

Kingdom of Saudi Arabia  
Deanship of Graduate Studies



محارير الإمتزاز الرطوبي الديناميكي والديناميكا الحرارية وحركية الإمتزاز للمسحوق الجاف لتمر السكري  
Dynamic vapor sorption isotherms, sorption thermodynamics and kinetics of dry Sukkari date  
powder

Thesis

By

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In partial fulfillment of the requirement for the Master's degree in Agricultural Engineering,

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November 2017 G/Rabie Awal1439 H

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Dynamic vapor sorption isotherms, sorption thermodynamics, sorption kinetics and some physical properties of dry Sukkari Date powder

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## **CERTIFICATE OF ORIGINALITY**

This is to certify that this thesis was carried out by Mustapha, Abdullateef Taiye (435107803), of the Department of Agricultural Engineering, College of Food and Agricultural Sciences, King Saud University, Riyadh. That the original work is my own except as specified in acknowledgements or appendices, and that neither the original work nor the thesis has been submitted to this or any other institution for a degree.

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## **DEDICATION**

*Dedicated to my lovely Mother, dearest wife, precious daughter and to all my family and friends.*

## ACKNOWLEDGEMENT

In the Name of Allah, the Most Merciful and the Most Compassionate, All praise are due to Allah, the Lord of the worlds; may peace and blessing of Allah be upon the noble prophet Mohammad, his household, companion and followers.

First of all, all praises and sincere appreciation be to Almighty Allah, who gave me the health, wisdom, knowledge, strength and endurance to accomplish this research. I profoundly express my appreciation to King Saud University for supporting my study. I wish to express my gratefulness to my thesis advisors, Prof. Bakri Hussein Hassan and Dr. Khaled Abdulwahed, for their guidance and support for this research. I would also like to extend my thanks to my thesis examination committee - Prof. Alhussein Mohammed Al-Awaadhand and Prof. Abdullah M. A. Alhamdan - for their help, support and valuable ideas. I also acknowledge the research center - College of Food and Agriculture sciences, Deanship of Scientific Research.

Special thanks to my colleagues for all their time and discussions. I convey my heartfelt appreciation to all my friends for their support and encouragement since the beginning of my studies

I would like to express my special gratitude to my parents, in-laws, siblings and family at large. Their unquantifiable support, prayers and encouragement have inspired me over the years. I would also express my sincere appreciation to my gorgeous and lovely wife, *Hajia Kafilat Lawal*, and my lovely Daughter, *Maryam Motunrayo*, for their kindness, prayer, perseverance, endurance, understanding, encouragement and support throughout my study. You will forever remain in my cerebellum.

## ABSTRACT

Sukkari date cultivar is one of the most important and distinctive dates produced in the Kingdom of Saudi Arabia. Some physical properties of the powder produced from Sukkari dates were determined at different particle sizes. Bulk density, tapped density, compressibility index, and Hausner ratio values of the produced Sukkari date powder at different particle sizes were in the ranges 623.68 – 634.97 kg/m<sup>3</sup>, 831.93 -901.77 kg/m<sup>3</sup>, 24.15- 30.12, and 1.32-1.43 respectively. Values of the physical properties increased as the particle sizes reduces, but decreased for very fine particle size. Moisture content increased with decreasing particle size and spanned in the range 2.97-3.41% d.b. Water activity also increased with reduced particle sizes in the range 0.16-0.18. Electrical conductivity was in the range 2.90-3.13 S/m and it decreased with the decrease of particle size. pH, showed no significant difference for the different particle sizes and it fell in the range 5.60-5.64 which means the powder can be classified as a low-acid product. The date powder color data analysis showed that the ranges of the color parameters lightness (L\*), a\* (greenness – redness), b\* (blueness–yellowness), chroma (C\*), hue angle (H°), Browning index (BI), and total color (E) were 64.56-69.26, 4.51-5.44, 24.44 -27.09, 24.96-27.45, 78.30-80.55 52.29-55.95 and 69.22-74.51 respectively. All color parameters increased as the particle sizes were reduced. Water Absorption Index sizes ranged from 0.81-1.74g/g dry matter and increased as the particle sizes were reduced with slight significant differences, while water solubility index and oil holding capacity also increased as the particles sizes were reduced but with no significant differences in the ranges 6.77-7.20 and 0.31-0.78 g/g of dry matter respectively.

Moisture adsorption isotherms of the Sukkari date powder were determined within the range of 0.1 to 0.9 water activity at three different temperatures (20, 40 and 60 °C ±0.2), using the standard dynamic gravimetric method. A curve of type III shape with a sigmoid shape was observed. As water activity increases, the moisture adsorption was found to increase especially at high water activity. At constant low water activity, the equilibrium moisture content (EMC) increases as temperature increases, but from around 0.70 water activity, the EMC increases as the temperature reduces. The data obtained were fitted to several moisture sorption models, namely, Modified BET, Modified GAB, Modified Oswin, Modified Halsey, Modified Henderson, Modified Smith, and Modified Chung-Phost. The first four sorption models fitted the experimental sorption data well throughout the entire range of water activity at the three studied temperatures.

However, Modified BET model was found to be the best model with percentage error of 6.30%,  $R^2$  of 0.997, SSE of 0.005 and RMSE of 0.014 and it was used for the thermodynamics analysis.

Sorption thermodynamic analyses was also carried out using moisture sorption data predicted by the Modified BET model. Net Isosteric heats of adsorption was found to decrease with an increase in moisture content and becoming stabilized at moisture content greater than 0.3 kg/kg d.b. The maximum value of the net isosteric heat of sorption (1.46 kJ/mol) was obtained at a low EMC of 0.05 kg/kg d.b, whereas the minimum value of 0.38 kJ/mol was obtained at EMC of 0.6 kg/kg d.b. Heat of sorption (differential enthalpy) and differential entropy showed a similar trend to net isosteric heat of sorption. A linear relationship was observed for the plot of enthalpy and entropy which indicates that compensation theory could be applied within the studied range of moisture contents. Also, Isokinetic temperature ( $T_B$ ) and harmonic mean temperature ( $T_{hm}$ ) of sorption, was found to be 290.67 K and 312.1 K, respectively, which thereby confirming the suitability of the theory because  $T_B$  is significantly different from  $T_{hm}$ , and since  $T_B < T_{hm}$ , therefore, the process can be characterized as entropy driven. Monolayer moisture content was found to decrease as the temperature increases. An increase in temperature causes a reduction of spreading pressure but not very significant. The spreading pressure also increases with increasing water activity but with a slow increment of less than 0.5  $a_w$ . Net integral enthalpy was found to decrease with increase in moisture content from a value of 689.45 kJ/mol at moisture content of 0.25 kg/kg d.b. to 113.40 kJ/mol at 0.5 kg/kg d.b. While net integral entropy was also found to decrease with increase in moisture content from a maximum value of 7.05 kJ/mol K at moisture content 0.025 (kg/kg d.b) to a minimum value of 0.999 kJ/mol K at the moisture content of 0.57 (kg/kg d.b.), but the reduction was very slow and becoming constant at higher water activity.

The applicability of four sorption kinetic models was investigated for predicting moisture adsorption process of Sukkari date powder, at different relative humidity (RH) within the range 10-90 % at a step of 10 %, and different temperatures (20, 40 and 60 °C). The water sorption rate of the Sukkari date powder quickly increased as the relative humidity increases and the time for equilibrium to be reached increased as the temperature decreases. Over the entire range of RH (10-90 %), the time for equilibrium to be reached increased as the temperature was decreased, and the approximate equilibrium time values were 148h, 63h and 28hr for the temperatures 20°C, 40°C and 60°C, respectively. All the four kinetic models adequately fitted the experimental data over the relative humidity and temperature ranges under study. Temperature dependence of the four

models' parameters were also investigated which indicated that the constants of Peleg model fitted well over the RH and temperature ranges and was used for determination of some thermodynamic properties. The Peleg rate constants decreased with an increasing temperature. At constant RH, the enthalpy decreases with increase in temperature with no significant difference. While entropy and free energy of activation increases with increase in temperature.

## ملخص الرسالة باللغة العربية

يعد صنف التمر سكري أحد أهم وأميز أصناف التمور المنتجة في المملكة العربية السعودية. وقد تم إيجاد بعض الخواص الطبيعية لمسحوق التمر المنتج من صنف السكري عند مقاسات مختلفة لحبيبات مسحوق التمر. قيم الكثافة الجمية والكثافة المضغوطة ومعامل الانضغاطية ونسبة هاوسنر (Hausner ratio) لمسحوق السكري المنتج عند مقاسات مختلفة لحبيبات المسحوق كانت في الحدود 623.68-634.97 كجم/م<sup>3</sup>، 831.93-901.77 كجم/م<sup>3</sup>، و24.15-30.12، و1.32-1.43، على التوالي. وقد زادت قيم الخواص الطبيعية مع انخفاض مقاسات حبيبات المسحوق، بيد أن قيمها نقصت لمقاسات حبيبات المسحوق الصغيرة جداً. أما المحتوى الرطوبي فقد زاد مع نقصان مقاس الحبيبات وكان في الحدود 2.97-3.41% على أساس جاف. كما زاد النشاط المائي بنقصان مقاس الحبيبات وكان في الحدود 0.16-0.18. وقد تفاوتت قيم الموصلية الكهربائية في الحدود 2.91-3.13 س/م حيث انخفضت قيمها بانخفاض مقاس الحبيبات. أما الرقم الهيدروجيني (pH) فلم يتغير معنوياً بتغير مقاسات حبيبات المسحوق حيث تفاوتت في الحدود 5.60-5.64 مما يشير إلى إمكانية تصنيف مسحوق تمر السكري كمنتج منخفض الحامضية. وقد بين تحليل نتائج اللون لمسحوق التمر أن حدود قيم معاملات اللون التي تمثل الأبيضاض (L\*)، والأخضرار-الأحمرار (a\*)، والأزرقاق-الأصفرار (b\*)، والصفاء اللوني (C\*)، وزاوية تدرج اللون (H°)، ومعامل الأسمرار (BI)، واللون الكلي (E)، كانت مساوية 64.56-69.26، 4.51-5.44، 24.44-27.09، 78.30-80.55، 52.29-55.59، و -69.22-74.51، على التوالي. وقد ازدادت جميع قيم معاملات اللون بانخفاض مقاسات حبيبات المسحوق. أما دليل الامتصاص المائي فقد تفاوتت في الحدود 0.81-1.74 جم/جم مادة صلبة حيث ازدادت قيمه مع انخفاض قيم مقاس الحبيبات بفروقات معنوية طفيفة، بينما ازدادت كذلك قيم مؤشر القابلية للذوبان في الماء وقيم سعة احتجاز الزيت في الحدود 6.77-7.20 و 0.3-0.78 جم/جم مادة صلبة، على التوالي، بنقصان مقاسات حبيبات المسحوق دون وجود فروق معنوية.

تم إيجاد محارير الامتصاص الرطوبي لمسحوق تمر السكري في حدود قيم النشاط المائي 0.1-0.09 عند ثلاثة درجات حرارة مختلفة (20 و 40 و 60 م°)، باستخدام الطريقة الديناميكية الوزنية. وقد تم الحصول على منحنيات امتزاز رطوبي سينية الشكل من النوع III. وبينت النتائج أنه كلما ازداد النشاط المائي يزداد الامتصاص الرطوبي خاصة عند قيم النشاط المائي العالية. وعند قيم النشاط المائي المنخفضة الثابتة فإن

المحتوى الرطوبي المتوازن يزداد بزيادة درجة الحرارة، ولكن عند حوالي قيمة النشاط المائي 0.70 فإن قيم المحتوى الرطوبي عند التوازن تزداد بانخفاض درجة الحرارة. وقد تم موازنة النتائج التي تم الحصول عليها باستخدام العديد من نماذج محارير الامتزاز الرطوبي، وعلى وجه التحديد، نموذج بي إي تي المعدل (Modified BET)، ونموذج قاب المعدل (Modified GAB)، ونموذج اوسوين المعدل (Modified Oswin)، ونموذج هالسي المعدل (Modified Halsey)، ونموذج هندرسون المعدل (Modified Henderson)، ونموذج سميث المعدل (Modified Smith)، ونموذج شنغ-فوست المعدل (Modified Chung-Phost). النماذج الأربعة الأولى واءمت النتائج التجريبية بصورة جيدة جداً في المدى الكامل لحدود النشاط لمائي عند درجات الحرارة الثلاثة التي تم اختبارها. بيد أن نموذج بي إي تي المعدل (Modified BET) اثبت انه النموذج الأفضل في موازنة النتائج التجريبية بنسبة خطأ تعادل 6.3% وقيمة معامل ارتباط ( $R^2$ ) تساوي 0.997 وقيمة مربع خطأ قياسي (SSE) تساوي 0.005 وقيمة جذر متوسط مربع الخطأ (RMSE) الذي يعادل 0.014، وبالتالي تم استخدام هذا النموذج في التحليلات الديناميكية الحرارية.

تم إجراء تحليلات الديناميكا الحرارية باستخدام بيانات الامتزاز الرطوبي التي تم التنبؤ بها باستخدام نموذج بي إي تي المعدل (Modified BET). وقد وجد أن قيم صافي الحرارة متساوية التوتر من الامتصاص تتخفض مع زيادة المحتوى الرطوبي ثم تصل الى مرحلة الاستقرار عند محتوى رطوبي أكبر من 0.3 كجم/كجم على أساس جاف. وقد تم الحصول على القيمة القصوى لصافي الحرارة متساوية التوتر من الامتصاص التي تساوي 1.46 ك جول/مول عند القيمة المنخفضة للمحتوى الرطوبي المتوازن التي تساوي 0.05 كجم/كجم مادة صلبة جافة، بينما تم الحصول على القيمة الدنيا لصافي الحرارة متساوية التوتر من الامتصاص التي تساوي 0.38 ك جول/مول عند المحتوى الرطوبي المتوازن الذي يساوي 0.60 كجم/كجم مادة صلبة جافة. وقد أظهرت حرارة الامتزاز (الانتالبي التفاضلي) وكذلك الانتروبي التفاضلي نمطاً مشابهاً لصافي الحرارة متساوية التوتر من الامتصاص. وتم ملاحظة وجود علاقة خطية عند رسم الانتالبي والانتروبي والتي تشير إلى إمكانية تطبيق نظرية التعويض في حدود قيم المحتوى الرطوبي التي تم اختبارها. كذلك فقد وجد ان قيم درجة حرارة الحركية المتساوية ( $T_B$ ) ودرجة حرارة الوسط التوافقي ( $T_{hm}$ ) كانت مساوية 291.67 و 312.1 ك ، على التوالي، والتي تؤكد بدورها ملائمة نظرية التعويض نظراً لأن قيمة  $T_B$  تختلف معنوياً من قيمة  $T_{hm}$ ، وبما أن  $T_b < T_{hm}$  فإن العملية يمكن وصفها كعملية يحركها الانتروبي. وقد وجد أن المحتوى الرطوبي للطبقة

الأحادية ينخفض مع ارتفاع درجة الحرارة. كذلك وجد ان زيادة درجة الحرارة يؤدي الى إنخفاض ضغط الانتشار ولكن ليس بصورة معنوية. كذلك يزداد ضغط الانتشار بازدياد النشاط المائي ولكن بزيادات بطيئة تعادل اقل من 0.5 من قيمة النشاط المائي. أما الانتالبي التكاملي الصافي فقد وجد انه يقل مع زيادة المحتوى الرطوبي من 689.45 ك جول/مول عند محتوى رطوبي 0.25 كجم/كجم مادة صلبة على أساس جاف الى 113.4 ك جول/مول عند محتوى رطوبي 0.50 كجم/كجم مادة صلبة على أساس جاف. أما الانتروبي التكاملي الصافي فقد وجد انه ينخفض مع زيادة المحتوى الرطوبي من قيمة قصوى تساوي 7.05 ك جول/مول ك عند محتوى رطوبي 0.025 كجم/كجم مادة صلبة على أساس جاف الى قيمة دنيا تساوي 0.999 ك جول/مول ك عند محتوى رطوبي 0.57 كجم/كجم مادة صلبة على أساس جاف، غير أن الانخفاض كان بطيئاً جداً ولكنه أصبح ثابتاً عند القيم الأعلى للنشاط المائي.

تم استقصاء قابلية التطبيق لأربعة نماذج لحركية الامتزاز بغرض التنبؤ بعملية الامتصاص الرطوبي لمسحوق تمر السكري عند قيم مختلفة للرطوبة النسبية في الحدود 10-90% وبزيادة خطوة منتظمة تعادل 10% عند درجات حرارة مختلفة (20 و 40 و 60 م°). وقد ازداد معدل الامتصاص الرطوبي لمسحوق تمر السكري بصورة سريعة مع ازدياد الرطوبة النسبية، كما ازداد زمن الوصول الى مرحلة الاتزان بانخفاض درجة الحرارة. وعلى المدى الكلي للرطوبة النسبية (10-90%) فإن الزمن اللازم للوصول لمرحلة الاتزان ازداد مع انخفاض درجة الحرارة، وكانت القيم المتوسطة للوصول الى مرحلة الاتزان مساوية 148 و 63 و 28 ساعة لدرجات الحرارة 20 و 40 و 60 م°، على التوالي. وتمكنت نماذج الحركة الأربعة من مواءمة النتائج التجريبية بصورة مرضية على مدى قيم الرطوبة النسبية ودرجات الحرارة التي تم اختبارها. كذلك تم استقصاء مدى اعتمادية معاملات النماذج الأربعة على درجة الحرارة، حيث وجد أن ثوابت نموذج بيليج (Peleg model) وامتت النتائج التجريبية بصورة مرضية وبالتالي تم استخدامها لايجاد بعض الخواص الثيرموديناميكية. وقد انخفضت ثوابت المعدل في نموذج بيليج مع زيادة درجة الحرارة. وعند رطوبة نسبية ثابتة انخفضت قيم الانتالبي مع زيادة درجات الحرارة ولكن دون اختلافات معنوية، بينما ازدادت قيم الانتروبي والطاقة الحرة للتنشيط مع زيادة درجة الحرارة.

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# CHAPTER ONE: Introduction, Importance, and Objectives

## 1.1 General Introduction

Date palm (*Phoenix dactylifera* L.) is the most successful and commercially important crop in the hot-arid regions of the world (Mahmoudi et al., 2008). Out of the total world production of 7.4 million tons of dates, 5.4 million tons are coming from Arab world. Saudi Arabia is one of the leading date producing countries with an annual production exceeding 1 million tons of dates from over 400 date cultivars (FAOSTAT, 2009). The Fruits are rich in sugars, fiber, mineral salts and vitamins and is an excellent material for producing liquid sugars, concentrated juice, confectionery pastes and fermentation products. Sukkari cultivar is one of the major date cultivars in the Kingdom of Saudi Arabia, which is processed and packaged in more than 120 date factories (Anonymous, 2006). The dry powdered form of Sukkari dates can be used as a sweetener and major ingredient in many food industries.

Several preservation processes have been developed in order to extend the shelf-life of foodstuffs by lowering the availability of water, micro-organisms and inhibiting some chemical reactions (Hasan & Nurhan, 2007). The purpose of drying food products is to allow longer periods of storage with minimized packaging requirements and reduced shipping weights. During the dehydration process, the quality of the product and its cost are greatly influenced by the drying operation, in addition to the quantity of physical and biochemical degradation. The drying time, temperature, and water activity influence the final product quality. Specific changes in color, flavor, texture, stability, and acceptability of raw and processed food have been associated with relatively narrow water activity ranges.

Establishing the relationship between equilibrium moisture content ( $X_e$ ) and water activity ( $a_w$ ), at constant temperature and pressure which is known as the sorption isotherm, is important to understand the stability of foodstuffs. For food materials, these isotherms give information about the sorption mechanism and the interaction of food biopolymers with water. The moisture sorption isotherms are extremely important in modeling the drying process, in design and optimization of drying equipment, in predicting shelf-life stability, in calculating moisture changes which may occur during storage and in selecting appropriate packaging material.

Several methods have been developed for moisture sorption determination in food. Most of these researches were carried out with the use of static gravimetric method associated with some

setbacks (Yazdani et al., 2006). Dynamic vapor sorption (DVS) method could overcome the drawbacks encountered with the discontinuous system (slowness of the equilibrium process, the possibility of mold or bacterial growth on samples at high relative humidity, and difficulty). The DVS system does not require the use of saturated salt solutions in order to provide the desired relative humidity, but instead, a mixture of dry nitrogen and saturated water vapor, whose proportions are precisely controlled by mass flow controllers is used (Gokhan, et al., 2012).

A number of models have been proposed in the literature to describe moisture isotherms (Nabil & Mohamed, 2000). These models can be classified in several categories: sorption models based on the monolayer theory, models based on the multilayer theory and empirical and semi-empirical models. Some of the equations take into account the effect of temperature. Several sorption models have been adopted as standard equations by the American Society of Biological and Agricultural Engineers (ASBAE) for describing sorption isotherms (ASBAE, 2006).

High sugar foods such as dehydrated fruits can undergo changes such as crystallization, clumping, sticking and caking during processing and storage, hence they must have good flow characteristics especially food powders (Tsami et al., 1990).Sukkari date cultivars are one of the major cultivars in Saudi Arabia that are usually dried due to their non-reducing sugar content (sucrose) (Alhamdan & Hassan,1999).Consequently, knowledge of the sorption characteristics of the dry Sukkari date powder is important to establish the packaging requirements, shelf life and stability of products containing this ingredient.

## **1.2 Rationale and Significance of the study**

Date palm (*Phoenix dactylifera* L.) is the most successful and commercially important crop in the hot-arid regions of the world (Mahmoudi et al., 2008). The Fruits contain carbohydrates (about 60%), most of which are in the form of sugars, they also contain significant amounts of dietary fiber, vitamins, carotenoids, anthocyanins, phenolics, and antioxidants (Al-Farsi and Lee 2012). Dates fruits are an excellent material for replacing added sugar, producing liquid sugars, concentrated juice, confectionery pastes and fermentation products (Manickavasagan, et al., 2015).

Production of free-flow powder from dates could improve handling, storage, and blendability with several products, including baked products in commercial manufacturing. Free-

flow powders offer natural and easy doseable ingredients in many foods and pharmaceutical products (Goula and Adamopoulos, 2010)

A fundamental property of a biomaterial that influences dehydration, shelf life predictions and storage stability is its moisture sorption characteristics (Chukwu and Ajisegiri 2006). This characteristics which are predicted by some models, is the relationship between water activity ( $a_w$ ) and moisture content at a given temperature.

For these and many other reasons, many researches have been carried out on dates and its products, but most of these researches that are related to moisture sorption isotherms are carried out on either dates' flesh, pastes or syrup Fikry & Al-Awaadh (2016) reported the moisture sorption isotherm of date powder rich in fibre. However, Mathlouthi; Rogé, (2003) stated that depending on the nature of food powder (crystalline or amorphous), the isotherms shape will be different. Carlos et al., (2005) confirm this behavior relating that the sorption characteristics were correlated with the degree of sugar crystallization. This means that for each product their exist a complex and unique relationship due to different interactions at different moisture contents between water and solid components (Gokhan, et al., 2012; Carter & Fotanna, 2008; Shafiur & Al-Belushi, 2006).

Therefore, actual determination of physical properties and moisture sorption characteristics of date powder parameters are required in order to find the best fit model(s), to determine the sorption thermodynamics and sorption kinetics. In addition, this information is required to predict the fundamental behavior of the product during handling, processing and storage.

### **1.3 Research Objectives**

The objectives of this study are:

- i. To produce Sukkari date powder and determine some of its physical properties and its vapor sorption isotherms at different temperatures, and fit experimental data to sorption models.
- ii. To determine the isosteric heat of sorption and differential entropy from the sorption data.
- iii. To evaluate sorption kinetics of the Sukkari date powder.

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## CHAPTER TWO: Literature Review

### 2.1 Water Activity

The importance of water to all life is well recognized, as well as the role of water in controlling the growth of microorganisms in foods and other biological systems (Labuza 1968). Water is an essential molecule of life; without it, there is no life. Practically all its properties are anomalous, which enables life to use it as building material for its machinery. Water is critically important to our daily lives—from survival and growth to temperature regulation, firefighting, food production, transportation, hydropower, cooking, cleaning, and bathing, and recreational activities, to name only a few needs and uses. Water can also be the cause of catastrophic situations, by its lack, overabundance, or impurity (Isengard, 2001a).

With regard to foods, water is present in all food ingredients and systems, from trace amounts, as in the case of crystalline sucrose, which has an average moisture content of 0.04% wet basis, to very high amounts, as in fresh fruits and vegetables, many of which have a moisture content greater than 90% wet basis (Iglesias & Chirife 1982). Water in foods is critically important because of its profound effect on the production, processing, microbial safety, and chemical and physical stability of food systems. Water's extensive involvement in food processing, stability, sensory perception, and, most important, safety has made it an essential focus of study in many fields of inquiry for numerous years. Most foods are multiphase systems with water being an important component. The role of water in food stability can be described to a significant extent by the potential of water to contribute to both physical and chemical deteriorative reactions through its ability to dissolve reactants, mobilize them, and participate in the reactions as well. Currently, there are three main water relations in foods research avenues: water activity ( $a_w$ ), molecular water mobility, and the food polymer science approach. A recent review by Schmidt (2004) critically examines and compares these three water relations in foods research avenues.

The measure of the state of water in foods called water activity, is a successful concept commonly used in correlation with food safety and quality. Water activity ( $a_w$ ) is a unique factor in food stability that enables the development of generalized limits within ranges where certain types of deteriorative reactions are dominant (Scott, 1957). One of the main preservation methods to ensure food safety against microbial and chemical deterioration is controlling the  $a_w$  in food, which can extend shelf-life and create convenience with new food products. Therefore, several

food preservation techniques rely on lowering the  $a_w$  so as to reduce the rates of microbial growth and chemical reactions.

