

Mass Transfer Kinetics During Osmotic Dehydration of Semi-refined Carrageenan

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ABSTRACT

*The study investigated the feasibility of introducing osmotic dehydration (OD) in the production of semi-refined carrageenan (SRC). It aimed to analyze mass transfer of water loss and solute uptake during OD as affected by temperature and agitation conditions. Semi-refined carrageenan from the seaweed *Kappaphycus alvarezii* were submerged in saturated sucrose solution at 30^o, 40^o, and 50^oC and in static and agitated (200 RPM) condition from 5-120 minutes. Destruction sampling was performed and mass transfer kinetics was analyzed using Page and Newton models. Results show that from an initial value of 92.23-94.45%, product moisture content was reduced to 33.55-47.85% after two hours of OD. The process was characterized by rapid water removal and sucrose uptake in the early stage, followed by slow rates until near-equilibrium condition was reached. Statistically, Page had better fit than Newton for both water loss and sucrose gain. Lastly, only temperature was found to have significant effect on mass transfer.*

Keywords: *osmotic dehydration; semi-refined carrageenan; mass transfer; diffusion; empirical models*

INTRODUCTION

Semi-refined carrageenan (SRC) is a type of seaweed hydrocolloid which is produced by a method in which carrageenan is never actually extracted from the seaweed. The parent material is simply heated in an alkaline solution of potassium hydroxide and then later washed, dried and milled. However, the seaweed flour produced has inferior quality compared to refined carrageenan (McHugh, 2003). Though several studies have already been conducted on mechanical and air drying of semi-refined carrageenan, the feasibility of applying osmotic dehydration on the product has never been fully explored.

Osmotic dehydration involves immersing the food in a hypertonic solution (Silva et al., 2012). Since the solution has higher osmotic pressure than the food, there is partial removal of water from the food tissues (Khan, 2012). Osmotic dehydration, which is effective even at ambient temperature, also preserves the color, flavor and texture of food from heat, and is used as a pre-treatment to improve the nutritional, sensorial and functional properties of food (Sing et al., 2007).

The study was conducted to investigate mass transfer, specifically sucrose gain and water loss, during osmotic dehydration of semi-refined carrageenan, as well as determine factors affecting its kinetics.

MATERIALS AND METHODS

Experimental Procedure

Procedures for extraction of carrageenan followed industry practices in the Philippines. Dried samples of the seaweed *Kappaphycus alvarezii* were acquired from local farmer. After soaking in distilled water for 30 minutes, rehydrated seaweeds were cooked in an alkali solution. For every one (1) kilogram of seaweed, 300 g KOH and 22.4 g KCl were dissolved in four liters of distilled water. Cooking was done for two hours in the temperature range of 80-85°C.

After washing in distilled water and chopping into uniform sizes of approximately one (1) inch and average thickness of 2.50 mm, the cooked seaweed was then subjected to osmotic dehydration at temperatures of 30°C, 40°C, and 50°C and in static and agitated (200 RPM) media of saturated sucrose solution. The ratio of the product and solution was 1:20. Chopped samples of weights 5.10 ± 0.10 grams were submerged into the solution at 5, 10, 15, 25, 35, 45, 60, 75, 95, and 120 min. Moisture content of the samples was then determined using oven (CENCO air oven) method.

Mass Transfer Modelling

Mass transfer during osmotic dehydration was evaluated using parameters on water loss (WL) and solid gain (SG):

$$WL = \frac{(MC_o)(W_o) - (MC_t)(W_t)}{W_o} \quad \text{equation (1)}$$

$$SG = \frac{S_t - S_o}{W_o} \quad \text{equation (2)}$$

where:

- W_o = initial weight of seaweed (g)
- W_t = weight of seaweed after osmotic dehydration at any time t (g)
- MC_o = initial moisture content of seaweed (%)
- MC_t = moisture content after osmotic dehydration at any time t (%)
- S_o = initial weight of the solids (g) = $(1 - MC_o)(W_o)$
- S_t = weight of solids after osmotic dehydration at any time t (g)
= $(1 - MC_o)(W_o)$

Kinetics of mass transfer was analyzed using Newton and Page models. In these models, the dependent variables are the dimensionless amount of water loss (W_A) and solute gain (W_S).

