±0.001	0.069±0.001
		45 ˚Bx	0.106±0.001	0.090±0.001
	R^2	25 ˚Bx	0.963	0.942
		35 ˚Bx	0.997	0.994
		45 ˚Bx	0.997	0.999
	RMSE	25 ˚Bx	0.404	0.344
		35 ˚Bx	0.161	0.217
		45 ˚Bx	0.240	0.145
Power Law	k	25 ˚Bx	0.079±0.028	0.103±0.039
		35 ˚Bx	0.048±0.004	0.048±0.007
		45 ˚Bx	0.110±0.015	0.078±0.007
	n	25 ˚Bx	0.895±0.078	0.832±0.083
		35 ˚Bx	1.079±0.017	1.080±0.033
		45 ˚Bx	0.992±0.029	1.032±0.018
	R^2	25 ˚Bx	0.969	0.958
		35 ˚Bx	0.999	0.997
		45 ˚Bx	0.997	0.999
	RMSE	25 ˚Bx	0.345	0.318
		35 ˚Bx	0.087	5.086
		45 ˚Bx	0.239	0.132

c.

Models	Parameters	Inıtıal Concentration (˚Bx)	Initial	1.Cycle
Bingham	σ_0	25 ˚Bx	-0.209±0.020	0.632±0.171
		35 ˚Bx	0.008±0.005	0.388±0.155
		45 ˚Bx	-0.073±0.018	0.006±0.114
	η	25 ˚Bx	0.020±0.001	0.028±0.002
		35 ˚Bx	0.038±0.002	0.071±0.001
		45 ˚Bx	0.085±0.002	0.116±0.001
	R^2	25 ˚Bx	0.953	0.949
		35 ˚Bx	0.970	0.996
		45 ˚Bx	0.994	0.999
	RMSE	25 ˚Bx	0.186	0.276
		35 ˚Bx	0.280	0.184
		45 ˚Bx	0.270	0.184

d.

Models	Parameters	Inıtıal Concentration (˚Bx)	2.Cycle	3.Cycle
Bingham	σ_0	25 ˚Bx	0.547±0.112	0.701±0.040
		35 ˚Bx	-0.149±0.087	-0.020±0.009
		45 ˚Bx	0.303±0.109	-0.022±0.009
	η	25 ˚Bx	0.043±0.001	0.040±0.001
		35 ˚Bx	0.071±0.001	0.069±0.002
		45 ˚Bx	0.103±0.001	0.090±0.001
	R^2	25 ˚Bx	0.990	0.992
		35 ˚Bx	0.998	0.994
		45 ˚Bx	0.998	0.999
	RMSE	25 ˚Bx	0.181	0.151
		35 ˚Bx	0.141	0.216
		45 ˚Bx	0.175	0.144

e.

Models	Parameters	Inıtıal Concentration (˚Bx)	Initial	1.Cycle
Herschel-Bulkley	σ_0	25 ˚Bx	0.060±0.007	0.060±0.012
		35 ˚Bx	0.360±0.096	0.658±0.138
		45 ˚Bx	0.381±0.078	0.380±0.052
	k	25 ˚Bx	0.012±0.001	0.148±0.076
		35 ˚Bx	0.008±0.002	0.041±0.009
		45 ˚Bx	0.037±0.008	0.073±0.004
	n	25 ˚Bx	1.533±0.164	0.675±0.101
		35 ˚Bx	1.321±0.146	1.112±0.047
		45 ˚Bx	1.165±0.044	1.094±0.010
	R^2	25 ˚Bx	0.986	0.969
		35 ˚Bx	0.985	0.998
		45 ˚Bx	0.998	1.000
	RMSE	25 ˚Bx	0.445	0.500
		35 ˚Bx	0.208	0.148
		45 ˚Bx	0.533	0.148

f.

Models	Parameters	Inıtıal Concentration (˚Bx)	2.Cycle	3.Cycle
Herschel-Bulkley	σ_0	25 ˚Bx	0.862±0.090	0.992±0.056
		35 ˚Bx	0.104±0.077	0.395±0.082
		45 ˚Bx	0.649±0.072	0.197±0.065
	k	25 ˚Bx	0.013±0.004	0.013±0.002
		35 ˚Bx	0.042±0.005	0.027±0.004
		45 ˚Bx	0.063±0.005	0.064±0.008
	n	25 ˚Bx	1.240±0.060	1.235±0.039
		35 ˚Bx	1.105±0.026	1.189±0.032
		45 ˚Bx	1.098±0.017	1.070±0.026
	R^2	25 ˚Bx	0.997	0.999
		35 ˚Bx	0.999	0.999
		45 ˚Bx	1.000	0.999
	RMSE	25 ˚Bx	0.096	0.123
		35 ˚Bx	0.079	0.087
		45 ˚Bx	0.081	0.116

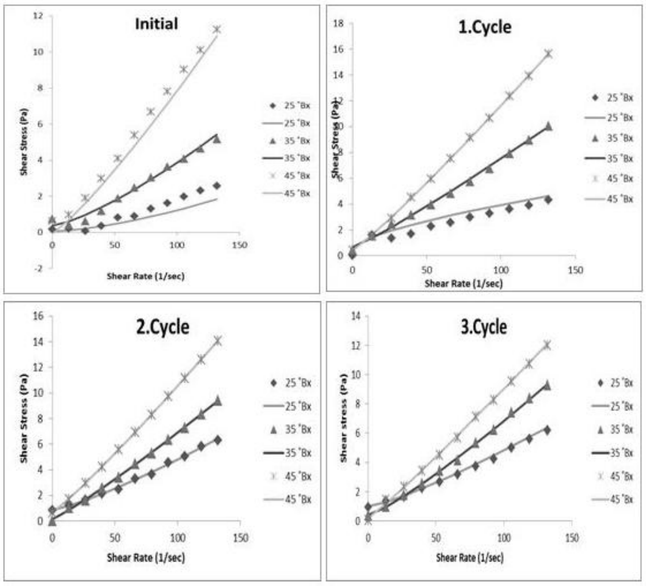

Figure 6
The experimental data and Herschel-Bulkley model predictions and experimental data for shear stress-shear rate relationship for original samples (a) and after each cycle (b, c, d) of freeze concentration (Symbols show the experimental data, lines show the model prediction)

Table 1 shows the statistical evaluation of the reological models by fitting the experimental data of samples. The best fit for all samples were observed with the Herschel-Bulkley Model. In Herschel-Bulkley Model, consistency coefficient (k) of the samples increased according to beginning. At the end of the third cycle, maximum increase of consistency coefficient was 0.064 Pa.s^n. Fig. 6 shows the model predictions and experimental data for shear stress-shear rate relationship for original samples (a) and after each cycle (b, c, d) of freeze concentration 25, 35 and 45 ˚Bx.

CONCLUSION

The aim of this study was to investigate of concentration of mulberry molasses by freeze concentration method assisted by centrifugation. Centrifugation technique is used improve the efficiency of processing for freeze concentration. By the increasing the number of cycles, the values of concentration, thawing fraction, percentage of concentrate, efficiency of concentration, recovered solute and viscosity increased. The rheological behaviour of molasses samples were best modeled with Herschel-Bulkley Model for both the original samples and after each cycle of freeze concentration.

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