Thus, water activity can be defined as an equilibrium property of water in foods and other materials. It is based on the chemical potential of water within a food system, which at equilibrium must be the same as the chemical potential of water in the surroundings of the food. This also means that the vapor pressure of liquid water in the food and the vapor pressure of water vapor in the surroundings must be equal. Hence,  $a_w$  can be obtained as the ratio of vapor pressure of water in a food and the vapor pressure of pure water at the same temperature and pressure conditions (Labuza, 1968). Therefore, the measurement of vapor pressure also gives  $a_w$ . The relationships between chemical potential, vapor pressure, and  $a_w$  indicate that  $a_w$  is a temperature-dependent property of food. The water content of food commodities are relatively constant and only the water activity of food is expected to change with temperature.

Mathematically, water activity ( $a_w$ ) is equal to the percent equilibrium relative humidity (% ERH), divided by 100. For this definition to hold; firstly, the food system must be in thermodynamic equilibrium and lastly, temperature and pressure must be constant. Unfortunately, these assumptions are often violated in food systems (Schmidt, 2004). This is because most foods experience physical, chemical, and microbiological changes over time and are therefore non-equilibrium systems (Schmidt, 2004). However, most food systems may exist practically in a steady state but not in a thermodynamic equilibrium state may undergo changes during storage (Fontana et al., 2008).

Labuza et al. (1970) and Labuza (1968) developed a global stability map (Fig. 1), which indicates that for reactions requiring an aqueous phase, such as non-enzymatic browning and enzyme reactions, there is a lower limit, usually at  $a_w$  between 0.2 and 0.3, below which the reactivity is 0; above that, the reaction rate increases until reaching a maximum at an  $a_w$  essentially between 0.6 and 0.8 and then decreases again, reaching 0 at  $a_w$  of 1.0 (Sherwin & Labuza, 2006). Lipid oxidation, on the other hand, shows a minimum in the 0.2 to 0.35  $a_w$  range and increases in rate on both sides (Labuza, 1971). The stability map also shows that molds can generally grow at lower  $a_w$  limits than yeast; such limits are lower than that for bacteria. Each of these organism types shows a minimum at both the high and low ends and a maximum in-between for growth rate as a function of  $a_w$ . Although this phenomenon has been attributed to “free” versus “bound” water

(Troller & Christian 1978), the control of growth rate is much more complex, being ruled by ionic balance, the amino acid pool each organism uses, and porin genes that manipulate water transport across the membrane. What is known is that no microbes can grow at 0.6  $a_w$ . However, although they cannot grow, they can survive at low  $a_w$  and, if added to a suitable medium, they may resuscitate and begin to grow again.

Long-term stability of food systems, however, can be obtained by freezing and dehydration. In both methods, food solids are concentrated either by separating water into another phase (ice) or by removing nearly all of the water (Roos 1995). Successfully processed and stored frozen and dehydrated materials are extremely stable (Chirife & Buera 1996). Water activity affects the stability, flow, and caking and clumping of powders during storage (Peleg & Mannheim 1977; Saltmarch & Labuza 1980; Chuy & Labuza 1994; Aguilera & del Valle 1995). Although  $a_w$  can be measured for most foods, their stability at the same  $a_w$  may vary significantly, e.g., from hours to years. For example, a food powder with sucrose as a main component becomes sticky and may crystallize at 0.3  $a_w$  within hours, whereas dairy powders with high lactose contents remain stable for years at the same  $a_w$  at typical storage temperatures. Foods with high  $a_w$  have a texture that is described as moist, juicy, tender, and chewy. When the  $a_w$  of these products is lowered, undesirable textural attributes such as hardness, dryness, staleness, and toughness are observed. Food low in  $a_w$  normally have texture attributes described as crisp and crunchy, while at higher  $a_w$ , the texture becomes soggy. The crispness intensity and overall hedonic texture of dry snack food products are a function of  $a_w$  (Katz & Labuza 1981, Hough et al. 2001). Critical water activities are found where the product becomes unacceptable from a sensory standpoint.

What is known is that no microbes can grow at 0.6  $a_w$ . However, although they cannot grow, they can survive at low  $a_w$  and, if added to a suitable medium, they may resuscitate and begin to grow again. Given this, it is important to know the relationship between the moisture content and  $a_w$  of a food. This relationship is called the moisture sorption isotherm, which is superimposed on the stability map (see Fig. 2.1).

The relationship derived between the moisture content of food components and the relative water vapor pressure ( $p/p_0$ ) of the atmosphere in equilibrium with the material can be used to compute the corresponding equilibrium relative humidity [ERH =  $100(p/p_0) = 100 a_w$ ]. Thus, under isothermal conditions, this equilibrium relationship is represented by the moisture sorption isotherm shown in Fig. 2.1.

Controlling  $a_w$  in a powder product below critical levels maintains proper product structure, texture, flowability, density, and rehydration properties (Fontana, 2008). Knowledge of the  $a_w$  of powders as a function of moisture content and temperature is essential during processing, handling, packaging, and storage to prevent the deleterious phenomenon of caking, clumping, collapse, and stickiness. Caking is dependent on  $a_w$ , time, and temperature and is related to the collapse phenomena of the powder under gravitational force (Chuy and Labuza 1994).

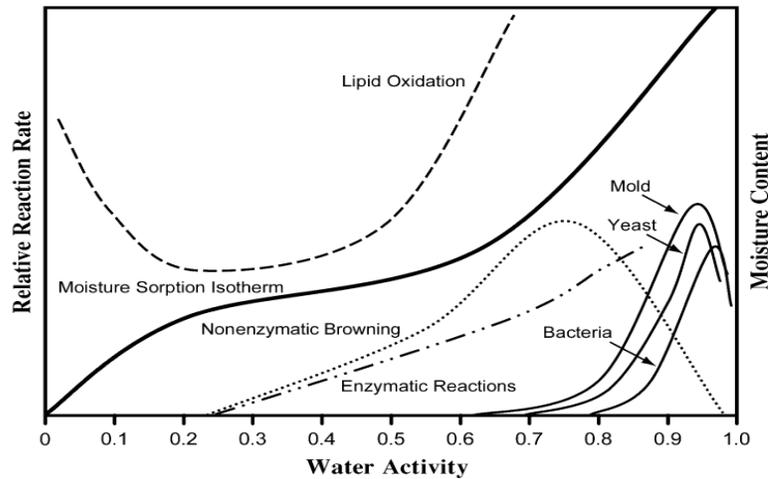


Figure 2.1 Food stability map as a function of water activity (Labuza et al. (1970); Labuza (1968)).

## 2.2 Equilibrium Moisture Content

Knowledge of the equilibrium moisture content of a biological material is essential for the efficient design and operation of systems for drying, wetting, or storing the material. The equilibrium moisture content for a given environment may be defined as the moisture content which the material would approach if left in that environment for an infinite period of time (Young & Nelson, 1967).

Equilibrium moisture content is directly related to drying and storing of hygroscopic materials which are likely to be influenced from atmospheric water vapor. Equilibrium relative humidity of the air, in contact with the material, determines whether it will gain or lose moisture in a particular environment (Dinçer & Esin, 1995).

## 2.3 Sorption Isotherms

Sorption isotherm is the plot of equilibrium moisture content of a material subjected to different relative humidities at a given temperature in closed environment. Depending on the direction of water transferred the process is named as adsorption or desorption. An adsorption isotherm can be obtained by subjecting a relatively dry material to an atmosphere of constant relative humidity and measuring the weight gained at equilibrium due to water and repeating this procedure for different relative humidities. The desorption isotherm is found by placing the wet material into an atmosphere of lower relative humidity and then again determining its equilibrium moisture content (Labuza, 1968). As shown in fig. 2.2, the moisture sorption isotherm curve can be generated from an adsorption or desorption process. The difference in moisture content between the adsorption and desorption curves for a given water activity value is due to hysteresis. This phenomenon could result in three different isotherms for the same food sample depending on the approach used. One reason for this difference is that during drying (desorption), some solutes may be supersaturated below their crystallization  $a_w$  and therefore hold more water as  $a_w$  is lowered. Also, capillaries can empty differently upon desorption, as the surface tension and wetting angle differ between adsorption and desorption, resulting in a higher moisture content for desorption. A working isotherm will fall in the middle of the two curves. Due to hysteresis, working isotherms are often used.

### 2.3.1 Types of Sorption Isotherms

Fellows (2009) stated that each food shows a unique set of sorption isotherms at different temperatures, however most sorption isotherms have a characteristic sigmoidal shape, similar to that shown in fig. 2.2. Brunauer (1940) first categorized sorption isotherms into five general types (fig. 2.3) based on the van der Waals adsorption of gases adsorbing on various nonporous solid substrates. Later, IUPAC (2004) categorized it into more practical classifications of six general types (fig. 2.4).

In general, type I isotherms are typical for substance that can hold a large amount of water at low  $a_w$  values, such as anti-caking agent. This can be seen as the isotherm increases significantly at the beginning and then reach a plateau at higher  $a_w$  values. This type of sorption isotherm is typically applicable in the process of filling the water monomolecular layer at the internal surface of a material. Most processed foods which have an  $a_w$  lower than 0.95 fall into the type II sorption isotherm category, which is a sigmoid-shaped curve. The resultant shape is caused by the additive

effects of Raoult's law, capillary effects, and surface water interactions (Barbosa-Canovas et al., 2007). The shape of the isotherm can be explained by the existence of multilayers at the internal surface of a material. Type III isotherm known as the Flory-Huggins isotherm, represents food systems which composed mainly of crystalline components, such as sugars and salts (Barbosa-Canovas et al., 2007). In this type, small amounts of water can be adsorb in the initial process because water interacts with hydroxyl groups on the surface of the material via hydrogen bonding. When crystalline materials reach their deliquescent point, the crystals begin to dissolve in the absorbed water. Type IV describes the adsorption of a swellable hydrophilic solid until a maximum of site hydration is reached. While Type V is the one observed in the adsorption of water vapour on charcoal which is related to the isotherms type II and III.

Mathlouthi & Rogé (2003) stated that most food systems exhibits Type II and IV sorption isotherm and Blahovec & Yanniotis (2009) gives the details of type II as shown in figure 2.2. The typical moisture sorption isotherm can be divided into three regions depending on the state of water present.

Region A ( $a_w < 0.25$ ) represents monolayer water which is strongly sorbed, unfreezable, and not easily removed by drying. The water in this region interacts most strongly with the solids and is least mobile. The Brunauer-Emmet-Teller (BET) monolayer moisture content is located at the end of Region A, which is considered to be a monolayer of water bound to specific polar sites on the dry solids. Region B ( $0.25 < a_w < 0.75$ ) represents water sorbed (both adsorption and absorption can occur in this region) in multi-layers within foods and solutions of soluble components. It is still slightly less mobile than bulk water. As water is added in the vicinity of the low-moisture end of Region B, it exerts a significant plasticizing action on solutes, lowers their glass transition temperatures and causes incipient swelling of the solid matrix (Yu, 2007). The third region is bulk or —free water, which is freezable and is easily removed by drying. It is also available for microbial growth and enzyme activity. Region C water is referred to as bulk-phase water

The effect of composition plays one of the most important roles that affect moisture sorption behavior in complex food systems. If assumed that the ingredients in a complex food system do not interact with each other, the isotherm of multi-component food systems could be estimated by using individual sorption isotherm (Figure 2.5). Many multi-component foods contain ingredients that have different water activities, and during storage, moisture will be exchanged until a final equilibrium  $a_w$  is reached.

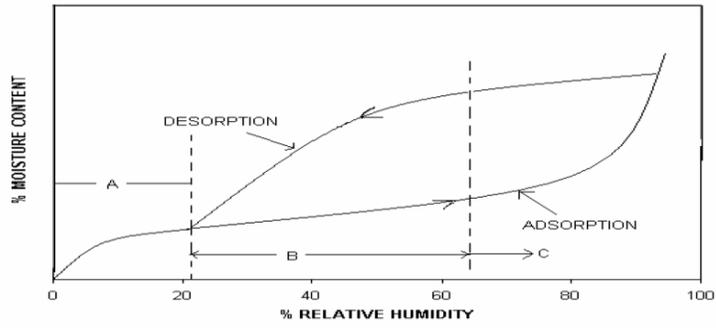


Figure 2.2-Typical Moisture Sorption Isotherm.

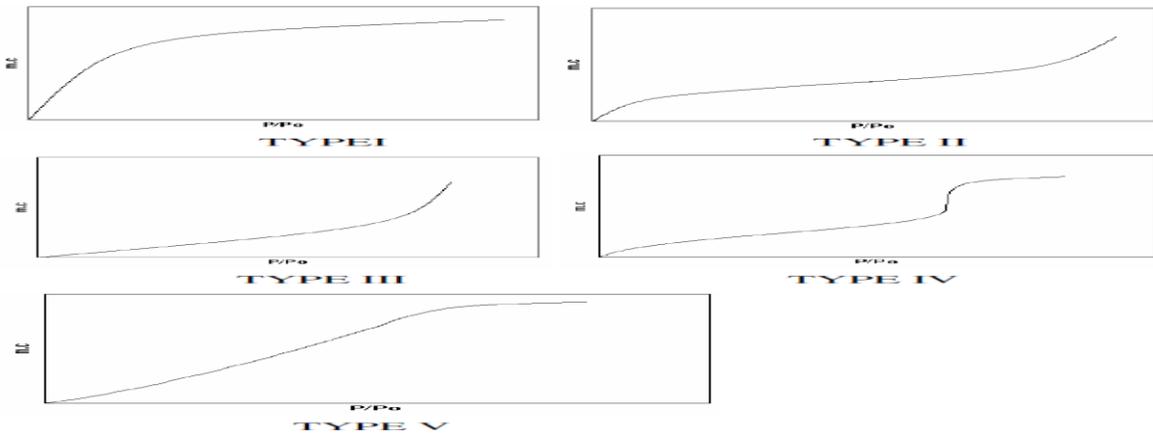


Figure 2.3 The Brunauer (1940) classification for adsorption isotherms.

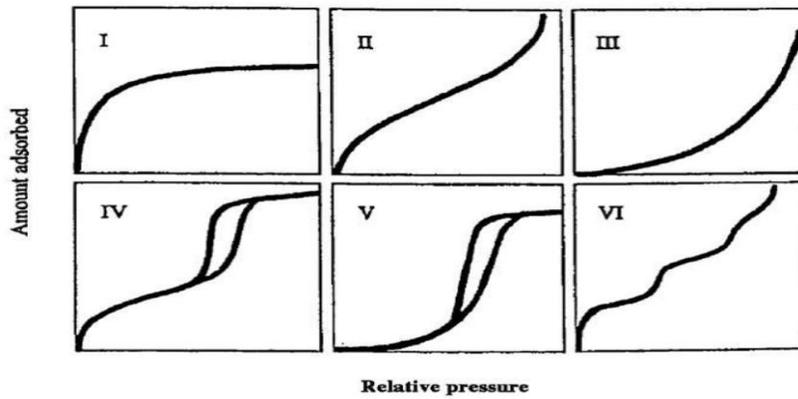


Figure 2.4 The IUPAC classification for adsorption isotherms (from Donohue, 2004).

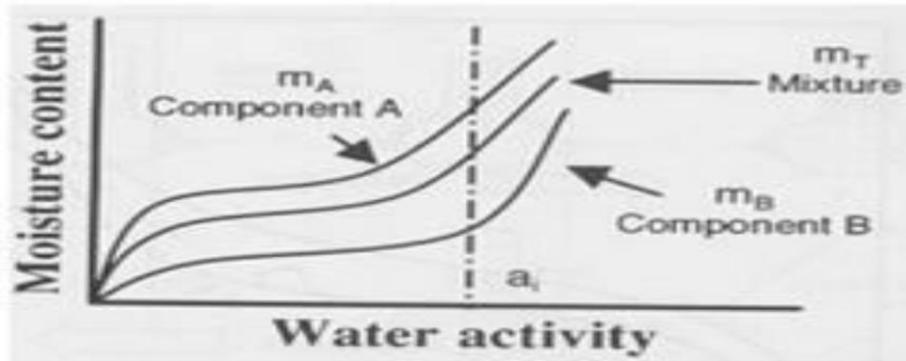


Figure 2.5 Weight average isotherms are used for multi-component food systems (from Labuza, 1984).

## 2.4 Isotherm prediction models

Isotherm prediction models are useful for establishing critical moisture content and predicting potential changes in food stability. Al-Muhtasib et al., (2002) proposed numerous models for predicting the relationship between  $m$ ,  $a_w$ , and temperature and each of these models had relative success in reproducing equilibrium moisture content, depending on the water activity range or the type of foodstuff. Rahman (2009) classified prediction models for moisture sorption isotherms into theoretical, semi-empirical, or empirical. However, before the advent of computers and the availability of nonlinear regression software, it was necessary to use two-parameter models that could be transformed into a linear equation, from which the fitting parameters could be determined. Also, due to the complex composition and structure of food, the mathematical prediction of sorption behaviour is difficult. Furthermore, since irreversible changes can occur at high temperatures, experimental measurements at these temperatures are required.

The equations usually applied for the food systems are;

### 2.4.1 BET Isotherm model

The BET isotherm model got its name from the initials of the scientist that first proposed it, that is Brunauer, Emmet and Teller in 1938. Labuza & Altunakar (2007) list BET models as one of the mathematical models with two parameters and have been found to be the most successful ways in all fields of interest to determine the monolayer moisture content of food. The BET equation gives a sigmoidal-type isotherm (particularly the types II and III.) similar to the type observed experimentally for biological materials and provides a good fit to the isotherm from 0 to  $0.5 a_w$  (Yu, 2007). However, Belarabi et al., (2000) stated that it depends on the method of data

analysis used, BET model it's not limited to the mentioned  $a_w$ . He stated that it can be used over wide range of water activity if direct non-linear regression is used without any data transformation.

Taher (2007) stated that BET theory is based on the concept of a sorbed molecule which is not free to move over the surface and which exerts no lateral surfaces on molecules sorbed on adjacent sites. He stated that when a surface is in equilibrium with a gas phase at a particular concentration, in general the number of molecules on each part of the surface will not be the same, but the net amount of surface associated with non-molecular layer, with a bimolecular layer, and so on, will be constant.

The general form of the BET equation is derived based on kinetic and statistical mechanics and also from thermodynamic considerations, which is given as;

$$M = \frac{M_o C a_w}{(1 - a_w)(1 + (C - 1)a_w)}$$

Where  $M_o$  is the monolayer moisture which content which is the moisture content at which the rate of quality loss is negligible (Labuza, 1984), and  $C$  is the energy constant related to the excess enthalpy of sorption.

#### 2.4.2 GAB Model

The Guggenheim-Anderson-de Boer (GAB) model is a semi-theoretical multi-molecular localized homogeneous adsorption model and has been considered the best fit model for many food materials over a wide range of relative humidity (Rahman, 1995). GAB model is the breakdown of the BET model at high  $a_w$  values which is considered the best-fit model for describing the full shape of a type II food moisture sorption isotherm (Rahman, 1995). Labuza and Altunakar (2007) stated that the GAB equation has been found to adequately represent experimental data in the range of 0 to 0.95  $a_w$  for most foods. The equation is given as;

$$M = \frac{M_o K C a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$$

Where  $M$  is the moisture content,  $M_o$  is the monolayer moisture content and  $K$  and  $C$  are constants. This equation can be solved by a nonlinear regression computer program or by rearranging into a polynomial form.

### 2.4.3 Smith Model

Smith (1947) developed an empirical model to describe the final curved portion of water sorption isotherm of bio-polymers with high molecular weight. He found out that there are two fractions of water that are sorbed onto a dry surface; the first fraction exhibits a higher condensation heat than the normal and it would be expected to follow the Langmuir model. Smith based his model on the second fraction, which only can be formed after the first fraction has been sorbed. He considered that the second fraction consists of multilayers of condensed water molecules, which effectively prevent any possible evaporation of the initial layer. He theorized that the moisture content in the second fraction was proportional to the logarithm of the difference between the  $a_w$  of the sample and pure water (Sahin, 2006; Da Silva et al., 2002). It has been found that this equation could be used between 0.5 to 0.95 relative humidity.

Smith equation was expressed as:

$$M = A + B \log(1 - a_w)$$

Where A and B are dimensionless constants for the material. The parameter 'A' represents moisture bound to the surface and the parameter 'B' represents the moisture in a uni-molecular layer of normally condensed moisture.

### 2.4.4 Henderson Model

Henderson (1952) has developed an empirical equation to cover the whole Isotherm by using 18 different hygroscopic products. A widely used model relating relative humidity and amount of sorbed water in food is;

$$M = \left(-\frac{\ln(1 - a_w)}{C}\right)^{1/n}$$

Where n is a constant

### 2.4.5 Halsey Model

Halsey (1948) equation is a good representation of adsorption data regarding isotherms type I, II, or III, which described the sorption behaviour of food products that contain starch (Levine & Slade, 1991). This model provides an expression for the condensation of multilayers at a relatively large distance from the surface, assuming that the potential energy of a molecule varies as the inverse nth power of its distance from the surface. It is expressed as;

$$M = M_o \left(-\frac{A}{RT \ln a_w}\right)^{1/n}$$

Where R is the universal gas constant; T is the absolute temperature.

#### 2.4.6 Oswin model

This is an empirical model developed by Oswin (1946) that consists of series expansion for sigmoid shaped curves and was used to relate the moisture content of fat free dry milk and freeze-dried tea up to a water activity of 0.5 as well as for various foods. This model can be written as;

$$M = C \left( \frac{a_w}{1 - a_w} \right)^n$$

#### 2.4.7 Modified models

The effect of temperature on the sorption isotherm is of great importance given that foods are exposed to a range of temperatures during storage and processing and water activity changes with temperature. Temperature affects the mobility of water molecules and the dynamic equilibrium between the vapour and adsorbed phases. In general, researchers have found that if the water activity is maintained constant, an increase in temperature causes a decrease in the amount of sorbed water. A lot of modification has been done by many researchers and some of the modified have been used and tested in many literatures, some of the modified models are given in table 2.1 below;

**Table 2.1** Some modified sorption isotherms predictive models.

Model Name	Equation	Eq. #	Reference
Modified GAB	$X = \frac{A(C/T)B a_w}{(1 - Ba_w)(1 - Ba_w + (C/T)B a_w)}$	1	(Van den Berg, 1984)
Modified Oswin	$X = (A + BT) \left[ \frac{a_w}{(1 - a_w)} \right]^C$	2	(Chen, 1971)
Modified BET	$X = \frac{(X_m + CT)K a_w}{(1 - a_w)(1 - a_w + K a_w)}$	3	(Brunauer, 1938; Iglesias & Chirife, 1976a,b)

Model Name	Equation	Eq. #	Reference
Modified Halsey	$X = \left[ -\frac{\exp(A + BT)}{\ln a_w} \right]^C$	4	(Iglesias & Chirife, 1982)
Modified Smith	$X = (A + B) - [(C + DT) \ln(1 - a_w)]$	5	(Smith, 1947)
Modified Chung-Pfost	$X = -\frac{1}{B} \ln \left[ -\frac{(T + C) \ln a_w}{A} \right]$	6	(Chung & Pfost, 1967a,b)

Where:

X = Dry basis moisture content  
X<sub>m</sub> = Dry basis monolayer moisture content  
a<sub>w</sub> = Water activity  
C, K, C<sub>0</sub>, K<sub>0</sub>, A, B, D = Constants  
T = Temperature, °C

## 2.5 Determination of moisture sorption isotherms

The moisture sorption isotherm of a material is obtained from the equilibrium moisture contents determined at several a<sub>w</sub> values at constant temperature. Food sorption isotherms are widely used in food processing, especially in drying, mixing, packaging, and for controlling spoilage by microorganisms (Lewicki & Pomaranska-Lazuka (2003). Many methods are available for determining vapor sorption isotherms. As knowledge about the importance of a<sub>w</sub> increased, food scientists needed a better measurement to quantify a<sub>w</sub> isotherm methods which classically used for most sample types are as stated by Rahman (2009) are; gravimetric method, colligative properties method and hygrometric method.

The accuracy of most of the methods lies in the range of 0.01–0.02 water activity units (Rizvi, 1995). The choice of one technique over another depends on the range, accuracy, cost, response time (speed), suitability, portability, simplicity, precision, maintenance and calibration requirements, and types of foods to be measured (Wiederhold, 1987; Rizvi, 1995; Rahman & Al-Belushi, 2006).

### 2.5.1 Gravimetric method

The gravimetric method involves the measurement of weight changes, which can be determined both continuously and discontinuously in dynamic (i.e. air may be circulated) or static systems (stagnant) (Al-Muhtaseb et al., 2004). Altunakar (2007) further summarized this method into two methods. The first method is based on the production of a range of samples of known moisture contents placed in a controlled humidity chambers at constant temperature. The water activity of each of these samples is recorded and the isotherm plotted from the collected data. This technique can require water activity determinations of many samples. Furthermore, the determination of desorption isotherm is almost impossible, and the method is thus considered impractical. An example of this method is the saturated salt slurry method. The second method entails exposure of a sample of known moisture content to a series of predetermined humidities. After a period of time at a particular humidity, the sample will equilibrate and the weight gain represents the water adsorbed. The humidity is successively raised to the next higher setting, and each equilibration weight is recorded. The adsorption isotherm is then plotted. The desorption isotherm is determined in a like manner except that the humidity series is reversed and is slowly dehydrated by lowering the humidity of the immediate atmosphere. This technique works well but the time to equilibration can take long time. The most common method of this is the dynamic vapour sorption method.

#### 2.5.1.1 Saturated salt slurry method

This method is an example of gravimetric static method which is the old and common method of measuring water activity of food. A saturated salt slurry is a slushy mixture composed of water and a saturated aqueous salt solution with salt crystals in a glass or plastic sealed container (Bells & Labuza 2000). In this method, a weighted sample of known mass (around 2–3 g) is stored in an enclosure and allowed to reach equilibrium with an atmosphere of known ERH (or  $a_w$ ) by the saturated salt solution, and reweighed at regular intervals until constant weight is established. The condition of equilibrium is thus determined in this manner. The moisture content of the sample is then determined, either directly or by calculation from the original moisture content and the known change in weight. A desiccator is commonly used as a chamber to generate controlled atmosphere (Figure 2.6). Fontana (2008) suggests a minimum of five different relative humidity values (i.e. choosing a series of appropriate salts) to cover the desired isotherm range since a given saturated salt slurry can provides only one relative humidity at any desired temperature. The details

of measuring water activity using this method are presented in Shafiur & Al-Belushi (2006), Lewicki & Pomaranska-Lazuka (2003), and Sablani et al. (2001). Several days, or even weeks, may be required to establish equilibrium under static air conditions, but results can be obtained for all relative humidity values simultaneously with little effort if the apparatus is replaced with different salt solutions (Smith, 1971).