Newton: $W_{A \text{ or } S} = \exp(-kt)$
Page: $W_{A \text{ or } S} = \exp(-kt^n)$

$$\text{where: } W_{A \text{ or } S} = \frac{MC_{t, A \text{ or } S} - MC_{eq, A \text{ or } S}}{MC_{O, A \text{ or } S} - MC_{eq, A \text{ or } S}} = \text{water loss (A) or solute gain (S) ratio}$$

$MC_{O, A \text{ or } S}$ = initial amount of water or solute, %

$MC_{t, A \text{ or } S}$ = amount of water or solute at time t, %

$MC_{eq, A \text{ or } S}$ = equilibrium amount of water loss or solute gain, %

t = time

k, n = constants

The goodness of fit was evaluated using coefficient of determination (R^2), chi-squared (χ^2), mean bias error (MBE), and root mean square error (RMSE). To determine which factors have significant influence on osmotic dehydration, two-way ANOVA analysis and Pearson product-moment correlation were used.

RESULTS AND DISCUSSION

Mass Transfer Kinetics

During osmotic dehydration, there was simultaneous water loss and sucrose gain happening in the product. From an initial value of 92.23-94.45%, the moisture content of osmotically dehydrated SRC was reduced to 33.54-47.82%. However, solids also increased from 6.41-6.84% to 52.18-66.46%. Regardless of temperature and agitation conditions, the two properties showed similar curves (Figure 1). As observed in the plots, there was rapid initial water removal and sucrose uptake followed by slower loss and gain in the latter stages. High moisture loss and solute gain in the beginning was apparently caused by the large osmotic gradient between the dilute water content of the modified seaweed and the surrounding hypertonic medium. As more water was incorporated into the solution while losing sucrose at the same time, there was slight reduction in the osmotic pressure, thereby slowing down both moisture loss and solute gain in the carrageenan. Furthermore, a high sugar subsurface layer was also formed over time (Lazarides et al., 1995). This layer interferes with the concentration gradients across the product-medium interface, acting as barrier against further removal of water and uptake of sugar.

In addition, rapid loss of water and gain of sugar near the surface in the early stage of osmosis result in structural changes such as shrinkage and collapse of surface cells, consequently leading to compaction of the surface layers and increased mass transfer resistance for water and solutes. This behavior was also observed in other food products subjected to osmotic dehydration (Agarry et al., 2008; Antonio et al., 2008; El-Aouar et al., 2006; Lazarides et al., 1995; Silva et al., 2012).

The curves in Figure 1 also show that though they both occur simultaneously, moisture loss happened at a much faster rate than sucrose gain. In agreement with the results of other works (Lazarides et al., 1995; Lenart, 1996; qtd in Azoubel & Murr, 2003; El-Aouar et al., 2006; Silva et al., 2012), water removal is often higher than the uptake of osmotic agent. This fact is attributed to the osmotic transport phenomenon occurring across the semi-permeable cellular membrane which restricts passage of solids but not of water.