An improvement to this technique came from Steinberg (1981) (Van Doore, 1985). His system used a small plastic chamber into the base of which was poured the saturated salt solution. The sample was suspended above this on a circle of filter paper. This modification drastically reduced the volume of the system, compared with the traditional desiccator, while at the same time it preserved a proven method.

The equilibrium methods outlined so far are tedious because the system comes to equilibrium mainly via molecular diffusion. An attempt was made to speed up this basic desiccator technique by the incorporation of a fan into the system. The instrument is called an isopiestic sorption apparatus. It uses a saturated salt solution in a center container to humidify the air, with a fan for circulation. This device has two major drawbacks. Firstly, the fan will always introduce a heating factor, thus possibly rendering the system thermally unstable. Secondly, to achieve rapid equilibration the sample sizes are limited to 10-100 mg.

The main advantages of this method are its simplicity, low cost, ability to handle many samples simultaneously, and easy operability (Lewicki & Pomaranska-Lazuka, 2003; Shafiur & Al-Belushi, 2006). The main disadvantages of this simple method are Slowness of the equilibrium process, which usually takes from 3 to 6 weeks and even months. Also, at high relative humidity values, the delay in equilibration can lead to mould or bacterial growth on the samples and consequent invalidation of the results. Although it is recommended to place toluene or thymol (which can be harmful if inhaled) in the chamber for slowing the microbial growth. In addition, it is always impossible to find salts, which could be used for each and every water activity ranging from 0 to 1. Using the static isopiestic method it is also difficult to measure adsorption and desorption isotherm for the same sample.

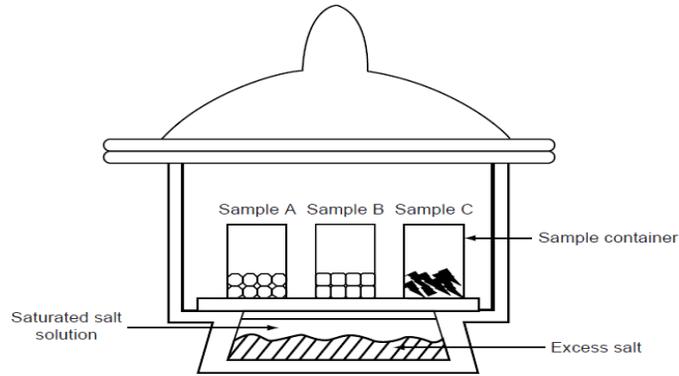


Figure 2.6 Static isopiestic method.

### 2.5.1.2 Dynamic Vapor Sorption

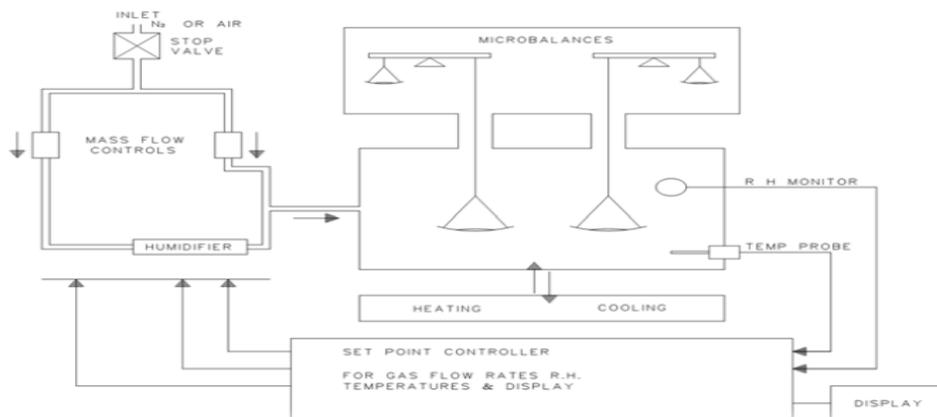
The dynamic vapor sorption (DVS) method could overcome major difficulties associated with the static gravimetric method. These instruments which are referring as humidity generating instrument have the ability to generate sorption isotherms in a relatively short period of time because they are based on a divided flow technology (Mermelstein, 2009). Most of the instrument under this category works on a principle of mass change with time which determined when equilibrium will be reached. As

Rate of change of mass with time approaches 0, the sample mass is changing less and therefore approaching equilibrium moisture content (Yu 2007). There are different types of commercial equipment based on dynamic method with automatic control and data analysis options, among which are; AQUADYNE Dynamic Vapor Sorption (DVS) 2000 (Quantachrome Instruments, 1900 Corporate Drive Boynton Beach, Florida, USA), DVS (Surface Measurement Systems, London, UK), Cisorp Water Sorption Analyzer (CI Electronics Ltd, Salisbury, UK), AquaSorp Isotherm Generator (Decagon Devices Inc., Pullman, WA), SPS Moisture Sorption Analyzers (Project Messtechnik, Ulm, Germany), and Hydrosorb™ 1000 Water Vapor Sorption Analyzer (Quantachrome Instruments, Boynton Beach, FL), IGA-Sorp (Hiden Analytical, Warrington, England), VTI and Q5000SA (TA Instruments, Delaware, USA) etc.

The Dynamic Vapor Sorption (DVS) instrument has been used by many researchers -such as; Buckton and Darcy (1995), Mackin et al., (2002), Bohn et al., (2005), Yu et al., (2008), Fikry, & Al-Awaadh (2016)- to determine moisture sorption isotherms.

AQUADYNE DVS 2000 (fig 2.8) produced by Quantachrome Instruments 1900 Corporate Drive Boynton Beach, Florida, USA is one of the latest dynamic gravimetric water sorption analyzer. Fig. 2.7 shows the symmetrical diagram of the analyzer. The instrument was specifically

designed to meet the needs of the small to mid-sized laboratories and plants and combines ease of use with a low capital investment and maintenance burden. The user selects a desired relative humidity or series of relative humidity values which are generated by mixing accurate amounts of selected dry and saturated air or nitrogen flows using sensitive mass flow controllers using a computer program. The relative humidity is automatically controlled by mass flow controllers, one for dry air and the other for water saturated air, by mixing them in the correct ratio to achieve the selected relative humidity. The system has a relative humidity sensor to verify its humidity generating performance and a temperature probe. Temperature flow and balance readings are displayed in the PC software as well as on the front panel of the AQUADYNE DVS (fig. 2.8). The sample mass reading is measured by an ultra-sensitive microbalance, which reflects the vapor sorption behavior of the sample. The microbalance can measure a mass change of up to 150 mg without the need of a counterweight with a resolution of  $\pm 0.1\mu\text{g}$ .



**Figure 2.7. Schematic diagram of the AQUADYNE DVS.**

The main advantages of the dynamic method are its ability to (1) equilibrate the sample rapidly, (2) use the same sample for the entire isotherm, (3) retain the sample in the controlled humidity chamber during the entire isotherm measurement, (4) easily measure the adsorption and desorption isotherms for the same sample, (5) use micro level sample in the order of milligrams, and (6) measure steps and oscillation mode at any increasing or decreasing water activity.

The reasons why this process gives fast equilibration (main advantage) could be due to the small sample size, the continuous circulation of gas, the surface area, and the small chamber or cell volume.

This DVS method is also defined as dynamic isopiestic method (Rahman & Al-Belushi, 2006).

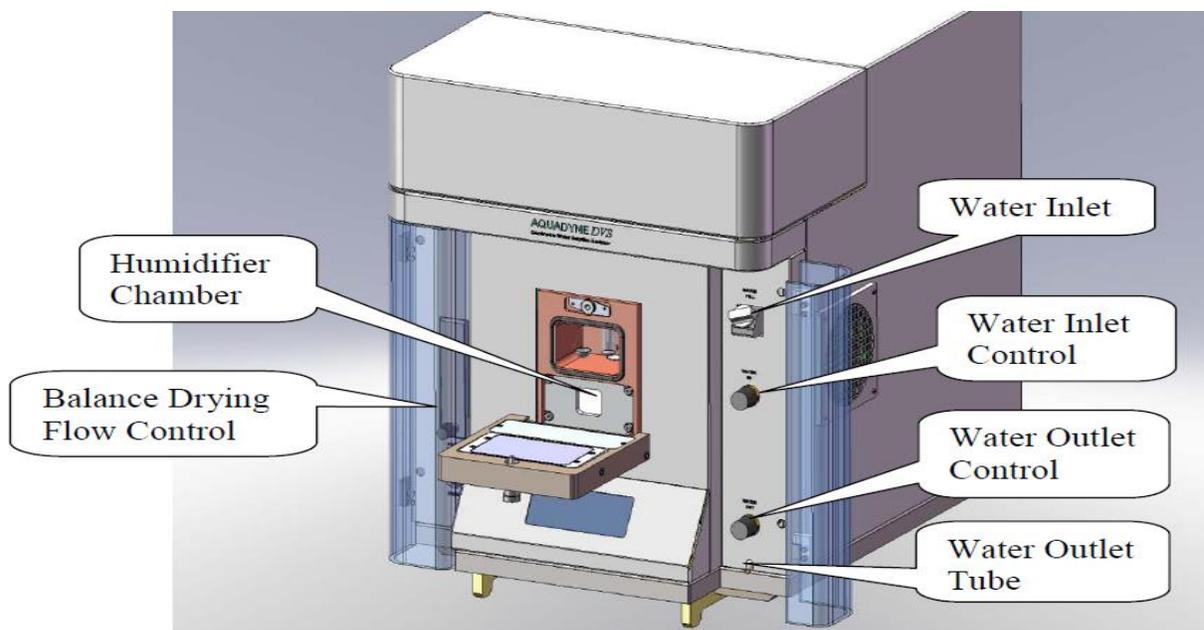


Figure 2.8. Front panel controls of AQUADYNE DVS.

### 2.5.1.3 Dynamic Dew-point Isotherms

Dynamic dew-point isotherm methods are also used to generate sorption isotherms, but unlike other previous mentioned methods, these methods do not require the sample to be at equilibrium. This method is also referred to as sorption rate technique. The sample is subjected to predetermined conditions of relative humidity at a fixed temperature, then the weight change, and in some cases the  $a_w$ , is measured before equilibrium is reached.

The Aqua-Sorp Isotherm Generator (Decagon Devices Inc., Pullman, WA) is an automated dynamic water vapor sorption instrument which uses the Dynamic Dew-point Isotherm (DDI) method for obtaining isotherms. This method does not control the %RH of the gas stream that is in contact with the sample. Instead, adsorption and desorption are accomplished by saturating the air with water and by passing the air through desiccant before both enter the sample chamber respectively. Either adsorption or desorption occurs depending on the user-selected final  $a_w$  (0.03-0.95). Both occur at a user-selected flow rate ranging from 10 to 1000 ml/min. After a small change in  $a_w$  (approximately 0.015), airflow is halted and a snapshot of the sorption process is obtained by directly measuring the sample  $a_w$  using a chilled mirror dew-point sensor and weight using a magnetic force balance, which is then converted to moisture content (Schmidt & Lee 2011).

The main advantage of this method over other method is that it generate numerous data points and are faster since they do not require the sample to equilibrate to a known humidity value.

### **2.5.2 Colligative Properties Methods**

This method involves estimation of water activity of food samples using a manometer (Rahman & Sablani, 2009). The estimation can be achieved by; (1) direct measurement of vapor pressure water in the vapour space surrounding the food; (2) estimation of the water activity at above 100°C and (3) the determination of water activity by cryoscopy or freezing point depression especially for water activity above 0.85. The details were provided by Bassal et al. (1993), Sahin, S., & Sumnu (2006) and Rahman & Sabani (2009).

### **2.5.3 Hygrometric method**

This is one of the methods used in measuring the equilibrium relative humidity of air in contact with a food material, at a given moisture content using hygrometers. Hygrometer is any instrument capable of measuring the humidity or psychometric state of air. In a hygrometer there are three zones: testing enclosure, sample environment, and sensor environment. The temperatures within the three zones need to be in equilibrium. Unless the temperature of the sample is known, the relative humidity in this region cannot be determined. Unless the temperature of the sensor is known, the relative humidity indicated the sensor cannot be converted into a reliable estimate of the vapor pressure throughout the system. Meaningful data cannot be collected when temperatures in the sample and the sensor are not carefully controlled and measured (Reid, 2001). The commonly used hygrometers are Dew-point hygrometers which detect the condensation of cooling water vapour, Electric hygrometers which measure the change in conductance or capacitance of hygrosensors and mechanical hygrometers which works based on the dimensional changes in natural or synthetic materials suitably amplified by mechanical linkage to indicate atmospheric humidity Rahman (2009). The details of measurement steps are provided in Rahman & Sablani (2009).

## **2.6 Importance of Sorption Isotherms**

Moisture sorption isotherms is of great importance to researchers especially food scientist or food related researchers. Damodaran et al., (2008) enumerates some of its importance as follows;

- i. It's useful for a variety of processing and product stability applications.
- ii. It can be used to determine water activity ( $a_w$ ) and associated moisture content that will inhibit growth of microorganisms and consequently help in increasing the shelf life of food and a safety product.
- iii. An isotherm helps in formulating food mixtures to avoid moisture transfer among ingredients and allows for ingredient selection to change the  $a_w$ .
- iv. From a processing standpoint, isotherms are useful to study and control the concentration and dehydration processes, since the ease or difficulty of removing water is related to the relative vapor pressure.
- v. Isotherms are important in packaging because it helps determine the moisture barrier properties needed in a packaging material to limit moisture gain or loss in a package

## 2.7 Moisture sorption thermodynamics

The thermodynamic properties of foods relate the concentration of water in the food to its partial pressure, which determine the end-point to which the food must be dehydrated in order to achieve a stable product with optimal moisture content, and the minimum amount of energy required to remove a given amount of water from the food (Aviara & Ajibola, 2002). Sorption isotherms are calculated from the thermodynamic functions, which are crucial in analysis of the heat and mass transport phenomena during dehydration (Rahman, 1999). The functions include differential heat of sorption, differential entropy, integral enthalpy, integral entropy and spreading pressure.

The heat of sorption of water often referred to as isosteric heat of sorption or differential heat of sorption, in high sugar foods, is valuable in modeling various food processes, food packaging, and storage stability. It provides important information on the state of water in food products (Tsami et al, 1990; Rizvi, 1995). Knowledge of the temperature dependence of sorption phenomenon provides valuable information about the changes related to energetic of the system. In designing equipment for dehydration processes, knowledge of the differential heat of sorption is important. The heat of vaporization of sorbed water may increase to, values above the heat of vaporization of pure water as food is, dehydrated to low moisture levels. The total heat of sorption in food minus the heat of vaporization of pure water at the system temperature is referred to as the net isosteric heat of sorption (Tsami et al, 1990). Several investigators determined the heat of

sorption of water in high sugar fruits such as sultana raisins, figs, prunes, apricot, apple, and dates using Clausius -Clapeyron equation (Bolin,1980; Saravacos et al., 1986; Maroulis et al., 1988; Tsami et al., 1990; Ayaranci et al.,1990; Tsami, 1991; Hamdi & Jandobi, 1994, Al-Muhtaseb et al, 2004).

Enthalpy, Entropy and Gibbs free energy are useful for explaining reactions and phenomena at the molecular level in materials. Also, the linear correlation of entropic and enthalpic mechanisms and the pore-water interaction can be used to explain the hydrophobic and hydrophilic interactions between water and other molecules (Azua & Beristain, 2006). The differential entropy of a material is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996). Differential entropy has been reported to be dependent on moisture content by many researchers. Rizvi & Benado (1983), Tolaba et al., (1997) and Al-Muhtaseb et al., (2004) reported an increase in differential entropy as the moisture content increases for grain sorghum, cereal grains and starch powders respectively.

The net integral enthalpy is an integral molar quantity which is calculated in a similar manner to the isosteric heat of sorption, but at constant spreading pressure instead of constant moisture content (Benado & Rizvi, 1985).

The thermodynamics of moisture sorption in alfalfa pellets, winged bean seed, gari and melon cassava and Starch powders have been studied by Fasina et al. (1997), Fasina et al., (1999), Aviara & Ajibola (2002), Al-Muhtaseb et al., (2004) respectively. The thermodynamic functions were determined from experimental sorption data by Aviara & Ajibola (2002). The dependence of differential and integral enthalpies and entropies of cereal grains on moisture content were determined by Tolaba et al. (1997).

Important parameters in interpretation of sorption thermodynamics data are spreading pressure, and its dependence on water activity and temperature. Babbit (1950) is one of the first authors to use this concept, where he stated that spreading pressure was the driving force responsible for diffusion in porous solids. Many researches have then been carried out on spreading pressure especially its effect on temperature and water activity. Fasina et al. (1999) reported that temperature had little effect on the spreading pressure values for gari and bean seeds in the range 40–70 °C while Aviara and Ajibola (2002), and Al-Muhtaseb et al., (2004) reported that the

spreading pressure of cassava decreased with increase in temperature and increased with increase in water activity.

## **2.8 Moisture sorption kinetics**

Understanding moisture sorption kinetics is valuable in selecting appropriate storage conditions, and evaluating moisture sorption during storage. Moisture sorption kinetics models are broadly classified into theoretical and empirical models. Theoretical models, based on Fick's law of diffusion, are generally considered as complex- involving numerous functions and parameters, hence are not convenient for practical calculations under most situations (Maskan, 2000; Igathenathane et al., 2009). Empirical moisture sorption kinetic models, such as the parallel exponential kinetic model (PEK), in addition to the Exponential, Page, and Peleg models, were successfully applied by several researchers (Maskan, 2002; Casada, 2002; Kohler et al., 2003; ASABE Standards, 2006; Igathinathane et al., 2009).

## **2.9 Moisture sorption of dates**

There is enormous potential for fresh dates and date products with better quality attributes. Date processing industries are producing various date products like date-paste, date-syrup, date-dip, date-honey, date-jam, date-vinegar, etc. therefore the needs for increasing the shelf life has been important to many researchers. Various studies have been done on dates and other food items and among is the sorption isotherms.

Robert (1998) performed studies on equilibrium moisture content of two varieties of Omani fresh dates at three temperatures (15, 25 and 45°C). The moisture sorption isotherms displayed a crossing effect due to the dissolution of crystalline sugars at higher temperatures and moisture contents. Guggenheim-Anderson and de Boer (GAB) equation were used which resulted to monolayer moisture contents ( $X_m$ ) of 13.9% for Fard and 14.4% for Khalas. Isothermic heat of sorption, for both varieties, varied from 9.4 to 1.6 kJ/mol as the moisture content changed from 5.0 to 40.0%. He stated that differences in moisture sorption behavior of the two varieties were attributed to compositional differences.

Studies on equilibrium moisture content of dates were also performed by Mayhara et al. (1998) at three different temperatures of 15, 25 and 45°C. Five-parameter GAB equation and a modified- GAB equation were used to model the sorption isotherm with the aid of a novel artificial

neural network (ANN) approach. The five-parameter GAB equation had a lower mean relative error (approximately 7%) than the modified-GAB equation (approximately 16%), in predicting equilibrium moisture content  $M$ . The effects of temperature on the water sorption isotherms were not evident with the five-parameter GAB equation but were evident with the modified GAB equation, the overall error was very high. An ANN model, optimized by trial and error, was superior to both GAB equations. It could predict  $M$  with a mean relative error of 4.31% and standard error of moisture content of 1.36 g/kg. The correlation coefficients ( $R^2$ ) of the relationships between the actual and predicted values of equilibrium moisture content and date varieties obtained by the ANN were 0.9978 and 0.9999 respectively. They stated that water activity and chemical compositional data had more impact upon the water sorption isotherms than temperature.

Alhamdan & Hassan (1999) investigated the water sorption isotherms of pastes of three date cultivars (Ruziz, Khudari, and Khlass) using the static method of saturated salt solutions at three storage temperatures: 5°C, 25°C and 40°C. They found out that the effect of temperature on sorption behavior was more pronounced than the effect of date cultivar. Equilibrium moisture content decreased with increasing temperature at water activities below 0.45-0.55. However, above 0.45-0.55, equilibrium moisture content increased with increase in temperature, mainly due to the additional dissolution of sugars at higher temperatures. The experimental data fitted well to GAB, Iglesias and Chirife, and Halsey equations, suitable for high sugar foods.

Nabil & Mohamed (2000) also studied the desorption isotherms of Tunisia Deglet Nour dates at four temperatures (30, 40, 50, 60°C). It was found that the desorption isotherms of Deglet Nour date gave the S-shaped characteristic curve, typical of many sorption isotherms of food. The GAB equation is suitable for representing the relationship between water activity and equilibrium moisture content of date in the range of water activity 0-0.9.

Belarbi et al., (2000) studied the water vapor desorption isotherms, at 25°C, of eleven date varieties from different locations, collected at full ripeness: Mech-Degla, Deglet-Nour and Haloua (Algeria), Barhi, Fardd, Khadrawi, Khalass, Madjol, Rizaiz (Saudi Arabia), Madjhoul (Palestine) and Kentichi (Tunisia). They used the static gravimetric method, according to the COST 90 recommendations. The overall shape of the curves describing the water content as function of the water activity was typical of sugar-rich materials. Experimental data were analyzed using the GAB

and the BET(Brunauer-Emmet-Teller) models, through direct nonlinear regression without any transformation of data. Both models correctly represented the whole set of data, in water activity range from 0.11 to 0.90, but the BET model was preferred since the values of its parameters were more realistic.

Houssein (2007) studied water sorption isotherms of two varieties of Libyan dates at 30°C, 40°C and 50°C, using the gravimetric method. Data were analyzed by applying the GAB, BET, Smith, Iglesias & Chirife, Halsey, Henderson and Oswin Models and It was found that the experimental data fitted well to, Smith, Iglesias and Chirife, Halsey, Hendreson and Oswin equations, which are suitable for high sugar foods. Isotheric heat of sorption value was also calculated using the Clausius- Clapeyron Equation and the result obtained varied from 0.9 to – 1.84 KJ/mol as moisture content changed from 11.0 to 18.0 %. In BET model, the constant C, which is related to the heat of sorption, was negative which is physically impossible.

Fikry, & Al-Awaadh (2016) studied the sorption isotherms for powder rich in fiber from Sifri Date cultivar at temperatures 25, 35 and 45 °C in a range of 0.09 –0.87 water activity. The obtained data were fitted to Peleg, GAB, BET, Halsey, Oswin, Smith, Modified Henderson, Adam and Shove, Modified Oswin and Modified Halsey models. The results indicated that Peleg model was found to be the best fitting model. The isotheric heat of sorption and the differential entropy decreased as the moisture content increases which can be predicted by polynomial functions. Glass transition temperatures ( $T_g$ ) decreased as the moisture content increased.

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## CHAPTER THREE: Physical Properties and Moisture Sorption Thermodynamics of Sukkari Date Powder

### ABSTRACT

Some related physical properties of date powder produced from Sukkari cultivar from Saudi Arabia were determined at different particle sizes. Bulk density, tapped density, compressibility index, and Hausner ratio increases as the particle sizes reduces but reduces for very fine particle size with ranges from 623.68 – 634.97 kg/m<sup>3</sup>, 831.93 -901.77 kg/m<sup>3</sup>, 24.15 to 30.12 and 1.32-1.43 respectively. Moisture content ranges from 2.97 to 3.41% d.b which increases as the particle sizes reduce. Water activity also increases as the particle sizes reduce except for very fine sizes which reduces with ranges from 0.16-0.18. Electrical conductivity reduces as the particle sizes decreases with a range from 2.90-3.13mS. pH, show no significant difference for the different particle sizes and it ranges from 5.60-5.64 which means the powder can be classified as low-acid products. For color analysis, lightness (L\*), a\* (greenness – redness), b\* (blueness–yellowness), chroma (C\*) hue angle (H°), Browning index (BI) and total color (E) increases as the particle sizes reduces and it ranges from 64.56-69.26, 4.51-5.44, 24.44 -27.09, 24.96-27.45, 78.30-80.55 52.29-55.95 and 69.22-74.51 respectively. Water Absorption Index sizes ranges from 0.81-1.74g/g dry matter increases as the particle sizes reduces with slight significant differences while Waster solubility index and oil holding capacity also increases as the particles sizes reduces but with no significant differences with ranges from 6.77-7.20 and 0.31-0.78 g/g of dry matter respectively.

Adsorption isotherm of the date powder were also determined within the range of 0.1 to 0.9(±0.4) water activity at three different temperatures (20, 40 and 60°C±0.2), using the standard dynamic gravimetric method. A curve of type III shape with a more or less sigmoid shape was observed. As water activity increases, the moisture adsorption was found to increase especially at high water activity. The effect of temperature result to that as equilibrium moisture content (EMC) increases, the temperature increases at constant low water activity, but from around 0.70 water activity, an increasing EMC as the temperature reduces was observed. The data obtained were fitted to Modified Bet, Modified Oswin, Modified Gab, Modified Halsey, Modified Henderson, Modified Smith and Modified Chungpost models. The first four mentioned models fit well to the experimental data throughout the entire range of water activity at the three-temperature ranges

studied. However, Modified Bet model was found to be the best model with Percentage Error of 6.30%,  $R^2$  of 0.997, SSE of 0.005 and RMSE of 0.014 and it was used for the thermodynamics analysis.

Net Isosteric heat of adsorption was found to decreased with an increase in moisture content and becoming stabilized at moisture content greater than 0.3 kg/kg d.b. The maximum value was obtained at a low EMC of 0.05 kg/kg d.b with a value of 1.46 kJ/mol to a minimum value of 0.38 kJ/mol at EMC of 0.6 kg/kg d.b. Heat of sorption (differential enthalpy) and differential entropy showed a similar trend to net isosteric heat of sorption. A linear relationship was observed for the plot of enthalpy and entropy which indicates that compensation theory could be applied within the studied range of moisture contents. Also, Isokinetic temperature ( $T_B$ ) and harmonic mean temperature ( $T_{hm}$ ) of sorption, was found to be 290.67 K and 312.1 K ( $T_{hm}$ ) which thereby confirming the suitability of the theory because  $T_B$  is significantly different from  $T_{hm}$ , and since  $T_B < T_{hm}$ , therefore, the process can be characterized as entropy driven. Monolayer moisture content was found to decrease as the temperature increase. An increase in temperature causes a reduction of spreading pressure but not very significant. The spreading pressure also increases with increasing water activity but with a slow increment of less than 0.5 $a_w$ . Net integral enthalpy was found to decrease with increase in moisture content from a value of 689.45 kJ/mol at moisture content of 0.25 kg/kg d.b. to 113.40 kJ/mol at 0.5 kg/kg d.b. While Net integral entropy was also found to decreased with increase in moisture content from a maximum value of 7.05 kJ/mol K at moisture content 0.025 (kg/kg d.b) to a minimum value of 0.999 kJ/mol K at the moisture content of 0.57 (kg/kg d.b.) but the reduction was very slow and becoming constant at higher water activity.

Keywords: Date Powder, Physical Properties, Sorption Isotherms, Modified Sorption Models, Sorption Thermodynamics.

### 3.1 Introduction

Date palm (*Phoenix dactylifera* L.) is the most successful and commercially important crop in the hot-arid regions of the world (Mahmoudi et al., 2008). The Fruits contain carbohydrates (about 60%), most of which are in the form of sugars; they also contain significant amounts of dietary fiber, vitamins, carotenoids, anthocyanins, phenolics, and antioxidants (Al-Farsi and Lee

2012). Dates fruits are an excellent material for replacing added sugar, producing liquid sugars, concentrated juice, confectionery pastes and fermentation products (Manickavasagan, et al., 2015).

Date fruits are harvested seasonally in abundance throughout the year in all parts of the world, thereby increasing the economy of a country. They are fruits with high moisture content and short shelf life, therefore in order to meet the market demand, there is needs for good preservation methods. One of the most preferable preservation means for fruits is drying and processing it into powder form. Production of free-flow powder from dates is highly desirable since it not only possesses long shelf life but also could improve handling, storage, and blendability with several products, including baked products in commercial manufacturing. Many foods and pharmaceutical industries prefer free-flow powders because it serves as natural and easy doseable components in their products (Goula and Adamopoulos, 2010). The flow properties of powders are important in handling and processing operations, which are determined by a combination of physical powder characteristics, e.g., moisture content, densities, particle size, size distribution, shape and surface properties, as these conditions dictate the behaviour of the powder during transportation by means of a hopper orifice, or during pile formation or through the die of a tablet compression machine (Sinka *et al.* 2004). Production of granular or powder materials usually result to variety of different physical properties, which thereby necessitate the measurement of these physical properties because they help to define the powder and intrinsically affect its (powder) behaviour during storage, handling and processing. The powders' flowability and flow behaviour under pressure, humidity and temperature are important in processing and handling operations, such as storage, transportation, compression and packaging (Knowlton, Carson, Klinzing & Yang, 1994). There have been a lot of researches on physical properties of food powders

With regard to handling of powders, particle size is one of the most important physical parameters, which can influence flow out of storage bins, compaction, the blending of different components and the segregation of a mixture which result to larger particles on top and smaller particles being at the bottom. Also, properties such as texture and appearance are influenced significantly by particle sizes. During drying process, particle surface area increases as the particle size decreases, thereby increasing the ability to agglomerate and higher affinity with moisture (Banu et al., 2012). Singh et al., (2013) reported a significant effect of particle size on hydration properties of corn bran which increases as the particle sizes reduces.

Bulk and tapped density are important parameters during storage, processing, packaging, and distribution conditions. The volumes of the solid and liquid materials and all pores are the bulk density which is used generally to define a final product obtained as a result of drying (Kurozawa et al. 2009). While the tapped density is an increased bulk density attained after mechanically tapping a container containing the powder sample; it is a measure of random dense packing (Sawant et al., 2013). Hausner ratio is an important bulk density related property which is the ratio of the tap bulk density to the loose bulk density. This property is important because it deals with properties relevant to moving, rather than static, powder. Using this ratio, powders can be grouped into two group i.e. Powders with Hausner ratios smaller than 1.25 (easily Fluidized), and powders with Hausner ratios greater than 1.4 (difficulty fluidized) (Fikry, 2016).

Color is one of the most important appearance characteristic due to its direct effect on consumers' preference and acceptability for food material. Certain defects or anomalies that may be present in food items can be detected through the color observation (Abdullah et al., 2004; Hatcher et al., 2004; Du & Sun 2004, Pedreschi et al., 2000). Color determination can be carried out by visual (human) inspection or by using a color measuring instrument. Color measuring instrument are recommended because of various advantages it has over human inspection. The colors of foods are usually measured in  $L^*a^*b^*$  units by either using an equipment called colorimeter or image processing and specific data acquisition systems (Trussel et al, 2005). The lightness ( $L^*$ ) is an indication of the brightness of the powder sample which ranges from 0 to 100. Parameters  $a^*$  (from green to red) and  $b^*$  (from blue to yellow) are the two chromatic components, which range from  $-120$  to  $120$  (Papadakis et al., 2000; Segnini et al., 1999, Yam & Papadakis 2004). Chroma ( $C^*$ ), hue angle ( $H^\circ$ ), browning index (BI) and total color (E) are important parameters that can be determined through the  $L^*a^*b^*$  system. The chroma ( $C^*$ ) values is proportional to strength of the color and indicates the degree of saturation of color (Akoy, 2014). The hue angle ( $H^\circ$ ) refers to the qualitative attribute of color, according to which colors have been defined as greenish, reddish, etc (Akoy, 2014). Browning index (BI) indicates the purity of brown color, which is reported to be an important parameter during enzymatic and non-enzymatic browning processes (Akoy, 2014). The total color (E) represents the total difference in respect to white standard where higher values represent a darker sample (Saricoban & Yilmaz, 2010). Fikry, (2016) reported that the colors of food powders are affected by the different variables, where he analyzed for the Date powder rich in fiber.

The water absorption index (WAI) and Waster solubility index (WSI) measures the volume occupied by powder sample after swelling in excess water, which maintains it's in aqueous dispersion. It describes the rate and extent to which the component of powder material or particles dissolves in water. Oil absorption capacity (OAC) similar to WAI but it's the measure of volume occupied by powder sample after swelling in excess oil. OAC is an important parameter in structure interaction in food such as flavor retention, improvement of palatability and shelf life extension (Nguyen et al., 2017). Sawant et al., (2013) stated that WAI is mainly influenced by the affinity of powder particles because a greater gel matrix with water will be trapped for finer particles. These properties have been widely studied for food functionality because of the importance of water in food.

Moisture sorption characteristics are fundamental property of a biomaterial which influences dehydration, storage stability and shelf life predictions (Ajisegiri et al., 2007). These characteristics which are predicted by some models, is the relationship between water activity ( $a_w$ ) and moisture content at a given temperature. The control of water content and  $a_w$  are needed for food product (such as Dates), subjected to transportation and storage before marketing for the biochemical and microbial stabilities.

The capacity of a powder when placed in atmospheres at different relative humidities and at a specified temperature to uptake or release water is illustrated in what is referred to as water sorption isotherm (Medeiros, 2006). The flowability and caking properties of powder is significantly affected by the presence of water. In general, as the water content of a powder increases, the cohesiveness of the powder increases and the more difficult it is to flow (Medeiros, 2006). In addition, there exists a value of relative humidity -called critical relative humidity- at a given temperature above which the powder (many food powders) will cake, and this is usually very detrimental to powder flowability (Teunoe et al., 1999).

Water sorption isotherms are useful in predicting the interaction of the solid with the water vapour in the atmosphere, during storage and after packaging. Types of packaging used must also be considered. They are also an important tool for understanding the behaviour of water during heat processing, such as drying (Rahman et al, 1997).

For these and many other reasons, many researches have been carried out on dates and their products, but most of these researches that are related to moisture sorption isotherms are carried out on dates' flesh, pastes or syrup. Fikry & Al-Awaadh (2016) reported the moisture sorption

isotherm of date powder rich in fibre. However, Mathlouthi; Rogé, (2003) stated that depending on the nature of food powder (crystalline or amorphous), the isotherms shape will be different. Carlos et al., (2005) confirmed that degrees of sugar crystallization were correlated with the sorption characteristics. This means that the relationship is complex and unique at different moisture contents for each product due to different interactions such as colligative, capillary, and surface effects between water and solid components (Gokhan, *et al.*, 2012; Carter & Fotana, 2008; Shafiur & Al-Belushi, 2006).

The concentration of water in food to its partial pressure is related to its thermodynamic properties, which determine the amount of water to be removed from the food in order to achieve a stable product with optimal moisture content, and the minimum amount of energy required to remove a given amount of water from the food (Aviara & Ajibola, 2002). Sorption isotherms are calculated from the thermodynamic functions, which are crucial in analysis of the heat and mass transport phenomena during dehydration (Rahman, 1999). The functions include heat of sorption, differential entropy, enthalpy-entropy compensation, spreading pressure, integral enthalpy and integral entropy.

The heat of sorption of water (usually known as isosteric or differential heat of sorption) in high sugar foods, is valuable in modeling various food processes, food packaging, and storage stability and provides crucial information on the state of water in food products (Tsami et al, 1990; Rizvi, 1995). Information on the temperature dependence of sorption phenomenon provides valuable information about the changes related to energetic of the system and also aid in the design of equipment for dehydration processes. The net isosteric heat of sorption is referred to as subtraction of heat of vaporization of pure water from total heat of sorption in food at temperature of the system (Tsami et al., 1990). As moisture content of food is reduced during dehydration, there might be an increase in heat of vaporization of sorbed water to a value above the heat of vaporization of pure water (Tsami et al., 1990). Several investigators determined the heat of sorption of water in high sugar fruits such as sultana raisins, figs, prunes, apricot, apple, and dates using Clausius -Clapeyron equation (Bolin,1980; Saravacos et al., 1986; Maroulis et al., 1988; Tsami et al., 1990; Ayaranci et al.,1990; Tsami, 1991; Hamdi and Jandobi, 1994, Al-Muhtaseb et al., 2004). Enthalpy, Entropy and Gibbs free energy are important parameters for explaining phenomena and reactions at the molecular level in materials. Also, the enthalpy-entropy compensation theory which is a linear correlation can be used to explain the hydrophobic and

hydrophilic interactions between water and other molecules (Azulara & Beristain, 2006). Differential entropy has been reported to be dependent on moisture content by many researchers and is proportional to the number of sorption sites available at a specific energy level (Madamba, Driscoll, & Buckle, 1996). Rizvi & Benado (1983), Tolaba et al (1997) and Al-Muhtaseb et al., (2004) reported an increase in differential entropy as the moisture content increases for grain sorghum, cereal grains and starch powders respectively. The net integral enthalpy is an integral molar quantity which is calculated in a similar manner to the isosteric heat of sorption, but at constant spreading pressure in place of moisture content (Benado & Rizvi, 1985). The thermodynamics sorption in alfalfa pellets, winged bean seed, gari and melon cassava and Starch powders have been studied by Fasina et al. (1997), Fasina et al. (1999), Aviara & Ajibola (2002), Al-Muhtaseb et al., (2004) respectively. The dependence of differential and integral enthalpies and entropies of cereal grains on moisture content were determined by Tolaba et al. (1997).

Important parameters in interpretation of sorption thermodynamics data are spreading pressure, and its dependence on water activity and temperature. Babbit (1950) is one of the first authors to use this concept, where he stated that spreading pressure was the driving force responsible for diffusion in porous solids. Many researches have then been carried out on spreading pressure especially its effect on temperature and water activity. Fasina et al. (1999) reported that temperature (40–70°C) had little effect on the values spreading pressure for gari and bean seeds while Aviara & Ajibola (2002), and Al-Muhtaseb et al., (2004) reported that the spreading pressure of cassava decreased with increase in temperature and increased with increase in water activity.

Therefore, experimental determination of physical properties and moisture sorption characteristics and thermodynamics of date powder is needed to predict the fundamental behavior of the product during handling, processing, packaging and storage.

## **3.2 Materials and methods**

### **3.2.1 Powder preparation**

Sukkari date cultivar was purchased from a local date factory, in Riyadh, Saudi Arabia. It was sorted, washed, and dried at room temperature. The Fruits was sliced to remove the seeds, then cut into small pieces and dried in a vacuum drying oven at  $60\pm 1^\circ\text{C}$  until attaining constant weight. The dried Sukkari flesh pieces were then grinded in a grinding machine to produce date

powder. The obtained date powder was sifted with a mechanical sifter to obtain homogenized particles of various groups and was further vacuum dried at  $60\pm 1^\circ\text{C}$  to produce bone dried Sukkari date powder. The bone-dried powder was immediately transferred into tightly closed glass jars to avoid any moisture gain from the surrounding air, and stored at  $5\pm 1^\circ\text{C}$  for further analysis.

## 3.2.2 Properties of the powder

### 3.2.2.1 Particle size distribution:

Particle size distribution (PSD) was carried out using a vibratory sieve shaker (Analysette 3 spartan model, Fritsch, Germany) with a series of nine sieves to determine the weighted mean diameter of particles as well as size distributions. The sieve sizes were 2, 1, 500, 355, 250, 180, 125, 90, 63  $\mu\text{m}$  mesh, and a pan. A known amount of powder was fed on top sieve and operated for 5 min and the weight of samples retained on each sieve was recorded. This procedure was repeated thrice and the average was recorded.

Particle size distributions of the powder were determined using a set of US standard sieves as stated by Fikry, (2016). The distributions are; coarse  $>355 \mu\text{m}$ , moderately fine (180–355  $\mu\text{m}$ ), fine (125–180  $\mu\text{m}$ ) and very fine ( $\leq 125\mu\text{m}$ ).

### 3.2.2.2 Moisture content

Moisture content (wet basis) was measured using moisture analyser. The moisture content was determined on each of the distribution of the powder and it was carried out in triplicate.

### 3.2.2.3 Bulk and tapped density

Bulk and tapped density of each of the classes of the powder were measured using a tapped density tester (Atlas AT-2000, UK) on the standard of American Society for Testing and Materials (ASTM). The test was triplicated for each sample.

### 3.2.2.4 Flowability and cohesiveness:

Flowability and cohesiveness of the powder were evaluated in term of Compressibility index (CI %). And Hausner ratio (HR) respectively. Both CI and HR were evaluated from the bulk and tapped densities of the powder using equations 1 and 2, respectively:

$$\text{Hausner Ratio, } HR = \frac{\text{Tapped density}}{\text{Bulk density}} \quad (1)$$

$$\text{Compressibility Index (\%), } CI = \frac{\text{Tapped density} - \text{Bulk density}}{\text{Tapped density}} \times 100 \quad (2)$$

### 3.2.2.5 Color evaluation

Surface colour of the samples were evaluated by measuring the L\*, a\* and b\* values (L is the degree of lightness which ranges from 0 (black) to 100(white), +a, -a, +b and -b are redness, greenness, yellowness and blueness respectively), by using Colorflex (Hunter Lab-Color Flex, Hunter Associates Laboratory, Inc-Reston, US). A white tile standard (L=96.33; a=+0.09; b=+1.98) was used as reference (standard) color. The color was evaluated using Chroma, hue angle, browning index and total color using equations below respectively (Palou et al, 1999; Akoy, 2014). The test was carried out for each sample and was done at three replicates.

$$\text{chroma} = \sqrt{a^{*2} + b^{*2}} \quad (3)$$

$$\text{hue angle} = \arctan(b^*/a^*) \quad (4)$$

$$BI = \frac{[100(x-0.31)]}{0.17} \quad (5)$$

Where

$$x = \frac{(a^* + 1.75L^*)}{(5.645L^* + a^* - 3.01b^*)} \quad (6)$$

$$E = \sqrt{L^{*2} + a^{*2} + b^{*2}} \quad (7)$$

### 3.2.2.6 Water absorption and solubility indices

Water Absorption Index (WAI) and Water Solubility Index (WSI) were determined as described by Semasaka et al., (2010) but with slight modification. 1g of each sample powder was suspended in 10mL of distilled water in a tared 50mL centrifuge tube and stirred with vortex, then left for 30 min at 20°C, followed by centrifugation 3,000 RPM for 15 min. The supernatants were then poured into a dry evaporator dishes of known weight and stored overnight at 120°C for the process of evaporation. WAI was determined from the weight of the remaining gel and expressed as grams of gel per gram of solid while WSI was calculated as grams of dry solid recovered after evaporating to the gram of original solid.

### 3.2.2.7 Swelling capacity (SC)

The SC is the volume occupied by a known weight of powder. 0.2 g of each sample was mixed with 10 ml distilled water and allowing it to hydrate for 18 h at 25°C. Then, the final volume attained by the sample was measured and SC was evaluated (Borchani et al., 2011).

### **3.2.2.8 Oil absorption capacity (OAC)**

OHC of the sample was measured by adding a 100 mg of sample to 10 ml of corn oil in a 50 ml centrifuge tube. The content was then stirred for 30 s every 5 min and after 30 min to disperse the sample in the oil, the tubes were centrifuged at 1500 g for 30 min. The free oil was then gently decanted and absorbed oil was then calculated by the difference. The OAC was expressed as grams of oil bound per gram of the sample on dry basis (Carine et al., 2010).

### **3.2.3 Water sorption isotherm**

The powders selected are 355-180 $\mu$ m (moderately fine), as handling and processing of the fine particles is a generic industrial problem due to its poor flowability as a result of the cohesion force from van der Waals attraction (Yang et al., 2005). The adsorption of moisture at different relative humidity (10–90%, applied in steps of 10%) and temperatures (20,40, and 60°C) was measured using a fully automated gravimetric dynamic vapor sorption (DVS) instrument (Aquadyne DVS, Quantachrome Instruments, Boynton Beach, FL, USA). Its two ultrasensitive microbalances can detect changes in mass during the adsorption process. The relative humidity is controlled by mixing dry and saturated (distilled water) nitrogen flows in the desired ratio using mass flow controllers and a calibrated humidity probe, this is achieved automatically by the equipment. Dry microcrystalline cellulose (CRM #302) powder was used for instrument calibration. In the experiment, pre-dried Sukkari date powder samples ( $54\pm 1$  mg each) was placed in the two ultrasensitive microbalances, which was bone dried (purging). Mass, temperature, and humidity data was recorded at 30 s time intervals. Equilibrium will be considered as have been reached when the change in mass is less than 0.001 mg/min and or 10080 hr (7 days). Each pair of samples in the two microbalances represents a replicate measurement. Two experiments (4 replicates) will be performed for each experimental condition. Hence the total numbers of experimental runs are: 3T (temperature) X 9 RH (relative humidity) X 2 experimental replicates = 54 experiments.

### **3.2.4 Sorption isotherm modeling**

Several sorption models used for high sugar fruits, as listed in Table 3 below, were tested for statistical adequacy in fitting the experimental dynamic vapor sorption data of Sukkari date

powder at different temperatures. Direct non-linear regression without data transformation was used for the analysis (Belarabi et al., 2000)

**Table 0.1 Sorption isotherms predictive models**

Model Name	Equation	Eq. #	Reference
Modified GAB	$X = \frac{A(C/T)B a_w}{(1 - Ba_w)(1 - Ba_w + (C/T)B a_w)}$	8	(Van den Berg, 1984)
Modified Oswin	$X = (A + BT) \left[ \frac{a_w}{(1 - a_w)} \right]^C$	9	(Chen, 1971)
Modified BET	$X = \frac{(X_m + CT)K a_w}{(1 - a_w)(1 - a_w + K a_w)}$	10	(Brunauer, 1938; Iglesias and Chirife, 1976a,b)
Modified Halsey	$X = \left[ -\frac{\exp(A + BT)}{\ln a_w} \right]^C$	11	(Iglesias and Chirife, 1982)
Modified Smith	$X = (A + B) - [(C + DT) \ln(1 - a_w)]$	12	(Smith, 1947)
Modified Chung-Pfost	$X = -\frac{1}{B} \ln \left[ -\frac{(T + C) \ln a_w}{A} \right]$	13	(Chung and Pfost, 1967a,b)

Where:

X = Dry basis moisture content (kg/kg d.b)  
 $X_m$  = Dry basis monolayer moisture content ((kg/kg d.b))  
 $a_w$  = Water activity  
C, K,  $C_0$ ,  $K_0$ , A, B, D = Constants  
T = Temperature, °C

### 3.2.5 Determination of Sorption Thermodynamic parameters

#### 3.2.5.1 Isosteric heat of sorption

The effect of temperature (T) on water activity ( $a_w$ ) at a constant moisture content (X) can be described by the Clausius-Claperon equation based on thermodynamic principles (Simal et al., 2007; Yu et al., 2008):

$$\left. \frac{\partial \ln a_w}{\partial (T)} \right|_X = \frac{Q_{st}^n}{RT^2} \quad (14)$$

Where  $Q_{st}^n$  is the net isosteric heat of sorption in ( $\text{kJ mol}^{-1}$ ), T is absolute temperature in (K), and R is the universal gas constant ( $8.314 \text{ J mole}^{-1} \text{ K}^{-1}$ ).

The relationship between the isosteric heat of sorption ( $Q_{st}$ ,  $\text{kJ mol}^{-1}$ ) which is the excess binding energy for removal of the water, and the net isosteric heat of sorption  $Q_{st}^n$  ( $\text{kJ mol}^{-1}$ ) and the latent heat of vaporization of pure water  $L_w$  ( $\text{kJ mol}^{-1}$ ) can be represented by the following equation:

$$Q_{st} = Q_{st}^n + L_w \quad (15)$$

Integrating equation (14) and assuming that the net isosteric heat of sorption  $Q_{st}^n$  is independent of temperature, gives the following equation;

$$\ln a_w|_x = -\frac{Q_{st}^n}{RT} + \text{constant} \quad (16)$$

Values of water activity ( $a_w$ ) were determined at the three temperatures of 20,40 and 60 °C and seven moisture levels in the range of 5–50%. By plotting  $\ln(a_w)$  vs.  $1/T$  in ( $\text{K}^{-1}$ ) at constant moisture content, the net isosteric heat of sorption  $Q_{st}^n$  can be calculated from the slope  $\frac{-Q_{st}^n}{R}$ , then the heat of sorption,  $Q_{st}$  (also known as differential enthalpy) is obtained from equation (15). The latent heat of vaporization of pure water  $L_w$  at 40°C was utilized for subsequent analysis; this represents the average temperature within the investigative range 20–60°C (Hasan & Nurhan 2007). To determine the dependence of  $Q_{st}$  on the equilibrium moisture content, the procedure was repeated for many values of equilibrium moisture content. This method requires sorption data at least three temperatures (Bahloul et al., 2008, Kaymak & Gedik 2004). And it assumes that isosteric heat of sorption does not change with temperature.

### 3.2.5.2 Differential Entropy

The differential entropy can be determined from equation (17) below;

$$-\ln a_w |_x = \frac{Q_{st}}{RT} - \frac{S_d}{R} \quad (17)$$

Where  $S_d$  is the differential entropy in ( $\text{J mol}^{-1} \text{K}^{-1}$ ).

Similar to net isosteric heat of sorption, by plotting  $\ln(a_w)$  vs.  $1/T$  in ( $\text{K}^{-1}$ ) at constant moisture content, the differential entropy  $S_d$  can be calculated from the intercept  $\frac{S_d}{R}$ , in eq. (17).

### 3.2.5.3 Enthalpy-Entropy Compensation Theory

Based on the compensation theory a linear relationship between enthalpy and entropy for a specific reaction can be, written as (Simal et al., 2007):

$$Q_{st}^n = T_\beta S_d + \Delta G_\beta \quad (18)$$

Where  $T_\beta$  is the isokinetic temperature at which all reactions in the series proceed at the same rate, and the free energy  $\Delta G_\beta$  at  $T_\beta$  provides a criterion to determine if water sorption is spontaneous ( $-\Delta G_\beta$ ) or non-spontaneous process ( $+\Delta G_\beta$ ), (Simal et al., 2007).

A parameter called harmonic mean temperature ( $T_{hm}$ ) has been used to check for validity of compensation theory. Enthalpy–entropy compensation requires that  $T_\beta \neq T_{hm}$ . The process is considered enthalpy driven if  $T_\beta > T_{hm}$ , while it is considered to be entropy driven if the opposite condition is observed (Leffer & Grunwald, 1963). The harmonic mean temperature can be obtained as follows:

$$T_{hm} = \left( \frac{n}{\sum_{i=1}^n (1/T)} \right) \quad (19)$$

Where  $n$  is the number of isotherms.

The net isosteric heat of sorption ( $Q_{st}^n$ ) decreases considerably when the moisture content is increased. Tsami et al., (1990) proposed the following empirical exponential correlation to describe the relationship between  $Q_{st}^n$  and moisture content  $X$ :

$$Q_{st}^n = Q_0 \exp\left(-\frac{X}{X_0}\right) \quad (20)$$

Where  $Q_0$  is the net isosteric heat of sorption of the first molecules of water in the food ( $\text{kJ mol}^{-1}$ ) and  $X$  is the equilibrium moisture content on dry basis, and  $X_0$  is the characteristic moisture

content of the food material on dry basis. It provides important information on both the physicochemical interactions of water with major food constituents and the state of water within the food system, and it is an invaluable parameter, for estimation of the energy requirements during drying (Al-Muhtaseb et al., 2002).

### 3.2.5.4 Spreading Pressure

The spreading pressure ( $\Phi$ ) is the force in the plane of a surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading (Hua et al., 2016). The spreading pressure can be obtained from the following relationship (McMinn et al., 2005):

$$\Phi = \frac{KT}{A_m} \int_0^{a_w} \frac{\theta}{a_w} d(a_w) \quad (21)$$

where  $\theta = \frac{M}{M_0}$ ,  $K$  is the Boltzmann constant=  $1.38E-23$ (J/K);  $A_m$  is the surface area of a water molecule= $1.06E-19$  ( $m^2$ ); and  $M$  is the moisture content, (kg/kg d.b) and  $M_0$  is the monolayer moisture content.