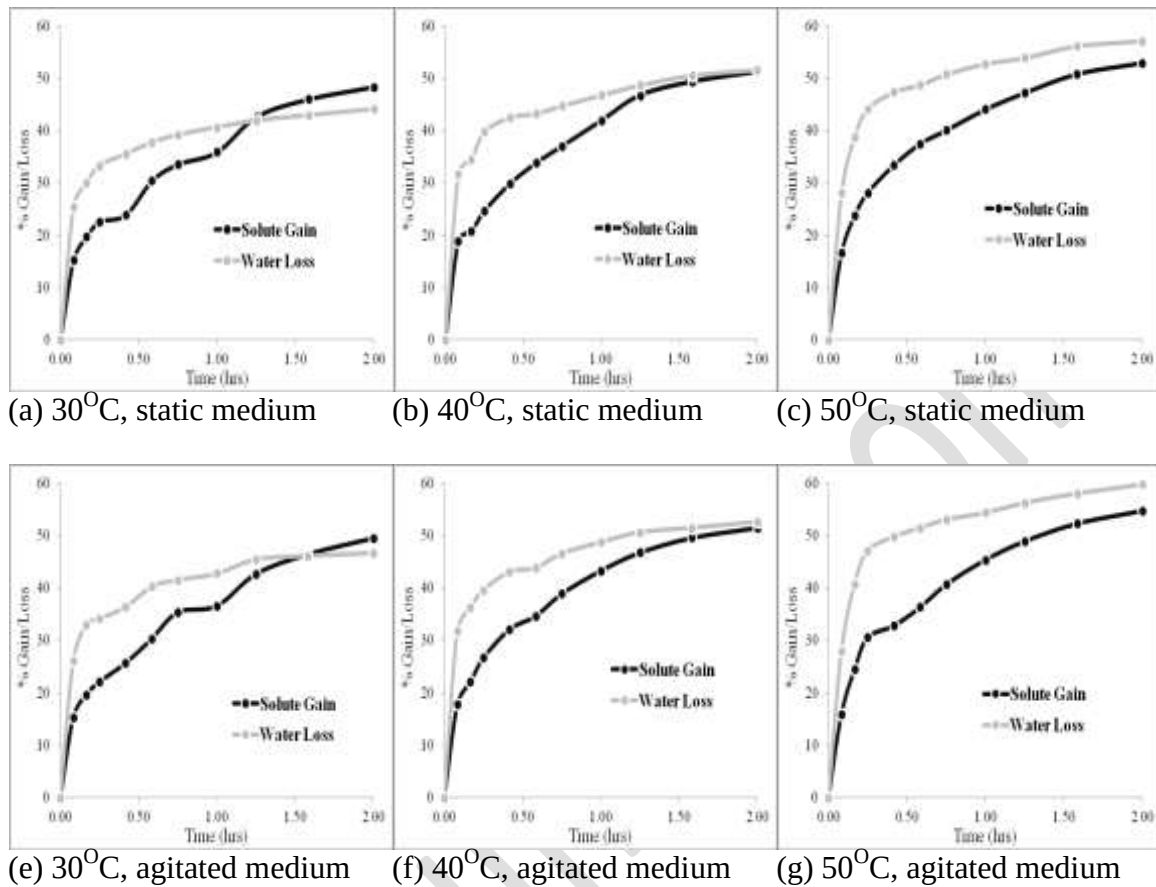


Figure 1. Solute gain and moisture loss

Mass Transfer Modelling

Drying models by Newton and Page were used to describe solute gain and water loss in the osmotically-dehydrated (OD) semi-refined carrageenan (Figures 2 and 3). Analysis of the relationship of temperature and agitation parameters is summarized in Table 1.

Based on the grand correlation value, Page had a better quality of fit for sucrose gain at an overall R^2 of 0.9479. Newton model followed closely behind at an R^2 value of 0.9477. However, both models demonstrated strong correlation. Differences between the models are much more pronounced with the other parameters. From the table, Page model had much lower values of χ^2 , MBE and RMSE than Newton. Hence, it can be said that the Page empirical model had the stronger fit for solute gain than Newton model.

For water loss, all models at different temperature and agitation conditions resembled Page. Page model also had a higher grand R^2 value of 0.9449 than Newton model. Similarly, Page appeared to have the stronger fit based on χ^2 , RMSE and MBE, and values for the parameters were also substantially spaced from Newton model.

In general, Page model had apparently the better fit for the data on both water loss and sucrose gain.