The monolayer moisture content  $M_0$  is an important parameter that has to be determined in order to obtain the spreading pressure. It can be obtained by applying the Brunauer, Emmett and Teller (BET) equation (Brunauer et al., 1940) to the experimental data on equilibrium moisture relationships of the Sukkari date powder. The BET equation is stated as;

$$\frac{a_w}{(1-a_w)M} \approx \frac{1}{M_0 C_2} + \frac{(C_2-1)a_w}{M_0 C_2} \quad (22)$$

Where  $C_2$  is a constant.

Plotting  $\frac{a_w}{(1-a_w)M}$  versus  $a_w$  at the three temperatures, should yield a straight line with slope and intercept from which  $M_0$  can be calculated.

The spreading pressure of moisture in date powder at different temperatures was then calculated using Eq. 21. However, the spreading pressure will be undetermined at  $a_w = 0$  (Using Eq. 21). Therefore, the lower limit was taken as  $a_w = 0.05$ , then the interval between  $a_w = 0.05$  and  $0.0$  was obtained by assuming a linear relationship known as Henry's law (eq. 23) between  $M$  and  $a_w$  (Fasina et al., 1999).

Therefore, for the water activity range of 0-0.05, eq. (21) becomes;

$$\Phi = \frac{KT}{A_m} \theta \quad (23)$$

To determine the effect of temperature, spreading pressure was plotted against water activity at various temperatures.

### 3.2.5.5 Net Integral Enthalpy and Entropy.

Net integral enthalpy is analogous to isosteric heat of adsorption. It is a measure of the food–water affinity which indicates the binding strength of water molecules to food particles. It is estimated in a similar way as differential heat of sorption but at constant spreading pressure rather than at constant moisture content.

These properties were carried out to estimate the properties at the maximum and minimum temperature levels in the study (Villa-Vélez et al., 2012; Cano-Higueta et al., 2015). The change in net integral enthalpy with moisture content has been derived from the first law of thermodynamics as given by Fasina et al., (1999):

$$\left. \frac{\partial \ln a_w}{\partial (1/T)} \right|_{\Phi} = - \frac{Q_{in}}{R} \quad (24)$$

Where,  $Q_{in}$  is the net integral enthalpy in J/mol;  $R$  is the gas constant of water vapour in J/mol K;  $T$  is the absolute temperature in K; and  $\Phi$  is the surface potential (spreading pressure) in J/m<sup>2</sup>.

By plotting  $\ln(a_w)$  against  $1/T$  at constant spreading pressure, the integral enthalpy was obtained from the slope of the straight line. Net integral enthalpy was then plotted against moisture content.

When values for  $Q_{in}$  are obtained, the changes in the molar integral entropy can be calculated from;

$$S_{in} = \frac{-Q_{in} - R \ln(a_w)}{T} \quad (25)$$

where  $S_{in}$  is the integral entropy of water adsorbed in the food (J/mol K) (Majd et al., 2012).

An indicator for the characteristics of the reaction of water sorption in the system known as free energy for water adsorption ( $\Delta G$ , kJ/mol), can be calculated by Gibbs equation (Eq. 26) (Rizvi, 2005):

$$G = -RT \ln(a_w) \quad (26)$$

## 3.3 Statistical Analysis

Data was analyzed using Excel and MATLAB. The goodness of fit of each model for the experimental data was evaluated by determining the coefficient of determination ( $R^2$ ), the sum of

the Standard Square Error (SSE), the Root Mean Square Error (RMSE), and the relative Percent Error (PE) (Viswanathan *et al.*, 2003; Menkov, 2000)

For a good fit, the values of  $R^2$  must be the greatest, and the SSE and RMSE values must be the lowest (Demir *et al.*, 2004; Goyal *et al.*, 2006). The PE below 10% indicate good fit (Roberts *et al.*, 2008). These will be analyze using the statistical function in Excel and MATLAB and are defined as follows;

The Standard error of estimate (Demir *et al.*, 2004):

$$SSE = \sum_{i=1}^N \left[ \frac{(MR_{exp,i} - MR_{pred,i})}{\sigma_i} \right]^2 \quad (27)$$

Root mean square error (Demir *et al.*, 2004):

$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^N (MR_{exp,i} - MR_{pred,i})^2 \right]^{1/2} \quad (28)$$

The relative percent errors (Roberts *et al.*, 2008):

$$PE = \frac{100}{n} \sum_{i=1}^n \frac{|MR_{exp,i} - MR_{pred,i}|}{MR_{exp,i}} \quad (29)$$

Where:

$MR_{exp,i}$  is the moisture ratio observed experimentally for instant i.

$MR_{pred,i}$  is the predicted moisture ratio for instant I for the same instant N.

The parameters N and n are the number of observations and constants.

$\Sigma_i$  is the standard deviation

## 3.4 Result and Discussion

### 3.4.1 Physical properties of Sukkari Dates powder

Results obtained for size distribution of the Sukkari date powder (SDP) is shown in Table 3.2 and the plot of percentage passing (%) with sieve sizes is shown in Fig 1. Based on the US standard sieve distribution, it can be- observed that about 81.5% of the powder produced are moderately fine particle sizes, i.e.,180-355mm, and 8.6%, 7.3% and 1.4% are coarse, fine and very fine particle sizes, respectively.

Table 3.3 shows the results of some of the physical properties of Sukkari date powder (SDP) at different particle sizes. The bulk density (BD) and tapped density (TD) are both significant characteristics for characterization, handling, and processing of powder systems. Bulk

density values were in the range 623.68 – 634.97 kg/m<sup>3</sup> with no significant differences for all the particle sizes of the SDP. The tapped density (TD) varied in the range 831.93 -901.77 kg/m<sup>3</sup> with the highest value (901.77 kg/m<sup>3</sup>) attained by the fine particles (<180-125 μm) and the lowest value (831.93 kg/m<sup>3</sup>) by the coarse particles (>355μm). No significant differences were observed between the coarse and the moderately fine particles, and between the fine, very fine, and bulk particles. These results were within the ranges obtained by Farahnaky et al., (2016).

The compressibility index (CI) and Hausner ratio (HR) both increased as the particle sizes were decreased and varied in the ranges 24.15% to 30.12% for CI and 1.32-1.43 for HR, respectively. The ranges are 24.15 to 30.12 and 1.32-1.43 for CI and HR, respectively. For CI there is a significant difference as the particle sizes decreases from moderately fine to very fine particle size, while there is no significant difference for HR of different particle sizes. The greater the compressibility of a bulk solid, the less flowable it is. The flowability ranges for both CI and HR are in the ranges classified by Lebrun et al., (2012) to be between passable – poor powders. This can be due to the sticky nature of the powder due to its very high sugar content.

Among the important physical attributes which may affect the processing and quality of powders during processing and storage are moisture content, water activity, pH, and Electrical conductivity (EC).

The moisture content (MC) ranges from 2.97 to 3.41% d.b and it increases as the particle sizes reduces. There is no significant difference for the different particle sizes except for the very fine particle sizes with slight difference. This shows that the powder is very dry.

The water activity ( $a_w$ ) of the system is generally defined as the amount of water available for microbial growth Sun (2005). A Low water activity reduces the growth of food spoilage or food-poisoning organisms. From the result,  $a_w$  show no significant difference for the different particle sizes except for a slight difference in very fine particle sizes. It was almost constant, and slightly increased as the particle sizes decreases but decrease for the very fine sizes within the range 0.16-0.18.

The pH of food is one of the main factors affecting the growth and survival of microorganisms. All microorganisms have a pH range in which they can grow and an optimum pH at which they grow best. It can be seen from the Table 3.3 that pH was almost constant for all particle sizes and fell in the range 5.60-5.64 with no significant difference for the different particle sizes. Its low value means the powder can be classified as a low-acid food product.

The electrical conductivity (EC) may reflect presence of ions or dipoles particles in the sample, meaning that the more EC, the more ions or conductive particles are in the sample (Fikry & Al-Awaadh, 2016). From the results obtained in this work, EC decreased as the particle sizes decreased and fell in the range 2.90-3.13mS with no significant difference among different particle sizes.

Color is an important quality factor related directly to the acceptability of food products, and is an important physical property to report for food powders. The lightness ( $L^*$ ) is an indication of the brightness of the powder sample. From the color analysis of the powder, it can be observed that the lightness increases as the particle sizes reduces and it was in the range 64.56-69.26. The range of  $a^*$  (greenness – redness) values was 4.51-5.44 with significant difference between different size categories. The parameter  $b^*$  (blueness–yellowness) showed no significant difference between the different particles sizes and its values varied in the range 24.44 -27.09, with very fine particles attaining the highest value. These values of  $L^*$ ,  $a^*$  and  $b^*$  were within the ranges reported by Farahnaky et al., (2016). The chroma ( $C^*$ ) values indicates the degree of color saturation and is proportional to strength of the color (Akoy, 2014). The  $C^*$  values were in the range 24.96-27.45 with the very fine particle size sample been the highest. The hue angle ( $H^\circ$ ) refers to the qualitative attribute of color, according to which colors have been traditionally defined as reddish, greenish, etc. The hue angle ( $H^\circ$ ) spanned in the range 78.30-80.55, with the highest value for very fine particle size powder. Browning index (BI) indicates the purity of brown color and is reported as an important parameter in processes where enzymatic and non-enzymatic browning takes place (Akoy, 2014). In this work BI values varied in the range 52.29-55.95, with fine particle sizes been the highest. It also increased with decreasing particles sizes. The total color (E) represents the total difference in respect to white standard where higher values represent a darker powder. It fell in the range 69.22-74.51, with very fine particle sizes been the highest. It also increased with decreasing particles sizes.

The water absorption index (WAI) and Water solubility index (WSI) measures the volume occupied by powder sample after swelling in excess water, which maintains it in aqueous dispersion. It describes the rate and extent to which the component of powder material or particles dissolves in water. The result obtained showed that WAI of the Sukarri date powder for the different particle sizes varied in the range 0.81-1.74g/g dry matter. WAI increased with decreasing particle size as the particle sizes reduces with slight significant differences. Waster solubility index

(WSI) is the amount of dried solid recovered by evaporating the supernatant from the WAI test expressed as the percentage of dry solid in the sample. Waster solubility index (WSI) ranges from 6.77-7.20 g/g of dry matter. It increases as the particles sizes reduces with no significant differences.

The oil holding capacity (OHC) of the powder for different particle sizes ranges from 0.31-0.78 g/g and it increases as the particle sizes reduces with no significant differences.

The property of swelling capacity (SC) indicates to what extent the powder samples swell as water is absorbed (Femenia et al., 2009). From the table it can be seen that SC increases as the particle sizes reduces and ranges from 2.08 – 3.14 ml/g dry matter with no significant differences between the particle sizes.

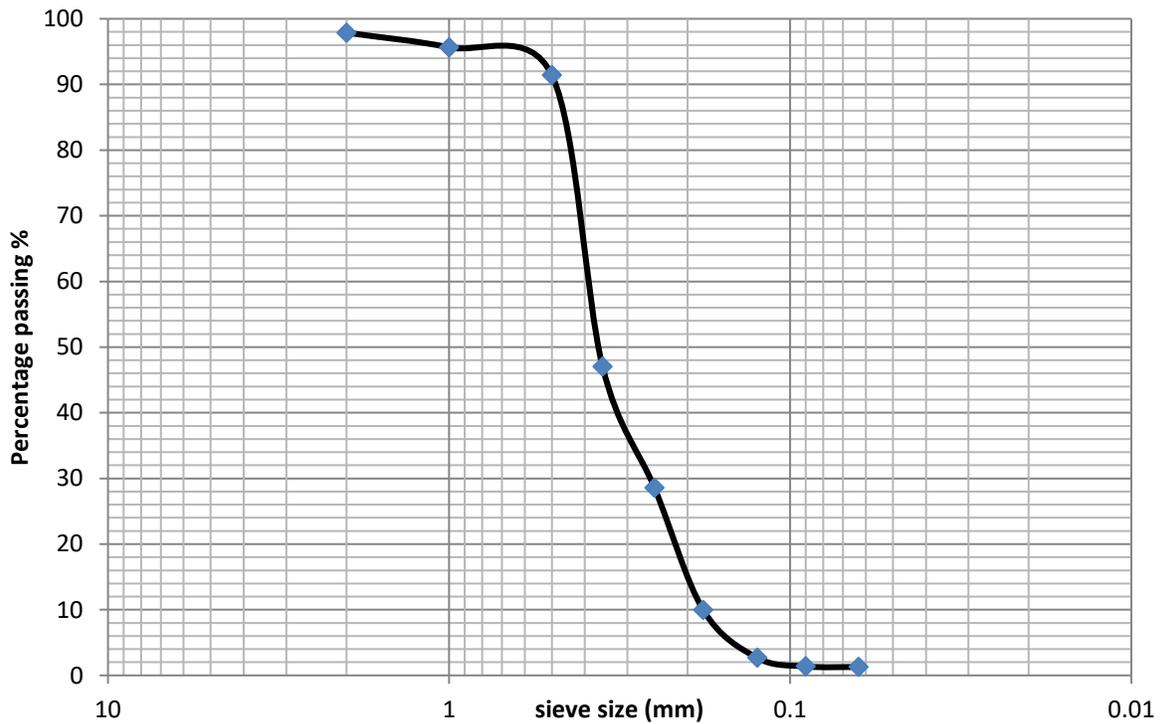


Figure 3. 1Particle Size distribution of Sukkari Date powder.

**Table 3. 2Particle Size distribution of Sukkari Date powder.**

Size Distribution	sieve sizes(μm)	Retained weight (g)	Retained percentage %	Cumulative weight (g)	Cumulative percentage %	passed percentage %	Amount (%)
Coarse	2	20.75(1.03)*	2.12	20.75	2.12	97.88	8.6
	1	21.96(2.59)	2.24	42.70	4.36	95.64	
	0.5	41.17(2.62)	4.20	83.88	8.56	91.44	
Moderately Fine	0.355	435.33(12.72)	44.40	519.20	52.96	47.04	81.5
	0.25	181.05 (10.36)	18.47	700.25	71.42	28.58	
	0.18	182.33(3.43)	18.60	882.58	90.02	9.98	
Fine	0.125	71.50(5.68)	7.29	954.09	97.31	2.69	7.3
Very Fine	0.09	12.94(1.89)	1.32	967.03	98.63	1.37	1.4
	0.063	0.95(0.34)	0.10	967.97	98.73	1.27	
	Pan	0.07(0.02)	0.01	968.04	98.74	1.26	

\* Values in parenthesis represent standard deviation

**Table 3. 3Some Physical properties of Sukkari Date Powder at different particle sizes**

	Particle size	Coarse (>355μm)	Moderately fine (355-180μm)	Fine (<180-125)	Very fine (<125 μm)	BULK (>355-125μm)	
<b>*PROPERTIES</b>	<b>BD (kg/m<sup>3</sup>)</b>	627.67 <sup>a</sup> ±3.67	633.00 <sup>a</sup> ±4.06	634.97 <sup>a</sup> ±2.66	623.68 <sup>a</sup> ±26.42	629.83 <sup>a</sup> ±12.46	
	<b>TD (kg/m<sup>3</sup>)</b>	831.93 <sup>a</sup> ±13.08	854.93 <sup>a</sup> ±16.40	901.77 <sup>b</sup> ±9.12	892.57 <sup>b</sup> ±4.71	870.30 <sup>b</sup> ±31.15	
	<b>CI (%)</b>	24.55 <sup>a</sup> ±0.79	25.95 <sup>a</sup> ±1.14	29.58 <sup>b</sup> ±1.00	30.12 <sup>b</sup> ±3.29	27.55 <sup>b</sup> ±2.93	
	<b>HR</b>	1.32 <sup>a</sup> ±0.01	1.35 <sup>a,b</sup> ±0.02	1.42 <sup>b,c</sup> ±0.02	1.43 <sup>c</sup> ±0.07	1.38 <sup>a</sup> ±0.06	
	<b>MC(%db)</b>	2.97 <sup>a</sup> ±0.17	3.37 <sup>a</sup> ±0.08	3.36 <sup>a</sup> ±0.41	3.93 <sup>b</sup> ±0.23	3.41 <sup>b</sup> ±0.42	
	<b>Aw</b>	0.16 <sup>a</sup> ±0.00	0.16 <sup>a</sup> ± 0.01	0.17 <sup>a</sup> ±0.00	0.22 <sup>b</sup> ±0.04	0.18 <sup>a</sup> ±0.03	
	<b>PH</b>	5.64 <sup>a</sup> ±0.05	5.60 <sup>a</sup> ±0.01	5.61 <sup>a</sup> ±0.02	5.62 <sup>a</sup> ±0.01	5.62 <sup>a</sup> ±0.03	
	<b>EC (mS)</b>	3.13 <sup>a</sup> ±0.58	3.09 <sup>a</sup> ±0.05	2.98 <sup>a</sup> ±0.07	2.90 <sup>a</sup> ±0.13	3.02 <sup>a</sup> ±0.27	
	<b>COLOUR</b>	<b>L*</b>	64.56 <sup>a</sup> ±0.73	64.86 <sup>a</sup> ±1.39	67.14 <sup>b</sup> ±0.55	69.26 <sup>c</sup> ±0.24	66.46 <sup>b</sup> ±2.11
		<b>a*</b>	5.06 <sup>b,c</sup> ±0.31	4.85 <sup>a,b</sup> ±0.31	5.44 <sup>c</sup> ±0.09	4.51 <sup>a</sup> ±0.08	4.96 <sup>a,b</sup> ±0.40
		<b>b*</b>	24.44 <sup>a</sup> ±0.36	24.71 <sup>a</sup> ±1.10	26.90 <sup>b</sup> ±0.16	27.09 <sup>b</sup> ±0.19	25.79 <sup>b</sup> ±1.37
		<b>C*</b>	24.96 <sup>a</sup> ±0.38	25.18 <sup>a</sup> ±1.14	27.45 <sup>b</sup> ±0.17	27.46 <sup>b</sup> ±0.20	26.26 <sup>b</sup> ±1.35
		<b>H<sup>o</sup></b>	78.30 <sup>a</sup> ±0.65	78.91 <sup>a</sup> ±0.20	78.58 <sup>a</sup> ±0.12	80.55 <sup>b</sup> ±0.10	79.08 <sup>a</sup> ±0.96
		<b>BI</b>	52.29 <sup>a</sup> ±1.50	52.35 <sup>a</sup> ±1.58	55.95 <sup>b</sup> ±1.05	53.19 <sup>a</sup> ±0.75	53.45 <sup>a</sup> ±1.89
		<b>E</b>	69.22 <sup>a</sup> ±0.66	69.58 <sup>a</sup> ±1.71	72.53 <sup>b</sup> ±0.45	74.51 <sup>c</sup> ±0.14	71.46 <sup>b</sup> ±2.42
	<b>WAI(g/g)</b>	0.81 <sup>a</sup> ±0.43	1.26 <sup>b</sup> ±0.11	1.41 <sup>b,c</sup> ±0.07	1.74 <sup>c</sup> ±0.09	1.31 <sup>b</sup> ±0.40	
	<b>WSI(g/g)</b>	7.20 <sup>a</sup> ±0.10	7.11 <sup>a</sup> ±0.41	6.77 <sup>a</sup> ±0.51	7.17 <sup>a</sup> ±0.91	7.07 <sup>a</sup> ±0.51	

<b>OHC(g/g)</b>	0.31 <sup>a</sup> ±0.02	0.44 <sup>a</sup> ±0.46	0.48 <sup>a</sup> ±0.29	0.78 <sup>a</sup> ±0.19	0.50 <sup>a</sup> ±0.30
<b>SC(ml/g)</b>	2.08 <sup>a</sup> ±0.46	2.60 <sup>a</sup> ±1.20	2.88 <sup>a</sup> ±0.39	3.14 <sup>a</sup> ±0.87	2.43 <sup>a</sup> ±0.85

\*For each property, values are expressed as means ± standard deviation. Values in the same row having the same letter are not significantly different by Duncan tests at a confidence level of 95%.

### 3.4.2 Vapor Sorption Isotherm

Data are plotted as equilibrium moisture content values, on dry basis, at different water activities in the range of 0.1 to 0.9(±0.4) for each temperature of 20°C, 40°C and 60°C (±0.2) as shown in fig 3.2. The curve is a type III shape with a more or less sigmoid shape which is general for high sugar food (Tsami et al., 1990). From the curve, as water activity increases, the moisture adsorption increases. It can be observed that the date powder absorbed less water at low water activities and absorbed much at high water activity. This is similar to what was reported by Telis et al., (1990) for food with higher sugar contents and by Sanni et al., (1997), McLaughlin & Magee, (1998), Arslan & Tog˘rul (2006) for different type of foods.

Generally, at constant water activity, moisture content is expected to increase with decreasing temperature (Rahman 1995). From fig. 3.2, clear temperature dependence can be observed on the isotherm with two main results. Firstly, as the equilibrium moisture content (EMC) increases, the temperature increases at constant water activity. Lastly, an overlap at approximately 0.7  $a_w$  occurred with an increasing EMC as the temperature reduces. Mohammad et al., (2012) reported a similar trend to the obtained first result for sorption isotherm of quince but at a higher  $a_w$ . He stated that this could be due to an increase or dissolution of solubility sugars in water. While the second result is similar to what has been reported by many researchers (Maroulis et al., 1988; Rahman, 1995; Rahman & Labuza, 1999; Tasmi et al., 1990, Wesley et al., 2000; Hossain et al., 2001; Prothon & Ahrne, 2004; Mohammad et al., 2012) as characteristics of high sugar foods. However, the obtained results are similar to what was obtained by Khaled et al., (2000) and they stated that it could be due to chemical and physical changes induced by temperature. Also, Weisser et al., (1982) and Mohammad et al., (2012) also stated that the intersection point depends on the composition of food and the solubility of sugars. For sultana raisin and currant, about 0.55 was the inversion point, 0.65 for fig and quince jam, 0.70 for prune and 0.75 for Quince and apricot. (Tsami et al., 1990; Sa & Sereno, 1993; Mohammad et al., 2012).

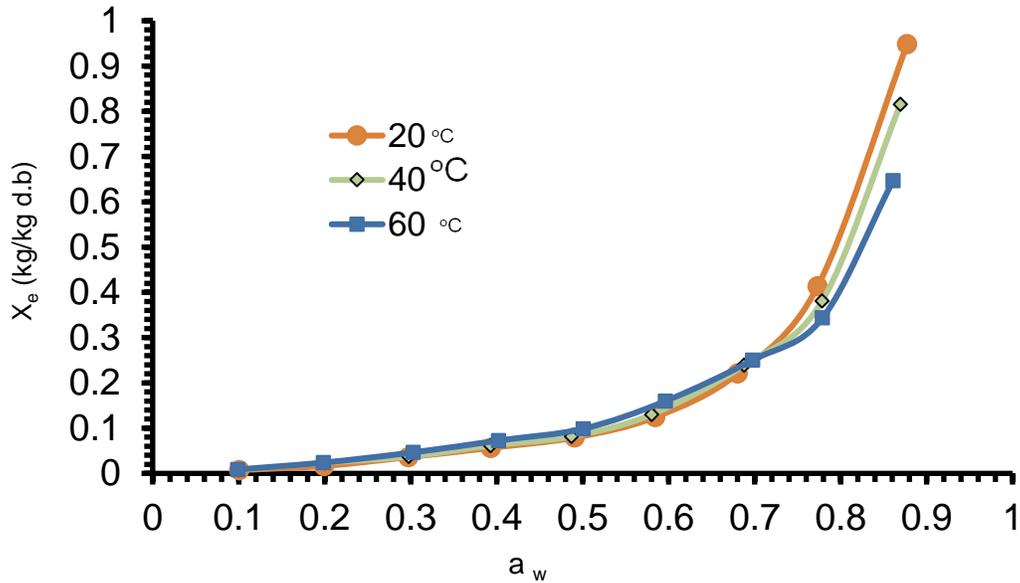


Figure 3. 2 Sorption Isotherm at 20°C, 40°C and 60°C for Sukkari Date Powder.

### 3.4.3 Isotherm Prediction Model

The result of the parameters for the sorption models of SDP and the statistical parameters are shown in Table 3.4. The best model was selected based on:  $Pe \leq 10$ ,  $R^2 > 0.95$  and low SSE and RMSE for all temperatures. Based on the goodness of fit criteria, from table 1 it can be seen that Modified Bet (MB), Modified Oswin (MO), Modified Gab (MG) and Modified Halsey (MH) models fit well to the experimental data for SDP throughout the entire range of water activity for the temperature range of 20-60°C. However, MB model is the best model with PE of 6.30%,  $R^2$  of 0.998, SSE of 0.005 and RMSE of 0.014 and it will be used for sorption thermodynamics. Modified Henderson, Modified Smith and Modified Chungpost were inadequate to represent the experimental data with PE of 11.52%, 18.26% and 24.52% respectively.

Hossain et al., (2001) and Belarabi et al., (2000) reported modified Bet to be the best fitting model to the sorption of pineapple and Dates. The MB model was used over the whole range of water activity under study as stated by Belarabi et al., (2000).

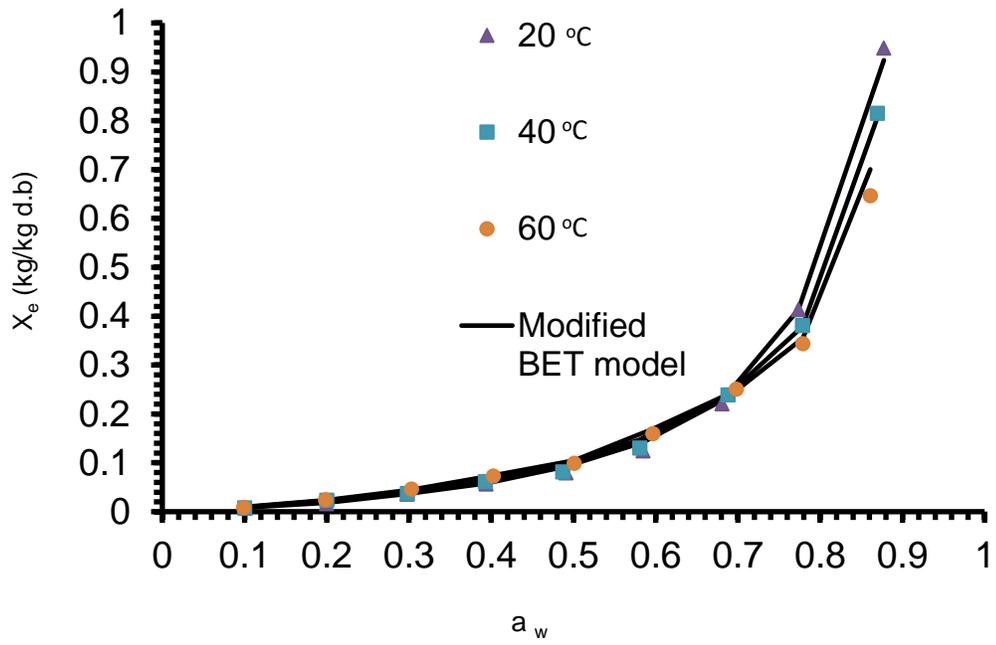


Figure 3.3 Sorption isotherm at 20°C, 40°C and 60°C for the experimental and predicted with modified Bet model.