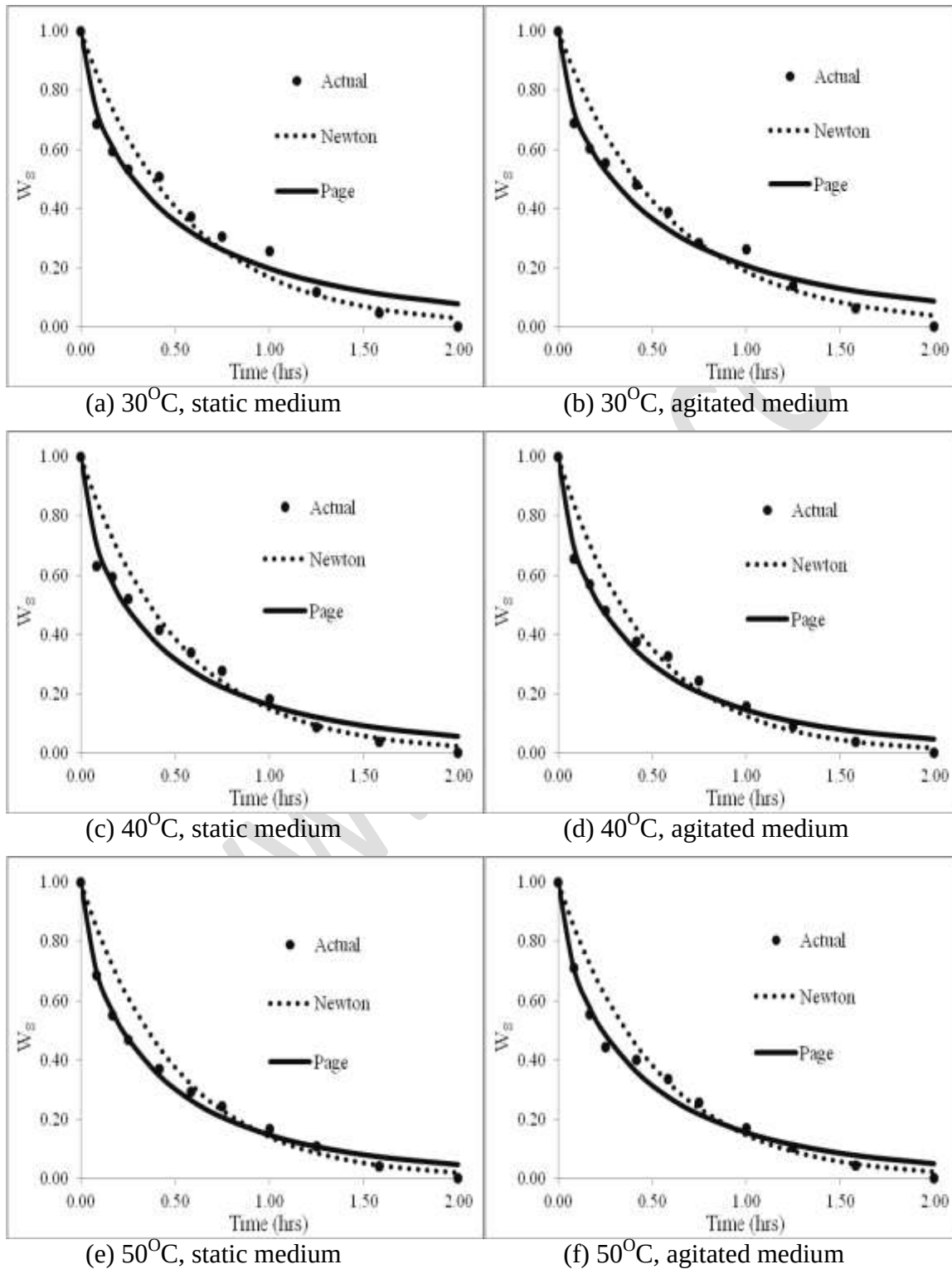


Figure 2. Curve models for solute gain

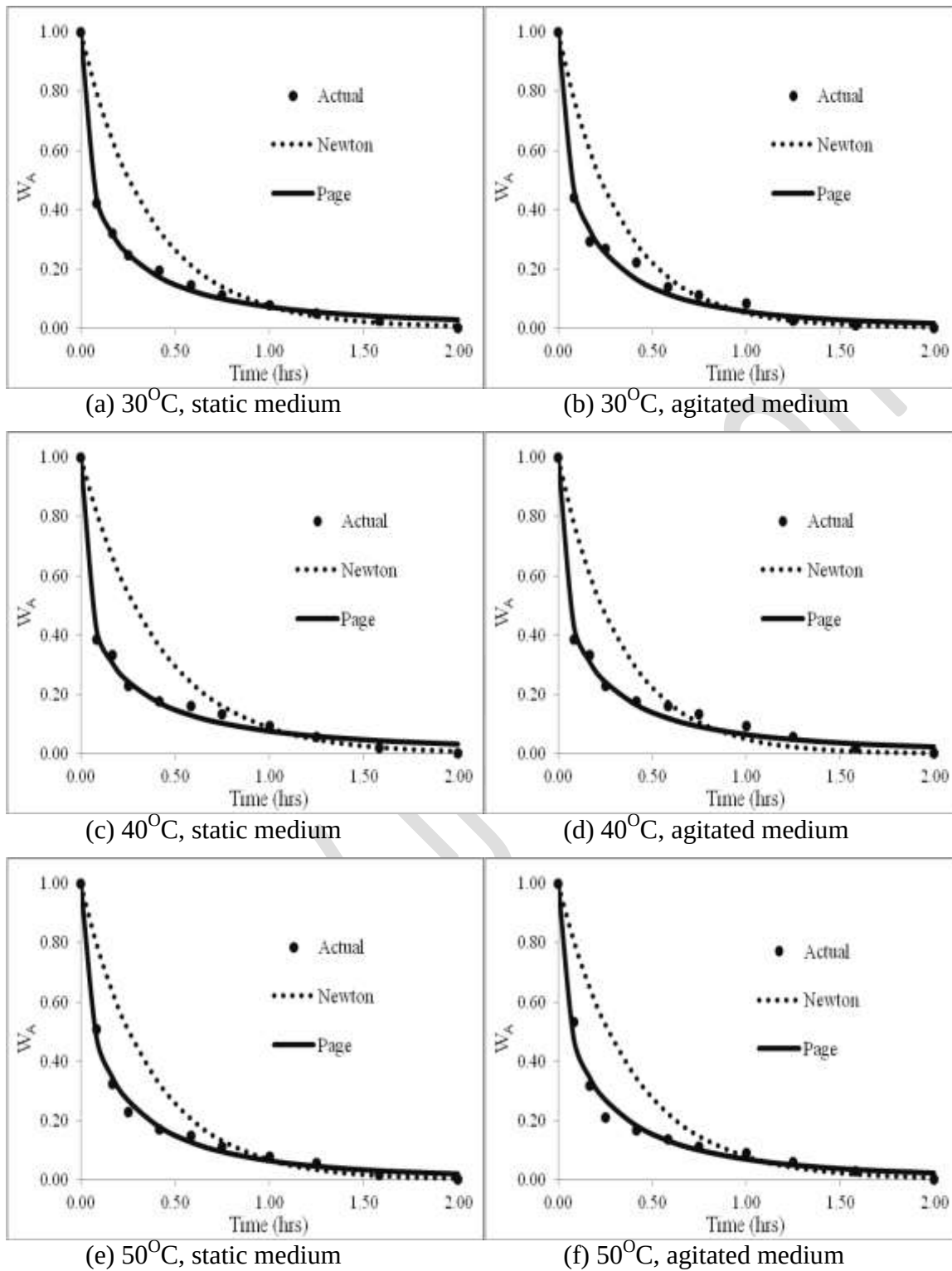


Figure 3. Curve models for water loss

Table 1. Mean values of statistical parameters for model fitting

Temp (°C)	Agitation Condition	Sucrose Gain		Water Loss	
		Newton	Page	Newton	Page
A. Based on R ²					
30	Static	0.9327*	0.9134	0.7869	0.9702*
	Agitated	0.9259	0.9285*	0.8846	0.9140*
40	Static	0.9626*	0.9203	0.7526	0.8975*
	Agitated	0.9661*	0.9579	0.8201	0.9453*
50	Static	0.9496	0.9736*	0.8152	0.9641*
	Agitated	0.9363	0.9642*	0.7123	0.9466*
Grand Mean		0.9477	0.9479*	0.8023	0.9449*
B. Based on χ^2					
30	Static	0.0084	0.0035*	0.0328	0.0005*
	Agitated	0.0094	0.0031*	0.0252	0.0010*
40	Static	0.0083	0.0026*	0.0439	0.0011*