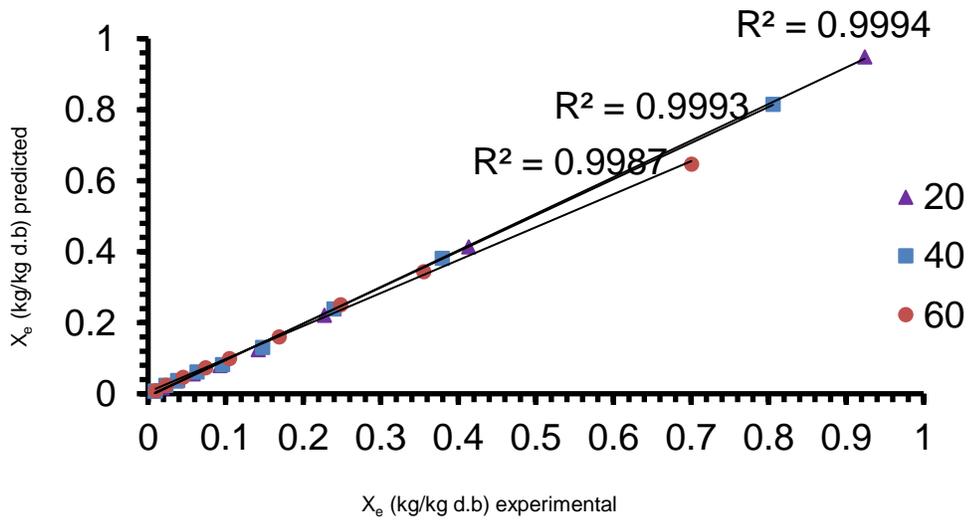
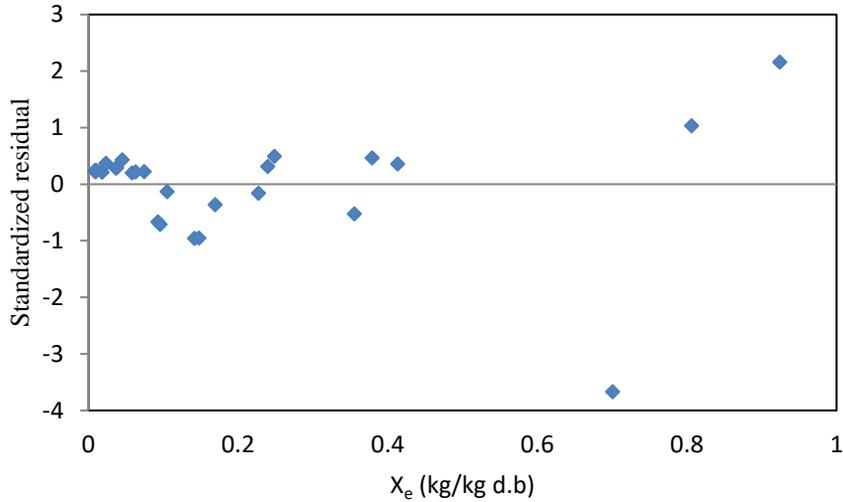


Figure 3.4 Comparison of experimental and predicted EMC using Modified BET model.



**Figure 3. 5**Plot of residuals fit of the Modified BET model to sorption data of Sukkari Date powder.

Figs. 3.3 and 3.4 show the correlation between the predicted and the experimental values at different temperatures using MB model of EMC. It can be seen from these figures the adequacy of the proposed model in describing the adsorption behaviour of SDP because the predicted data band around the straight line closely. The plot of standardized residual against the predicted values of EMC in fig. 3.5 was used to further verify the fitness of the model. It can be seen that the error variance is constant with a random distribution; therefore, the Modified Bet model is suitable for the evaluation for the adsorption behaviour of SDP.

The standardized residual is defined as

$$R = \frac{e_i - e_{average}}{RMSE} \quad (30)$$

where  $e_i = emc_{experimental} - emc_{predicted} = Residual$

and  $e_{average} = average\ of\ the\ residual$

**Table 3. 4. Estimated parameter for the EMC models for the temperature range of 20-60°C with the statistical parameters.**

Model	Parameters	Values
Modified Oswin	A	0.11258 *(0.01116)
	B	-0.00034 (0.000269)
	C	0.899517 (0.010961)
	SSE	0.004
	R <sup>2</sup>	0.9967
	RMSE	0.012386
	PE%	6.64
	Modified Smith	A
B		-0.08087 (0.222574)
C		0.197185 (0.027954)
D		-0.00061 (0.000444)
SSE		0.764
R <sup>2</sup>		0.8952
RMSE		0.168207
PE%		17.80
Modified Halsey	A	-1.94542 (1.758474)
	B	-0.0016 (0.002498)
	C	0.677391 (0.029153)
	SSE	0.0650
	R <sup>2</sup>	0.9898
	RMSE	0.049036
	PE%	8.50
Modified Gab	A	0.081313 (0.011896)
	B	1.04574 (0.010373)
	C	43.85062 (13.07492)
	SSE	0.0113
	R <sup>2</sup>	0.9932
	RMSE	0.020415
	PE%	8.56
Modified BET	C	-0.00041 (0.000448)
	K	0.5942 (0.04728)
	X <sub>M</sub>	0.148026 (0.022045)
	SSE	0.005
	R <sup>2</sup>	0.9977
	RMSE	0.013608

	PE%	6.30
Modified Chungpfof	A	546.3129 (104.9285)
	B	11.32271 (0.573007)
	C	228.8762 (50.759)
	SSE	1.148
	R <sup>2</sup>	0.7948
	RMSE	0.206219
	PE%	24.51
Modified Henderson	A	0.006882 (0.002368)
	B	386.9928 (91.57376)
	C	0.618331 (0.016431)
	SSE	0.204055
	R <sup>2</sup>	0.9294
	RMSE	0.086934
	PE%	11.52

\* Values in parenthesis represent standard deviation.

### 3.4.4 Sorption Thermodynamic Parameters

#### 3.4.4.1 Net isosteric heat of sorption

The thermodynamic properties were determined by calculating the energy requirements of heat and mass transfer in biological systems (Rizvi & Benado, 1984). The plot observed between  $\ln a_w$  and  $1/T$  at constant moisture contents shows linear relationship (Fig. 3.6), from its slope, the net isosteric heats of sorption were calculated at different moisture contents as shown in Fig. 3. 7. It can be seen that the net Isosteric heats of adsorption decreased with an increase in moisture content and becoming stabilized at moisture content greater than 0.3 (kg/kg d.b). The maximum net isosteric heat of sorption was obtained at a low EMC of 0.05 with a value of 1.46 kJ/mol to a minimum value of 0.38kJ/mol at EMC of 0.6 (kg/kg d.b). Similar ranges of results have been reported for the net isosteric heats of some foods at 5% moisture contents (1.45 kJ/mol for sesame seed (Aviara et al., 2002); 1.47 kJ/mol for cowpea (Ajibola et al., 2003); 1.7 kJ/mol for potato (McMinn & Magee, 2003). The little differences could be due to the difference in the chemical composition and structural makeup of the crops.

The heat of sorption (differential enthalpy),  $Q_{st}$ , was calculated using eq. 15 and its effect on moisture content is as shown in fig. 3.8 with a similar trend to net isosteric heat of sorption. The increasing  $Q_{st}$  at low moisture content means that maximum energy is being used to remove the water present in the product. It also indicates the existence of highly active polar sites on the

surface of the food material which are covered with water molecules forming a mono-molecular layer Tsami (1991). The decrease in enthalpy with increasing moisture content indicates covering of less favourable locations and the formation of multi-layers.

The effect of moisture content on isosteric heat of sorption of water in Sukkari powder can be expressed mathematically as power function as shown in eq. 31, This mathematical relationship may be used to calculate the heat of sorption of SDP for various moisture contents.

$$Q_{st} = 43.47X_e^{-0.01} \quad R^2 = 0.993 \quad (31)$$

#### 3.4.4.2 Differential Entropy

Entropy change plays an important role in the energy and exergy analysis of food processing systems. From Eq. 17 and the slope from fig. 3.5, at different moisture contents, the differential entropy ( $S_d$ ) were obtained as shown in fig 3.8. The differential entropy showed a strong dependence on moisture content with a power trend (eq.32) similar to that exhibited by differential enthalpy. Similar observations have been reported for some foods (Al-Muhtaseb et al., 2004b; Goula et al., 2007; Igathinathane et al., 2007; Mohammad et al., 2012).

Large values of heat of sorption and differential entropy associated with low moisture values represent bound moisture Igathinathane et al., (2007).

$$S_d = 0.1735X_e^{-1.074} \quad R^2 = 0.995 \quad (32)$$

#### 3.4.4.3 Enthalpy-Entropy compensation theory

To verify the compensation theory, a plot of enthalpy and entropy shows a linear relationship as shown in fig. 3.9. This indicates that the theory could be applied within the studied range of moisture contents. Eq. 33 is the linear regression of the fig. 3.9 and comparing it with eq. 17, gives the isokinetic temperature ( $T_B$ ) of sorption, which was found to be 290.67 K. Also, the harmonic mean temperature ( $T_{hm}$ ) was calculated from eq. 19 as 312.1 K, which is significantly different from  $T_B$ , thereby confirming the suitability of the theory for water sorption in SDP and since  $T_B < T_{hm}$ , therefore, the process can be characterized as entropy driven.

The constant  $\Delta G_\beta$  of the linear differential enthalpy-entropy fit (i.e. comparing eq. 18 with eq. 32) was 43.73 kJ/mol which are in the same range as obtained for leaf, stalk skin, and stalk

pith 44.30, 44.02 and 44.15 kJ/mol respectively (Igathinathane et al., (2007), which indicates a non-spontaneous reaction.

$$Q_{st} = 290.67S_d + 43.73 \quad R^2 = 0.97 \quad (33)$$

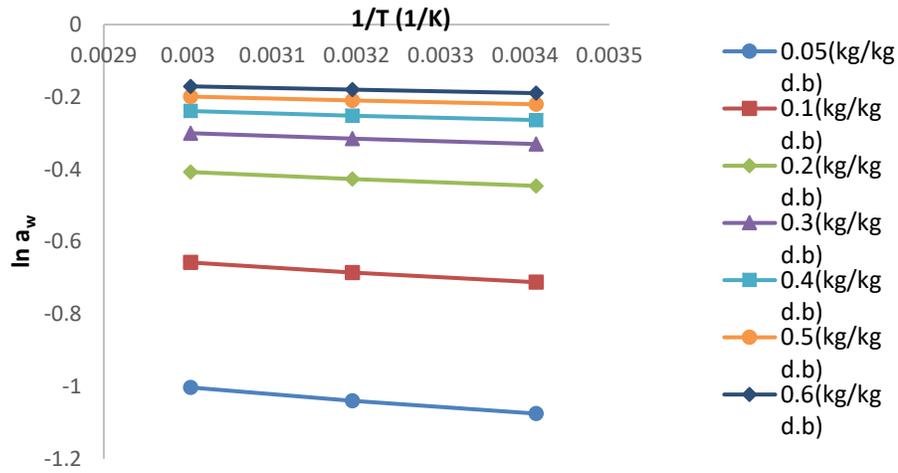


Figure 3.6- $\ln a_w$  against  $1/T$  at constant moisture content.

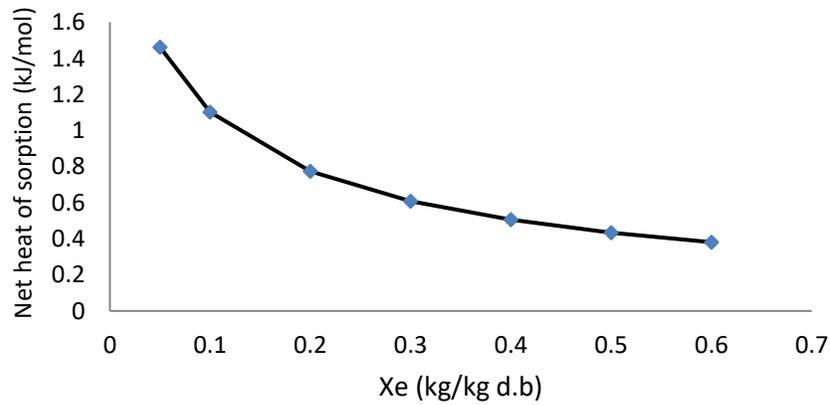


Figure 3.7-Net Isosteric heat of adsorption of Sukkari Date powder as a function of equilibrium moisture content.

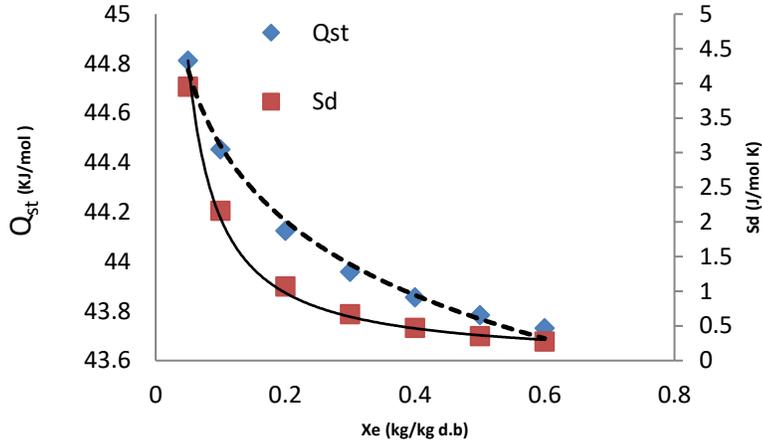


Figure 3.8-Isosteric heat of adsorption and Differential entropy of Sukkari Date powder as a function of equilibrium moisture content.

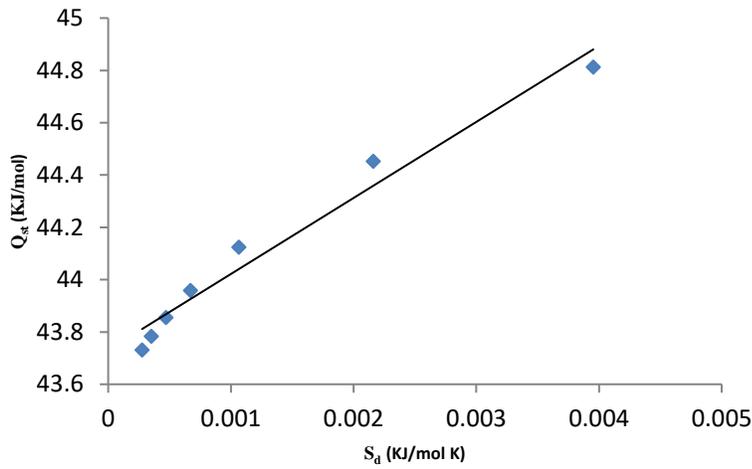


Figure 3.9 – Relationship between isosteric heat of sorption and differential entropy of sorption for Sukkari Date powder.

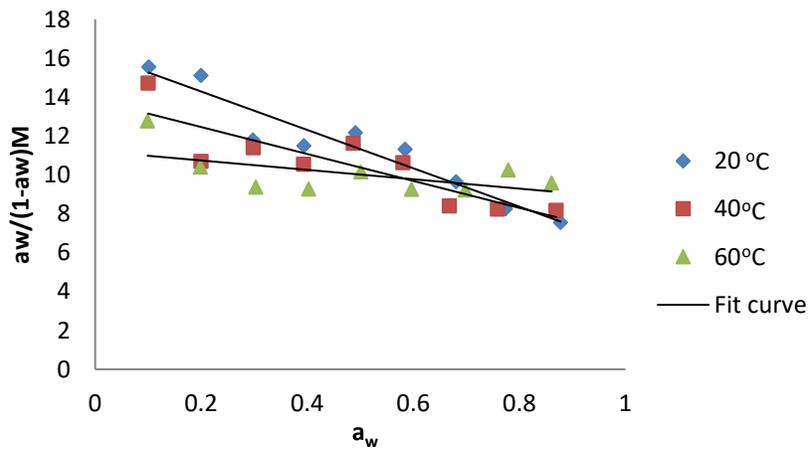
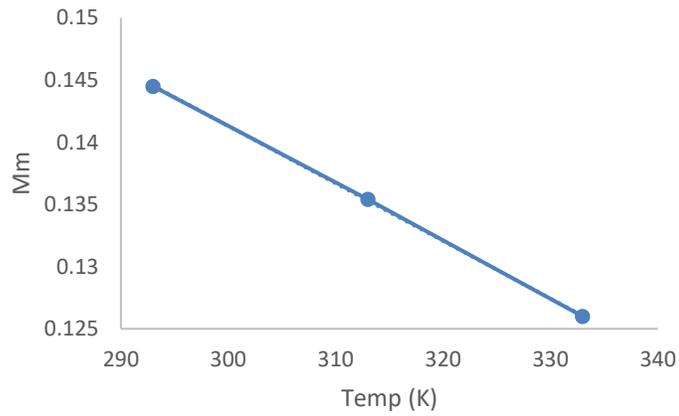


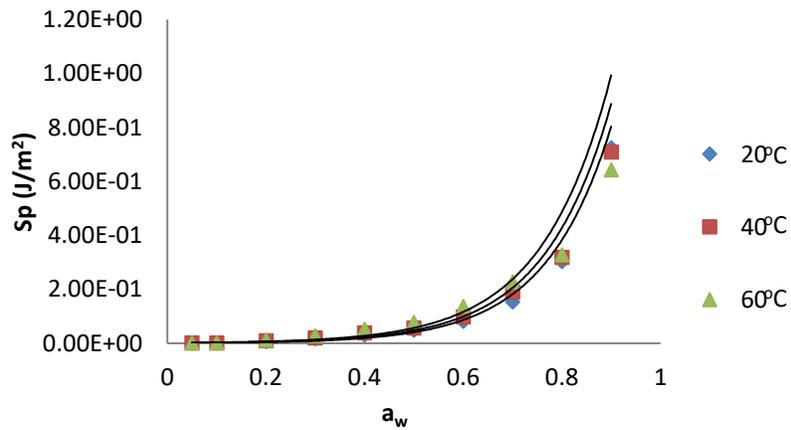
Figure 3.10- plot of  $(a_w/((1-a_w)M))$  versus  $a_w$ .

**Table 3. 5 Monolayer moisture content at different temperatures**

Temperature (K)	Monolayer Moisture content kg/kg d.b
293	0.145
313	0.135
333	0.126



**Figure 3.11- Plot of monolayer moisture content of Sukkari date powder as a function of temperature.**



**Figure 3.12- Variation of spreading pressure with moisture content and temperature of Sukkari Date powder.**

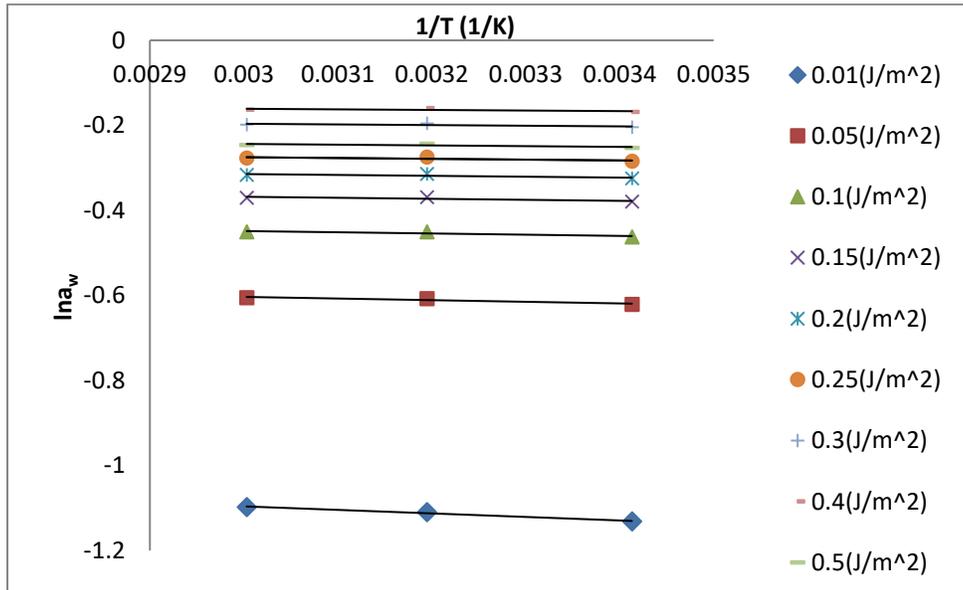


Figure 3.13-  $\ln a_w$  against  $1/T$  at constant spreading pressure.

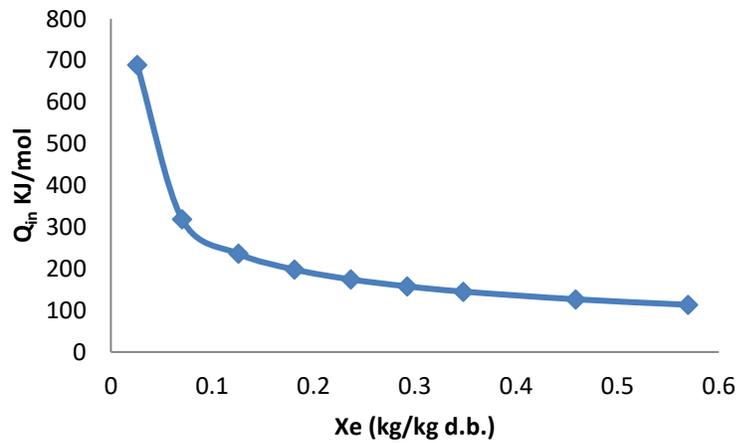


Figure 3.14- Net integral enthalpy of Sukkari Date powder as a function of equilibrium moisture content.

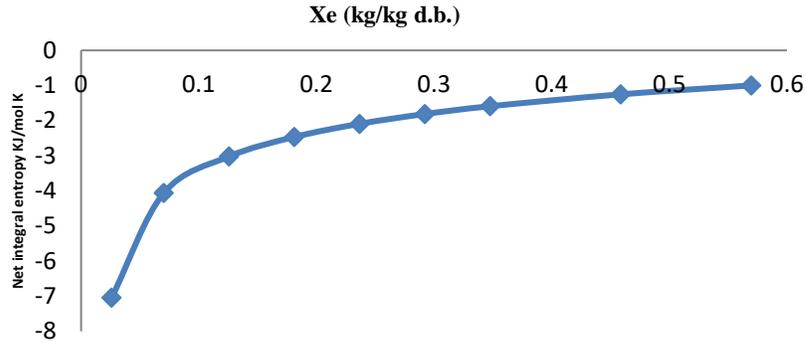


Figure 3.15 Net integral entropy of Sukkari Date powder as a function of equilibrium moisture content.

#### 3.4.4.4 Monolayer moisture content and spreading pressure

The monolayer moisture content was determined by comparing eq. 34-35, which is the linear relationship of the plot of  $\left(\frac{a_w}{(1-a_w)M}\right)$  versus  $a_w$  at the three temperatures (fig. 3.10) with eq. 22 and the results obtained are shown in table 3.5. Fig. 3.11 shows the plot of monolayer moisture content of SDP as a function of temperature. It can be seen that as the temperature increases, the monolayer moisture content decreases. This relationship can be represented mathematically by eq. 37. This follows a similar trend for dehydrated food which has been ascribed to a reduction in the number of active sites due to physical and chemical changes induced by temperature (Rizvi 1986; Sopade et al., 1996). Diosady et al., (1996) also stated that as the absorbed molecules gain kinetic energy  $M_m$  should decrease with increasing temperature.

$$\left(\frac{a_w}{(1-a_w)M}\right) = -9.8696a_w + 16.258 \quad (34)$$

$$\left(\frac{a_w}{(1-a_w)M}\right) = -6.9276a_w + 13.843 \quad (35)$$

$$\left(\frac{a_w}{(1-a_w)M}\right) = -2.412a_w + 11.221 \quad (36)$$

$$M_m = -0.0005T + 0.2801 \quad (37)$$

Where  $M_m$  is the monolayer moisture content (kg/kg d.b), T is temperature (K)

The spreading pressure of SDP was determined using eq. 21. The spreading pressure increased with increasing water activity as shown in fig. 3.12. The increment was very slow at water activity of less than 0.5. An increase in temperature causes a reduction of the spreading

pressure but not very significant. Similar results have been reported by Fasina et al., (1999); Aviara & Ajibola, (2000); Aviara et al., (2002); Aviara et al., (2004) and Noshad et al., (2012) for winged bean seed and gari, plantain, sesame seed, soya bean and quince respectively.

#### 3.4.4.5 Net integral enthalpy and entropy

The plot observed between  $\ln a_w$  and  $1/T$  at constant spreading pressure shows linear relationship (Fig. 3.13), from its slope, the Net integral enthalpy ( $Q_{in}$ ) were calculated at different moisture contents as shown in Fig. 3.14.  $Q_{in}$  of SDP decreased with increase in moisture content from a value of 689.45KJ/mol at moisture content of 0.25 kg/kg d.b. to 113.40KJ/mol at 0.5 kg/kg d.b. Similar trends have been reported for the enthalpy of sugar beet root, its insoluble fraction and sucrose (Iglesias et al., 1976), plantain (Aviara & Ajibola, 2000), Soya beans (Aviara et al., 2004) and walnut kernels (Arslan & Tog̃rul, 2006). This behaviour may be due to the fact that as the moisture content of the food material increased, the sorptive sites get saturated, and by surface tension, water molecules bind to the particles than by chemical adsorption. Therefore, it results to lower integral enthalpy due to the weakness of surface tensional forces which break easily.

The relationship of net integral entropy with moisture content is shown in Fig. 3.15. Net integral entropy of SDP decreased with increase in moisture content from a maximum value of 7.05KJ/mol K at moisture content 0.025 (kg/kg d.b) to a minimum value of 0.999KJ/mol K at the moisture content of 0.57 (kg/kg d.b.). The reduction was very slow and becoming constant at higher  $a_w$ . A similar trend has been reported for the entropy of winged bean seed and gari (Fasina et al., 1999), plantain (Aviara & Ajibola, 2000), cassava (Aviara & Ajibola, 2002), sesame seed (Aviara et al., 2002), walnut kernels (Arslan & Tog̃rul, 2006) and deffated sesame meal (Majdi et al., 2007). Oliveira (2009) reported that the decrease of entropy in the low  $a_w$  range may be due to lateral interaction in the adsorbed film arising from loss of rotational freedom (restrictive effect) of the water molecules adsorbed which makes the available sites to be saturated.

### 3.5 Conclusion

Majority of the powders produced from Sukkari Date cultivar are moderately fine particle sizes. Bulk density, tapped density, compressibility index, Hausner ratio, moisture content and water activity were found to increase as the particle sizes reduces except for very fine sizes which reduces. Color analysis parameters [lightness ( $L^*$ ),  $a^*$  (greenness – redness),  $b^*$  (blueness–

yellowness), chroma ( $C^*$ ), hue angle ( $H^\circ$ ), Browning index (BI) and total color (E)] also increases as the particle sizes reduces. While Electrical conductivity reduces as the particle sizes decreases and pH, show no significant difference for the different particle sizes. Water Absorption Index, Water Solubility Index and Oil Holding Capacity were also found to increase as the particle sizes reduce sizes with slight significant differences for the first and no significant differences for the latter two.

Adsorption isotherm of the date powder determined within the range of 0.1 to 0.9 ( $\pm 0.4$ ) water activities and at three different temperatures (20, 40 and  $60^\circ\text{C} \pm 0.2$ ) shows a curve of type III shape with a more or less sigmoid shape. As water activity increases, the moisture adsorption was found to increase especially at high water activity. The effect of temperature result to that as equilibrium moisture content (EMC) increases, the temperature increases at constant low water activity, but from around 0.70 water activity, an increasing EMC as the temperature reduces was observed. The Modified Bet, Modified Oswin, Modified Gab and Modified Halsey fitted well to the experimental data throughout the entire range of water activity at the three temperatures range studied, however, Modified Bet model was found to be the best model. For sorption thermodynamics, net Isostatic heats of adsorption, Heat of sorption (differential enthalpy) and differential entropy was found to decrease with an increase in moisture content. Monolayer moisture content and spreading pressure was found to decrease as the temperature increases. However, spreading pressure increases with increasing water activity but with a slow increment at less than  $0.5a_w$ . While Net integral enthalpy and Net integral entropy were found to decrease with increase in moisture content.

Generally, it can be concluded that particle sizes have significant effect on most of the aforementioned physical properties. Also, for good storage, Sukkari Date powder should be stored at RH of less than 50%, less than 10% d.b. moisture content and a temperature of less than  $40^\circ\text{C}$ .

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# CHAPTER FOUR: Water Vapor Sorption Kinetics of Sukkari Date Powder at Different Temperatures

## Abstract

The applicability of four sorption kinetic model was investigated for predicting adsorption process of Sukkari date powder, at different relative humidities Rh of 10-90% at step of 10 and temperatures (20, 40 and 60°C). The water sorption rate of the powder quickly increased as the relative humidity increases and the time for equilibrium to be reached increases as the temperature decreases which takes approximately 148h, 63h and 28hr for 20°C, 40°C and 60°C respectively. All the four models fit to the experimental data over the relative humidities and temperature ranges under study. Temperature dependence of the four models' parameters were also investigated which indicated that the constants of Peleg model fitted well over the RH and temperature ranges and was used for determination of some thermodynamic properties. The Peleg rate constants decreased with an increasing temperature. At constant RH, the enthalpy decreases with increase in temperature with no significant difference. While entropy and free energy of activation increases with increase in temperature.

Keywords: Sorption kinetics, Kinetic model, Relative humidity, Temperature.

## 4.1 Introduction

Understanding moisture sorption kinetics of food is valuable in selecting appropriate storage conditions, and evaluating moisture sorption during storage. Numerous kinetic models have been used for the kinetic sorption of foods which are broadly classified into theoretical and empirical models (Garcia et al., 2006). In general, theoretical models involve numerous functions and parameters which makes it to be complex, and thereby making it difficult to be used under most situations for practical calculations (Maskan, 2000; Igathenathane et al., 2009). On the other hand, Empirical models, such as the parallel exponential kinetic model (PEK), Exponential, Page, and Peleg models, are analytical models for prediction that have been successfully applied by several researchers due to their simplicities (Maskan, 2002; Casada, 2002; Kohler et al., 2003; ASABE Standards, 2006; Igathinathane et al., 2009).

PEK model have been used to accurately described sorption behaviour of some food (Madamba *et al.*, 1996, Rahman *et al.*, 1998, Tang *et al.*, 2008). Fast and slow exponential kinetics

processes which have characteristic times and moisture contents can be represented from the sorption kinetics (Morton & Hearle 1997). Okubayashi *et al.*, (2004) proposed that at the site of 'external' surfaces and 'amorphous' regions, the fast kinetic process is related to the fast moisture sorption, while at the 'inner' surfaces and 'crystallites' the sorption is related to slow kinetic process. However, Hill *et al.*, (2010) stated that there has not been a clear view and exact explanation as to what the two processes physically represent. The reciprocals of the characteristic times for the two kinetic processes are used to obtain rate constants.

Exponential model is another empirical model been used to describe the sorption kinetics of food. It is derived from first-order rate kinetics which states that rate of moisture sorption is proportional to the amount of departure of the instantaneous moisture from the final equilibrium moisture (Casada, 2002).

Another empirical model that is simple to use is the Page model (*ASABE Standards*, 2006), which is usually used in drying modeling. It is two parameter exponential model which was developed to overcome the shortcomings of exponential model by the introduction of exponent "n" (Iguaz *et al.*, 2003b). It has been applied to simulate the sorption kinetics of some foods such as carrots, vegetables and kiwi fruits (Iguaz *et al.*, 2003a; Doymaz, 2004; Simal *et al.*, 2005).

A two-parameter non-exponential empirical model was proposed by Peleg (1988) known as Peleg model. This is one of the most used models for water absorption kinetics of agricultural product due to its simplicity (Jideani & Mpotokwana, 2009). Its prediction accuracy had been tested for sorption processes of various food (Sopade & Obekpa, 1990; Palou *et al.*, 1994; Lopez *et al.*, 1995; Sopade & Kaimur 1999; Turhan *et al.*, 2002; Azoubel, & Murr, 2004.; Corzo, & Bracho, 2006; Cunningham *et al.*, 2007; Ganjiloo *et al.*, 2012). The constants of Peleg model have been used by many researchers to determine rate of sorption and some thermodynamics properties during sorption (Jideani & Mpotokwana, 2009; Shafaei *et al.*, 2016).

From literature research so far, it has been observed that there are little or no information about the sorption kinetics of Date fruits. As a result, due to the importance of sorption kinetics at some stages of food processing, there is a need for its determination. The objective of this work is to compare the suitability of parallel exponential kinetics (PEK) model, Exponential model, Page model and Peleg model for describing sorption kinetics of Sukkari Date Powder (SDP) over different temperature and relative humidity ranges. Furthermore, the evaluation of applicability of the model will also be discussed.

## 4.2 Materials and Methods

### 4.2.1 Sorption kinetics

In this study the Dynamic Vapour Sorption (DVS) apparatus was used to measure the water vapour sorption of Sukkari Date powder (SDP). It was carried out at temperatures of 20, 40 and 60°C within the range of 10-90% relative humidity (RH). A full description of the apparatus and the methodology has been reported by Abdullateef T. M. (2017). The kinetic curve is obtained by plotting mass gain (kg/kg db) against time.

### 4.2.2 Sorption kinetics model

The data obtained are then analysed and fitted with each target relative humidity level evaluated separately by considering the initial time  $t_0=0$  and sample mass  $M_0=0$  using four sorption kinetics models with the aid of curve fitting function in MATLAB.

#### 4.2.2.1 Parallel exponential kinetics (PEK) model

The evaluation of mass gain during the adsorption process will be based on the assumption of two parallel, independent sorption processes (slow and fast) by fitting the PEK model (eq.1) to the experimental data (Kohler et al., 2003). The mathematical form of the PEK model is given as:

$$M_t = M_1 \left(1 - e^{-\frac{t}{t_1}}\right) + M_2 \left(1 - e^{-\frac{t}{t_2}}\right) \quad (1)$$

$$EMC = EMC_0 + EMC_1 + EMC_2 \quad (2)$$

Where  $M_t$  is the mass at time  $t$  (kg/kg d.b),  $t$  is the time (hour),  $M_1$  and  $M_2$  are the masses at equilibrium at infinite time and  $t_1$  and  $t_2$  are the characteristic times for the two parallel sorption processes respectively.

PEK model can be used to determine the moisture content at infinite time ( $EMC$ ) by summing the cumulative moisture contents associated with the fast and slow kinetic processes and the moisture content at time zero as given by eq. 2

From eq. 1, the fast and slow processes are represented as eq. 3 and 4 respectively (Hill & Xie, 2010)

$$M_1 \left(1 - e^{-\frac{t}{t_1}}\right) \quad (3)$$

$$M_2 \left( 1 - e^{-\frac{t}{t_2}} \right) \quad (4)$$

#### 4.2.2.2 Exponential model

The experimental data was fitted to eq. 5

$$M_t = M_e - (M_e - M_0) \cdot \exp(-k_e \cdot t) \quad (5)$$

where  $M_e$  is the Pseudo Equilibrium Moisture Content (PEMC), which is the stable moisture content of the material after sufficient time of exposure to the test environment.  $M_t$  is the instantaneous moisture content of the material on dry basis (d.b) at any time  $t$ ,  $t$  is time of sorption (h),  $M_0$  the initial moisture content of the material (d.b), and  $k_e$  the sorption rate constant ( $\text{h}^{-1}$ ).

#### 4.2.2.3 Page model

Page model was fitted to the experimental data as reported by Igathinathane et al., (2009)

$$M_t = M_e - (M_e - M_0) \cdot \exp(-k \cdot t^n) \quad (6)$$

where  $k$  is the sorption rate constant ( $\text{h}^{-1}$ ) of Page model, and  $n$  is the exponent (dimensionless) of Page model.

#### 4.2.2.4 Peleg model

This model (eq. 7) was also fitted to the experimental data as described by Turhan et al., (2002) with little modification

$$M_t = M_0 + t / (k_1 + k_2 \cdot t) \quad (7)$$

where  $k_1$  is Peleg rate constant ( $(\text{mass of dry matter}) \cdot (\text{mass of water})^{-1} \cdot \text{h}$ ) that is inversely related to the initial rate of water absorption.  $k_2$  is Peleg capacity constant which is related maximum attainable moisture content ( $(\text{mass of dry matter}) \cdot (\text{mass of water})^{-1}$ )

The Peleg model has the advantage of determining the EMC and initial rate of sorption. The rate of sorption ( $R$ ) can be obtained from first derivative of the Peleg equation (Pavelkić et al., 2015).

$$R = \frac{dM}{dt} = \frac{k_1}{(k_1 + k_2 t)^2} \quad (8)$$

But at  $t = t_0$ , initial sorption rate,  $R_0$  gives a relationship (eq. 9) related to the Peleg's rate constant  $k_1$  which is the adsorption rate at the beginning (Turhan et al., 2002).

$$R_0 = \left. \frac{dM}{dt} \right|_{t_0} = \frac{1}{K_1} \quad (9)$$

And as  $t \rightarrow \infty$ , eq. 7 gives the relation between equilibrium moisture content ( $M_e$ ) and  $K_2$  which is the maximum attainable moisture content (Azoubel, & Murr, 2004.; Corzo, & Bracho, 2006).

$$M|_{\infty} = M_e = M_0 + \frac{1}{K_2} \quad (10)$$

### 4.2.3 Temperature dependence of model parameters

Arrhenius equation has been used by several researchers to explain the dependence of temperature on the fitted parameters of sorption models (Perry & Green, 1984, Igathinathane et al., 2009; Hill et al., 2010). The Arrhenius equation (eq. 11) is used to quantified the variation of each fitted models parameters (eqs. 1, 5, 6 and 7) with temperature.

$$P = A. \exp\left(\frac{E_a}{RT}\right) \quad (11)$$

where P is the parameter modelled and takes the parameters  $1/t_1$ ,  $k_e$ ,  $k$ ,  $n$ , and  $1/k_1$  with consistent units, A is the collision factor,  $E_a$  is the activation energy, R is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and T is the absolute temperature (K).

Taking natural logarithms of both sides of eq.11 gives;

$$\ln(P) = \ln(A) - \frac{E_a}{RT} \quad (12)$$

Thus, a plot of  $\ln(P)$  against  $(1/T)$  will yield a straight line of slope  $-E_a/R$ , from where the activation energy will be obtained.

Using the activation energy, other thermodynamic properties such as changes in enthalpy (eq. 13), entropy (eq. 14) and free energy of activation (eq. 15) is determined (Shafaei et al.,2016).

$$H = E_a - RT \quad (13)$$

$$\Delta S = R \left( \ln A - \ln \frac{K_B}{h_p} - \ln T \right) \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

where  $R$ , is universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) ;  $\ln A$ , is intercept of the curve from Eq. (12);  $K_B$ , is Boltzmann constant ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ );  $h_p$ , is Planck's constant ( $6.626 \times 10^{-34} \text{ J s}$ ); and  $T$  is absolute temperature (K).

### 4.3 Statistical Analysis

The criteria used to evaluate the best fitting model are coefficient of determination ( $R^2$ ), the sum of the Standard Square Error (SSE), the Root Mean Square Error (RMSE), and the relative Percent Error (PE) (Menkov, 2000; Viswanathan *et al.*, 2003).

For a good fit, the values of  $R^2$  must be the greatest, and the SSE and RMSE values must be the lowest (Demir *et al.*, 2004; Goyal *et al.*, 2006). The PE below 10 % indicate good fit (Roberts *et al.*, 2008). These are evaluated using the statistical function in Excel and MATLAB.

## 4.4 Results and Discussion

### 4.4.1 Sorption kinetics

Fig. 4.1 shows a change of the steps of relative humidity and the related kinetic sorption curves for the SDP at  $20^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $60^\circ\text{C}$ . It's worth noting that at equilibrium, the actual RH was slightly lower than the target RH. The water sorption rate of the powder quickly increased as the relative humidity increases as can be seen from fig.4.1. However, within any specific relative humidity range, the sorption rate gradually decreased with the elapse of time. Also, there is a finite time during which the RH changes from one stable value to the next. A typical example is shown in fig. 4.2 where it can be seen that a change of RH from 10 to 20% does not occur instantaneously. During this period, the moisture content of the sample is not moving towards a static equilibrium point, so the kinetics curve is affected during the transition time which can last for the first few minutes. Furthermore, with respect to temperature, over the full range of RH, the time for equilibrium to be reached increases as the temperature decreases (approximately 148h, 63h and 28hr for  $20^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $60^\circ\text{C}$  respectively). These trends have been similarly reported by many researchers (Kohler *et al.*, 2003; Hill *et al.*, 2010; Haerifar & Azizian, 2013). At constant RH (example 39.8%), the observed PEMC are 2.03%, 2.228% and 2.261% for  $20^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $60^\circ\text{C}$  respectively as can be seen in fig. 4.3. Furthermore, from fig 4.3-4.5, at constant RH, the time taken for the sorption kinetics reduces with increase in temperature and the moisture absorption rate was rapid at the initial period but slower in the following stages. This trend is a commonly

observed characteristics of agricultural materials (Abu-Ghannam & McKenna,1997; Maskan, 2002; Resio et al.,2006; Cunningham et al., 2007; Igathinathane et al., 2009; Shafaei et al., 2016).

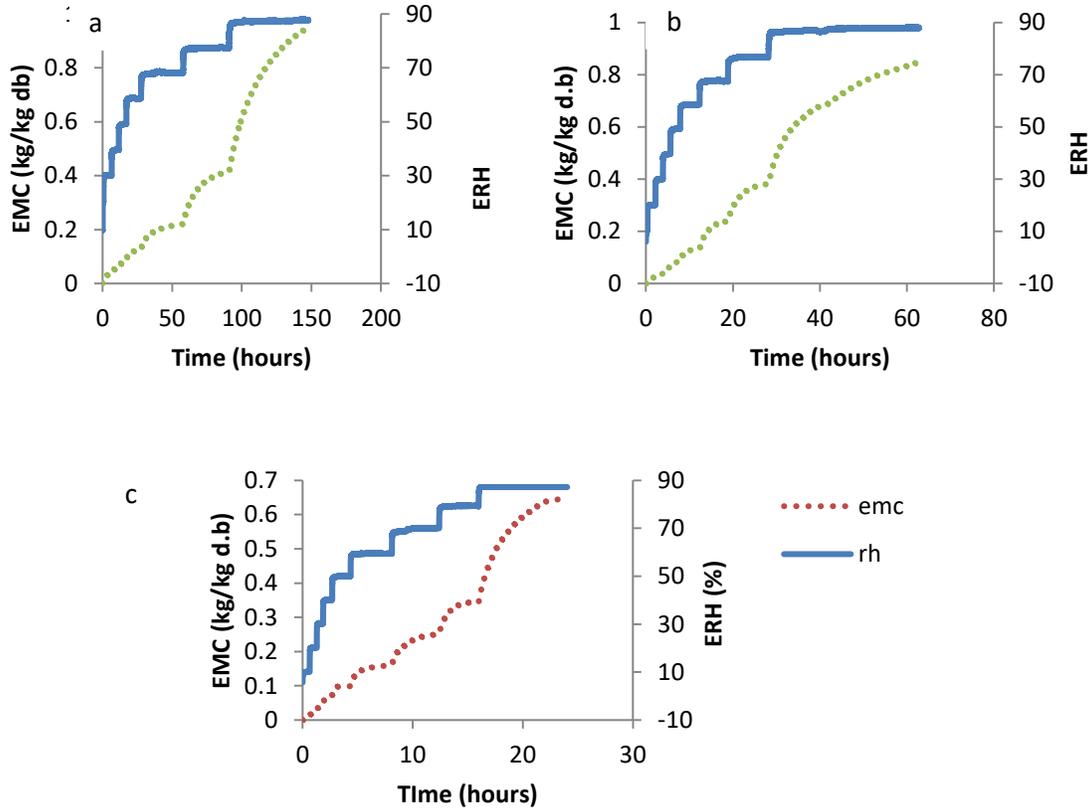


Figure 4.1 Kinetics of moisture content for Sukkari Date Powder over time profile of isotherm at different relative humidity and at a) 20 °C b) 40°C and c)60 °C.

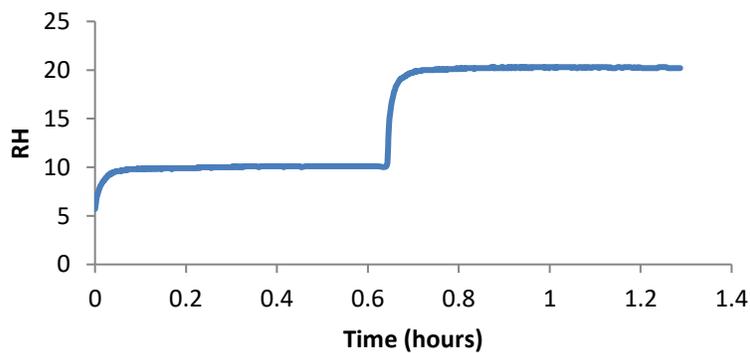


Figure 4.2 Typical example changes of relative humidity from 5 to 10 % and subsequently 10 to 20% during sorption process at 60 °C.

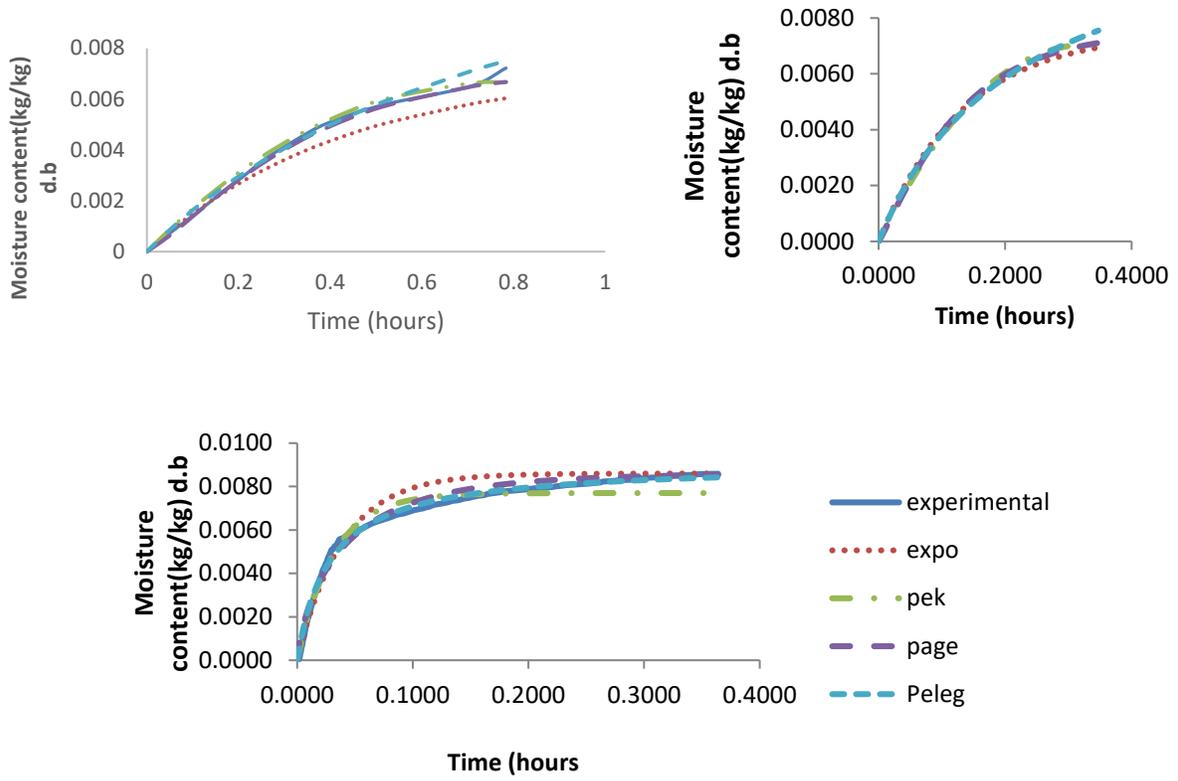
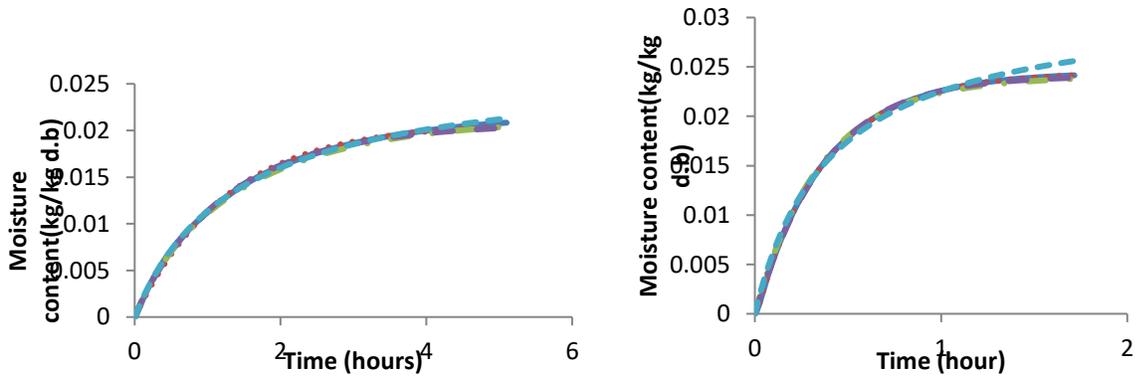


Figure 4.3 A representative example for a kinetic curve fit of the experimental data measured at RH level of 10% and at a) 20 °C b) 40°C and c) 60 °C the Sukkari Date powder.



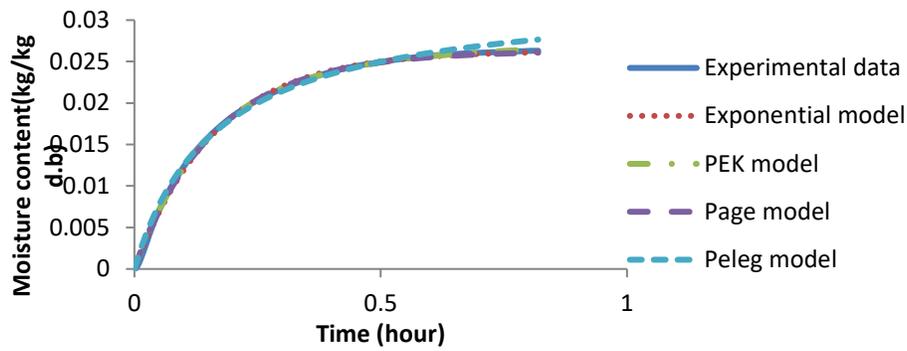


Figure 4.4 A representative example for a kinetic curve fit of the experimental data measured at RH level of 39.8% and at a) 20 °C b) 40°C and c) 60 °C the Sukkari Date powder.