	Agitated	0.0075	0.0014*	0.0293	0.0007*
50	Static	0.0088	0.0009*	0.0283	0.0006*
	Agitated	0.0010	0.0021*	0.0318	0.0010*
Grand Mean		0.0083	0.0021*	0.0303	0.0008*
C. Based on RMSE					
30	Static	0.0887	0.0575*	0.1755	0.0211*
	Agitated	0.0938	0.0537*	0.1538	0.0303*
40	Static	0.0884	0.0495*	0.2032	0.0326*
	Agitated	0.0841	0.0365*	0.1659	0.0251*
50	Static	0.0907	0.0283*	0.1629	0.0205*
	Agitated	0.0967	0.0441*	0.1729	0.0305*
Grand Mean		0.0905	0.0461*	0.1731	0.0276*
D. Based on MBE					
30	Static	0.0252	-0.0019*	0.1065	0.0010*
	Agitated	0.0351	0.0011*	0.0824	-0.0028*
40	Static	0.0415	-0.0033*	0.1245	-0.0001*
	Agitated	0.0347	-0.0016*	0.0883	-0.0009*
50	Static	0.0491	0.0005*	0.0990	0.0014*
	Agitated	0.0450	0.0004*	0.1077	0.0028*
Grand Mean		0.0384	-0.0008*	0.1014	0.0002*

*better fit

Effects of Factors to Osmotic Dehydration

Temperature and agitation conditions were the factors considered in the osmotic dehydration of semi-refined carrageenan. Their effect on the water loss and sucrose gain during the process was evaluated based on the constants (Table 2) in the empirical models generated. Based on Table 3, there was very weak direct correlation between agitation condition and the constants in the two models for sucrose gain. Meanwhile, only the constant k in the Page model had reasonably strong correlation with temperature which was significant at 5% level.

Results of ANOVA confirmed the observation that only the differences of constant k in the Page model were significantly different.

Table 2. Mean values of constants in the models

Temperature (°C)	Agitation	Page		Newton
		k	n	k
Sucrose Gain				
30	Static	1.6319	0.6670	1.8052
	Agitated	1.6065	0.6647	1.7190
40	Static	1.8271	0.6683	1.8992
	Agitated	1.9263	0.6785	2.0801
50	Static	1.9141	0.6792	1.9561
	Agitated	1.8677	0.6873	1.9215
Water Loss				
30	Static	2.7850	0.4857	2.7290
	Agitated	2.9262	0.5454	3.0455
40	Static	2.6434	0.4447	2.4344
	Agitated	2.7445	0.4776	2.9850
50	Static	2.7665	0.5353	2.7060
	Agitated	2.6998	0.5194	2.5790

As to water loss, there was weak negative inverse to weak direct relationship between the constants and temperature. As to agitation condition, the factor had generally very weak to moderate correlation with the constants. In other words, both factors had no clear association with moisture loss.

The results satisfied the assumption of constant solution concentration. At the product-solution ratio of 1:20, the concentration is high enough so that the external resistance is negligible compared to the internal one and that the driving force becomes more or less uniform (Rastogi et al., 2014), thereby effecting non-significant difference between static and agitated media.

Table 3. Correlation between factors and constants in the models

Factor	Page		Newton
	k	n	k
Sucrose Gain			
Temperature	0.566*	0.100	0.348
Agitation	0.023	0.038	0.048
Water Loss			
Temperature	-0.138	0.091	-0.270
Agitation	0.081	0.240	0.334

*means that correlation is significant at 5%

The case is different for temperature. As implied in the Page model, the factor significantly affected solute gain but not moisture loss. The driving force of mass transfer during osmotic

dehydration is the pressure gradient which in turn depends upon concentration and temperature of the osmotic solution. An increase in either or both factors leads to greater osmotic pressure, resulting to an increased mass transfer (Rastogi, 1997). This increased in mass mobility in food systems during osmosis at higher processing temperature has been observed in previous works (Herman-Lara, 2013; Lazarides, 1995). The solid gain increased with temperature is due to membrane swelling and plasticizing effect, which improves the cell membrane permeability to sugar molecules (Ganjloo et al., 2012). Moreover, the osmotic medium also becomes less viscous at higher temperature, thereby promoting better mass transfer on the surface (Azoubel & Murr, 2003).

CONCLUSION

Page model was found to be the best fit to describe sucrose gain and water loss during osmotic dehydration of SRC with temperature posing significant influence.

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