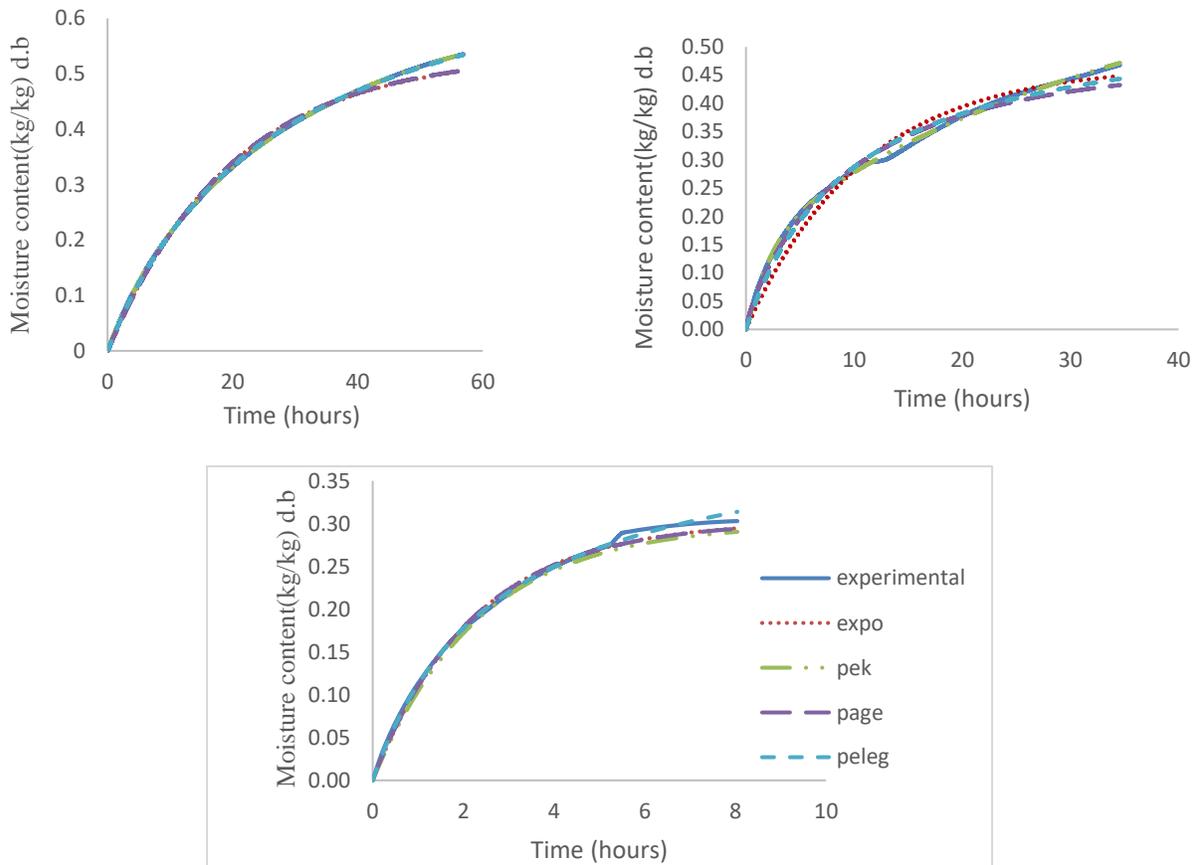


Figure 4.5 A representative example for a kinetic curve fit of the experimental data measured at RH level of 87.57% and at a) 20 °C b) 40°C and c) 60 °C the Sukkari Date powder.

#### 4.4.2 Performance and application of Sorption kinetics model in estimating moisture content of SDP

A representative example for the correspondence of the experimental data with the four sorption kinetic models at the three temperatures under study and RH level of 10%, 39.8%, and 87.57% for the SDP are presented in Fig. 4.3, 4.4 and 4.5 respectively. It can be observed through the statistical parameters as shown in table 4.1 that all the four models fit to the experimental data at constant RH ( $R^2 > 0.99$ , low SSE and RMSE).

PEK-model provides two distinct processes (i.e. fast and slow process), each with its characteristic times  $t$ , and equilibrium mass  $M_t$ , which allow the two processes and the total sorption curve for each humidity level to be calculated. The sorption isotherm obtained from the PEK fitting was used to determine the EMC using eq. 2 which was obtained by summing the cumulative moisture contents associated with the fast and slow kinetic processes and the moisture content at time zero in the adsorption (see Table 4.2). This shows that vapour sorption kinetic behaviour on SDP can be accurately described by the parallel exponential kinetics (PEK) model. The little differences which are not very significance can be associated to error due to transition time during change of RH from one step to another.

The sorption constants ( $k_e$ ,  $k$  and  $n$ ) of exponential and Page models indicate the ease of moisture sorption in the SDP, where quicker moisture uptake is indicated by their higher values (Igathinathane et al., 2009). Both  $k_e$  and  $k$  increase with increasing temperature while no significant effect of temperature was observed on  $n$ . These trends are common for moisture sorption of most agricultural products (Igathinathane et al., 2009).

Peleg rate constant  $k_1$  is stated to be related to the rate of mass transfer and is inversely proportional to initial moisture absorption rate i.e. the lower the value of  $k_1$ , the higher the initial absorption rate (Turhan et al., 2002). The  $k_1$  decreased with increasing temperature indicating increase in the initial water absorption. Since the reciprocal value of  $k_1$  describes the initial mass transfer rate (eq. 9), observed results indicate an increase of the initial mass transfer rate with increasing the temperature. Also, the Peleg capacity constant,  $k_2$  is related with emc, that is, the higher the emc, the lower the  $k_2$  (Corzo & Bracho, 2006; Mišljenović et al., 2010; Ganjloo et al., 2012).  $k_2$  increases with increasing temperature which indicates an increase in emc with temperature. Generally, it can be observed from table 1 that  $k_1$  and  $k_2$  showed inverse relation with

temperature. Similar trends have been reported for these constants by several researchers (Lopez et al., 1995; Sayar, Turhan, & Gunasekaran, 2001; Igathinathane et al., 2009).

#### **4.4.3 Temperature dependence of models constants**

Table 4.3 shows a typical example of the fitted constants of sorption models on Arrhenius equations for the SDP at constant RH of 39.8%. From the  $R^2$  values ( $>0.98$ ), all the four models fit well to the Arrhenius equation. However, further verification of all the models on other ranges of RH indicates that Peleg fits well than the other three models  $0.98 < R^2 \leq 0.998$ . Therefore, Peleg model was used for further calculations.

#### **4.4.4 Activation energy**

Fig 4.6 shows the activation energy for each RH step change, where the end values are represented as the RH value, i.e. a step change of 10-20% is represented by 10% and so on. The ranges of the activation energy ranges between 11.29-73.28 kJ/mol at lower RH values which then decrease at higher RH values. This could be as a result of presence of high proportion of water in the cell wall nanopores that is not intimately associated with the macromolecular OH content as reported by Hill et al., (2010). The reduced  $E_a$  at lower RH was also reported by Harding et al., (1998), where he stated that a reduction in  $E_a$  can be attributed to complete filling of pores by water.

#### **4.4.5 Effect of temperature on enthalpy, entropy and released energy**

The effects of temperature changes on enthalpy, entropy and released energy of the sorption process of SDP is presented in Tables 4.4. At constant RH, there is a positive reduction of enthalpy as the sorption temperature is increased showing no significant difference ( $P > 0.05$ ). During the sorption process, entropy increased with negative values (exothermic reaction) as the temperature increased, with no significant difference ( $P > 0.05$ ). The free energy of activation increases with as the temperature increased, with also no significant difference ( $P > 0.05$ ). The increment of the free energy of activation indicates the absorption of energy from surrounding area (Reusch, 2007). Similar trends have been reported by other researchers for bean, chickpea and barley (Jideani & Mpotokwana, 2009; Montanuci et al., 2013; Shafaei 2016).

Table 4.1 Sorption kinetic models at three different temperature and at different RH.

TEMPERATURE (°C)	MODELS	Constants	RELATIVE HUMIDITY (%)								
			10	20	30	39.8	49.5	58.89	68.53	77.83	87.57
20	Parallel Exponential Kinetic model	m <sub>1</sub>	3.307	-0.00021	0.01206	-0.01856	0.002836	0.03296	0.03035	0.02028	0.5385
		m <sub>2</sub>	-3.836	0.02429	0.002683	0.03869	0.01852	0.009708	0.06384	0.1829	0.1014
		t <sub>1</sub>	0.4707	0.1716	2.037	1.102	0.4615	2.252	1.412	1.488	34.63
		t <sub>2</sub>	0.5605	5.337	0.2787	1.255	1.677	0.004012	10.63	11.06	7.112
		SSE	7.19E-07	2.28E-08	3.17E-06	0.000104	1.54E-05	0.001096	0.000899	0.000268	0.007675
		R <sup>2</sup>	0.9875	1	0.9999	0.9982	0.9998	0.9964	0.9998	1	1
		RMSE	0.00032	1.50E-05	4.66E-05	0.000239	8.77E-05	0.000585	0.000357	0.000166	0.000587
		PE%	8.64	0.5	3.08	3.75	3.48	2.19	1.48	0.99	1.65
	Exponential model	k <sub>e</sub>	25.00281	0.530192	0.7242	0.6965	0.7255	0.5968	0.1749	0.1153	0.05018
		SSE	2.57E-06	4.56E-05	0.000231	8.40E-05	9.50E-05	0.03563	0.1652	0.102	1.601
		R <sup>2</sup>	0.9384	0.9401	0.9903	0.9986	0.9986	0.8838	0.9632	0.9965	0.9968
		RMSE	0.000594	0.000663	0.000397	0.000215	0.000218	0.003333	0.004843	0.003247	0.00848
		PE%	9.19	13.96	9.76	3.57	3.92	13.94	13.4	5.44	3.35
	Page model	k	78.12632	0.5302	0.7547	0.7049	0.7354	0.7319	0.2674	0.1329	0.04866
		n	1.29	0.9999	0.8629	0.9639	0.9574	0.6368	0.7479	0.9326	1.011
		SSE	3.63E-07	7.80E-06	4.27E-05	5.31E-05	4.76E-05	0.003457	0.006682	0.04587	1.579
		R <sup>2</sup>	0.9937	0.9898	0.9982	0.9991	0.9993	0.9887	0.9985	0.9984	0.9969
		RMSE	0.000201	0.000275	0.000171	0.000171	0.000154	0.001038	0.000974	0.002178	0.00842
		PE%	3.77	0.01	5.65	3.33	4.14	3.72	5.66	3.04	3.56
	Peleg model	k <sub>1</sub>	5.440894	181.1	77.33	59.94	54.39	22.69	41.83	37.8	34.81
		k <sub>2</sub>	70.24786	64.41	57.98	37.13	37.28	21.52	9.942	3.922	1.26
SSE		4.00E-07	4.04E-06	2.89E-05	3.98E-05	9.22E-05	0.009863	0.01361	0.01256	0.04676	
R <sup>2</sup>		0.9916	0.9947	0.9988	0.9993	0.9986	0.9678	0.997	0.9996	0.9999	
RMSE		0.000211	0.000198	0.000141	0.000148	0.000214	0.001754	0.00139	0.00114	0.001449	
PE%		6.33	8.27	4.86	3.15	4.84	6.98	4.11	2.14	1.97	
40	Parallel Exponential Kinetic model	m <sub>1</sub>	0.087322	0.005269	-0.8315	0.002645	-0.3485	0.01999	0.08441	0.007165	0.1598
		m <sub>2</sub>	-0.37964	0.0104	0.8432	0.02046	0.02509	0.02948	0.01406	0.141	0.5206
		t <sub>1</sub>	0.658874	0.8283	0.9434	0.2717	488.9	0.4268	2.154	0.3583	2.399
		t <sub>2</sub>	4.414	0.344	0.9118	0.4329	0.3963	1.202	0.3605	2.892	37.86
		SSE	2.87E-05	5.95E-06	0.000163	1.25E-05	5.97E-05	2.93E-05	0.001765	0.000446	0.2447
		R <sup>2</sup>	0.9267	0.9995	0.9923	0.9996	0.9986	0.9999	0.9991	0.9999	0.999
		RMSE	0.000607	8.97E-05	0.000448	0.000122	0.00024	0.000126	0.000704	0.000304	0.00364
		PE%	5.01	4.38	7.15	4.87	7	5.5	2.07	1.43	1.71
	Exponential	k <sub>e</sub>	7.495	2.293	2.617	2.506	2.624	1.266	0.6217	0.4027	0.09242

60		SSE	2.49E-06	1.78E-05	1.16E-05	1.52E-05	4.03E-05	0.00116	0.01106	0.01053	8.89
		R <sup>2</sup>	0.9936	0.9986	0.9995	0.9995	0.999	0.996	0.9947	0.9985	0.9624
		RMSE	0.000175	0.000155	0.000119	0.000134	0.000197	0.000793	0.001761	0.001475	0.02194
		PE%	8.41	5.08	5.3	4.92	6.95	6.79	53.8	2.57	9.94
	Page model	k	9.602	2.206	2.581	2.546	2.594	1.249	0.6455	0.4024	0.1487
		n	1.115	0.9569	0.9843	1.02	0.9857	0.9075	0.9366	1.001	0.8063
		SSE	7.05E-07	8.04E-06	9.68E-06	1.07E-05	3.74E-05	0.000145	0.007508	0.01052	3.421
		R <sup>2</sup>	0.9982	0.9994	0.9995	0.9997	0.9991	0.9995	0.9964	0.9985	0.9855
		RMSE	9.39E-05	0.000104	0.000109	0.000113	0.00019	0.000281	0.001451	0.001475	0.01361
		PE%	2.56	5.43	5.6	4.26	7.47	8.93	3.24	2.59	5.59
	Peleg model	k <sub>1</sub>	17.94	23.95	16.31	14.47	12.07	12.08	14.01	15.24	17.22
		k <sub>2</sub>	80.77	50.42	40.55	33.56	33.68	17.05	8.295	5.155	1.757
		SSE	8.83E-07	1.25E-05	6.65E-05	0.000173	0.000342	0.00068	0.003161	0.006664	3.464
		R <sup>2</sup>	0.9977	0.999	0.9969	0.9945	0.9918	0.9976	0.9985	0.999	0.9853
		RMSE	0.000105	0.00013	0.000286	0.000453	0.000575	0.000608	0.000942	0.001174	0.01369
		PE%	6.99	6.43	8.64	9.04	12.36	8.53	2.04	2.05	5.76
	Parallel Exponential Kinetic model	m <sub>1</sub>	-0.4852	0.004565	0.04226	0.01795	-0.00072	0.02656	0.08778	11.76	49.15
		m <sub>2</sub>	0.4929	0.01163	-0.5627	0.009298	0.02695	0.02461	0.01555	-11.65	-48.85
		t <sub>1</sub>	0.03104	0.2135	0.4059	0.1293	0.3749	0.2119	1.361	0.7756	2.175
		t <sub>2</sub>	0.03104	0.09572	45.79	0.3221	0.1775	0.9998	0.1207	0.7735	2.174
		SSE	0.000673	8.59E-06	0.000671	1.50E-05	1.31E-05	4.86E-05	0.001279	0.007283	0.1216
		R <sup>2</sup>	0.981248	0.9986	0.9471	0.9993	0.9996	0.9999	0.9991	0.9965	0.9959
		RMSE	0.001587	0.000158	0.001432	0.001572	0.000124	0.000163	0.000695	0.001622	0.004987
		PE%	4.52	8.42	14.92	6.57	4.09	2.58	2.17	4.8	4.99
Exponential model	k <sub>e</sub>	25.58	8.726	5.983	6.083	5.734	2.077	1.047	0.9454	0.4454	
	SSE	7.88E-05	1.08E-05	4.06E-05	2.58E-05	1.27E-05	0.007774	0.01956	0.004302	0.1468	
	R <sup>2</sup>	0.972958	0.9982	0.9968	0.9988	0.9996	0.9674	0.9867	0.9979	0.9951	
	RMSE	0.00054	0.000176	0.000351	0.000237	0.000122	0.002058	0.002715	0.001246	0.005478	
	PE%	8.61	8.3	12.78	6.39	4.53	6.87	6.11	2.95	3.43	
Page model	k	10.2649	8.392	6.785	5.863	5.744	1.817	1.06	0.9514	0.4511	
	n	0.7434	0.9809	1.076	0.9773	1.001	0.759	0.89	0.9783	0.9867	
	SSE	3.72E-05	9.99E-06	1.57E-05	2.16E-05	1.27E-05	0.000442	0.0109	0.003927	0.1446	
	R <sup>2</sup>	0.977078	0.9984	0.9988	0.999	0.9969	0.9981	0.9926	0.9981	0.9951	
	RMSE	0.000372	0.00017	0.000219	0.000218	0.000122	0.000491	0.002027	0.001191	0.005438	
	PE%	5.98	8.93	8.39	6.93	4.08	6.13	4.5	2.82	3.13	
Peleg model	k <sub>1</sub>	3.072	5.671	6.701	4.962	4.467	5.771	7.866	7.915	6.526	
	k <sub>2</sub>	110.3	50.51	31.52	30.33	32.95	17.87	8.136	7.164	2.375	
	SSE	1.74E-05	3.97E-05	5.68E-05	9.23E-05	0.000674	0.000118	0.006915	0.003167	0.02966	

	R <sup>2</sup>	0.9885	0.9935	0.9955	0.9957	0.9798	0.9995	0.9953	0.9985	0.999
	RMSE	0.000254	0.000338	0.000416	0.000449	0.00089	0.000253	0.001615	0.001069	0.002463
	PE%	4.22	12.76	14.91	9.79	10.66	2.43	3.85	2.35	1.57

PE% is percentage error, RMSE is Root mean square Error, SSE is the sum square error

**Table 4.2 Comparing the EMC of fast and slow process of PEK model with experimental data.**

Temp (°C)	RH (%)	Fast	Slow	EMC	
		EMC <sub>1</sub> (kg/kg d.b)	EMC <sub>2</sub> (kg/kg d.b)	EMC <sub>1</sub> + EMC <sub>2</sub> (kg/kg d.b)	EMC* (kgkg/ d.b)
20	10(0.004) <sup>a</sup>	0.0040	0.0028	0.0068(0.0006)	0.0066(0.0005)
	20(0.0025)	0.0062	0.0029	0.0092(0.0002)	0.0092(0.0021)
	30(0.0025)	0.0161	0.0030	0.0191(0.0001)	0.0191(0.0019)
	39.6(0.0025)	0.0172	0.0032	0.0204(0.0031)	0.0208(0.0021)
	49.3(0.002)	0.0171	0.0057	0.0227(0.001)	0.0228(0.0081)
	58.7(0.0025)	0.0327	0.0097	0.0424(0.0012)	0.0438(0.00241)
	68.2(0.0015)	0.0654	0.0300	0.0954(0.0031)	0.0962(0.00984)
	77.4(0.0005)	0.1759	0.0174	0.1933(0.0082)	0.1931(0.0327)
	87.7(0.0005)	0.4344	0.1014	0.5358(0.0012)	0.5356(0.0687)
40	10(0.001)	0.0040	0.0034	0.0074(0.0002)	0.0075(0.0003)
	20(0.0034)	0.0107	0.0051	0.0158(0.0024)	0.0158(0.00016)
	30(0.002)	0.0078	0.0062	0.0140(0.0008)	0.0139(0.0038)
	39.7(0.004)	0.0180	0.0058	0.0238(0.001)	0.0241(0.0012)
	49.2(0.005)	0.3947	0.0031	0.3977(0.001)	0.0203(0.0031)
	58.5(0.0045)	0.0288	0.0200	0.0488(0.005)	0.0486(0.0069)
	67.4(0.013)	0.0973	0.0122	0.1094(0.024)	0.1083(0.012)
	76.6(0.013)	0.1354	0.0072	0.1425(0.014)	0.1417(0.0024)
	87.8(0.0085)	0.3118	0.1598	0.4716(0.12)	0.4676(0.104)
60	10(0.002)	0.0007	0.0084	0.0091(0.008)	0.0086(0.0004)
	20(0.0035)	0.0080	0.0073	0.0154(0.001)	0.0152(0.0037)
	30(0.001)	0.0213	0.0015	0.0228(0.004)	0.0225(0.0015)
	40.1(0.0015)	0.0179	0.0086	0.0265(0.0002)	0.0263(0.0031)
	50(0.0025)	0.0527	0.0291	0.0817(0.0001)	0.0261(0.0042)
	59.4(0.002)	0.0266	0.0239	0.0505(0.0004)	0.0509(0.017)
	70(0.002)	0.0822	0.0155	0.0977(0.0001)	0.0907(0.004)
	79.5(0.011)	0.0904	0.0039	0.0944(0.0002)	0.0932(0.018)
	87.2(0.006)	0.2686	0.0427	0.3113(0.002)	0.3030(0.02)

a- values are represented by their means and the one in parenthesis represent standard deviation

\*From experimental data (Abdullateef, T.M., 2017)

**Table 4.3 Arrhenius type relationship fitted constants of models parameters of Sukkari Date Powder at 39.3% RH.**

Models	Constants	E <sub>a</sub> (KJ/mol)	R <sup>2</sup>
Exponential model	k	44.06	0.9954
PEK	1/t <sub>1</sub>	43.70	0.9809
Page	k	43.10	0.9928
Peleg	1/k <sub>1</sub>	50.61	0.998

**Table 4.4 Thermodynamic parameters of Sukkari Date Powder**

RH*	Temperature (°C)	ΔH (KJ/mol)	ΔS (J/Kmol)	ΔG (KJ/mol)
10.00%	20	8.86	-317.63	101.92
	40	8.69	-318.18	108.28
	60	8.52	-318.7	114.65
20.00%	20	70.85	-38.40	82.10
	40	70.68	-38.95	82.87
	60	70.51	-39.46	83.66
30.00%	20	47.38	-110.22	79.68
	40	47.22	-110.77	81.89
	60	47.05	-111.28	84.11
39.80%	20	48.17	-105.81	79.18
	40	48	-106.36	81.3
	60	47.84	-106.87	83.43
49.50%	20	48.40	-104.01	78.88
	40	48.24	-104.56	80.97
	60	48.07	-105.08	83.06
58.89%	20	25.24	-176.50	76.96
	40	25.08	-177.05	80.49
	60	24.91	-177.56	84.04
68.53%	20	31.63	-159.01	78.22
	40	31.46	-159.56	81.41
	60	31.30	-160.07	84.60
77.83%	20	29.34	-166.32	78.07
	40	29.17	-166.87	81.40
	60	29.01	-167.38	84.74
87.57%	20	31.35	-159.435	78.07
	40	31.19	-159.984	81.26
	60	31.02	-160.499	84.47

\*mean value of RH

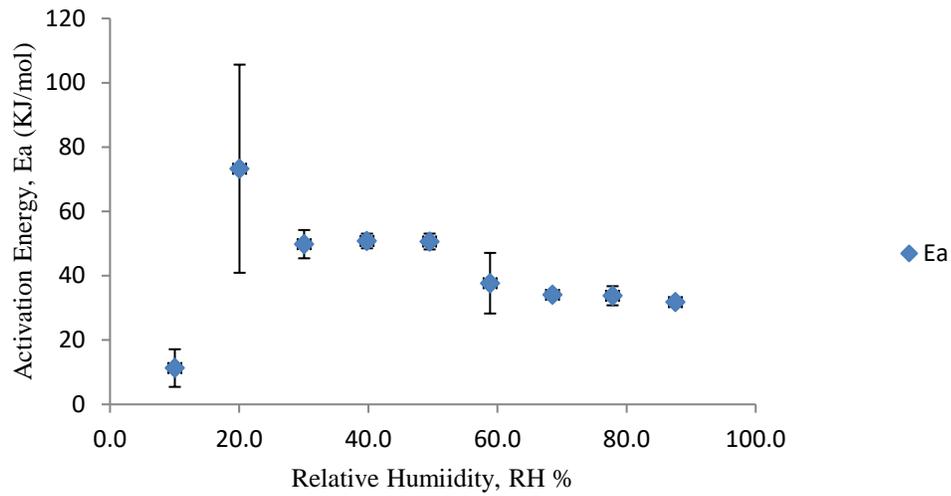


Figure 4.6 Activation energy of Sukkari Date powder at different RH.

#### 4.5 CONCLUSION

All the four models fit well to the experimental data which indicates that they can be used to predict the sorption kinetics of Sukkari Date powder. Peleg model is the best model for describing the effect of temperature over the RH under studied which was obtained with the aid of Arrhenius equation. Activation energy of sorption process of SDP ranges between 11.29-73.28 kJ/mol at lower RH values which then decrease at higher RH values. At constant RH, the enthalpy decreases with increase in temperature with no significant difference. While entropy and free energy of activation increases with increase in temperature.

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## CHAPTER FIVE: Conclusion and Recommendations

### 5.1 Summary and Conclusion

The objectives of this research was achieved as Sukkari date powder was produced in pilot-scale and some of its physical properties, vapor sorption isotherms, thermodynamic properties and sorption kinetics were determined. This research can be summarized in the following points;

The majority of the powders produced from Sukkari Date cultivar are moderately fine particle sizes. Bulk density, tapped density, compressibility index, Hausner ratio, moisture content and water activity were found to increase as the particle sizes reduces except for very fine sizes which reduces. Color analysis parameters [lightness ( $L^*$ ),  $a^*$  (greenness – redness),  $b^*$  (blueness–yellowness), chroma ( $C^*$ ), hue angle ( $H^\circ$ ), Browning index (BI) and total color (E)] also increases as the particle sizes reduces. While Electrical conductivity reduces as the particle sizes decreases and pH, show no significant difference for the different particle sizes. Water Absorption Index, Water Solubility Index and Oil Holding Capacity were also found to increase as the particle sizes reduce sizes with slight significant differences for the first and no significant differences for the latter two.

Adsorption isotherm of the date powder determined within the range of 0.1 to 0.9 ( $\pm 0.4$ ) water activities and at three different temperatures (20, 40 and  $60^\circ\text{C} \pm 0.2$ ) shows a curve of type III shape with a more or less sigmoid shape. As water activity increases, the moisture adsorption was found to increase especially at high water activity. The effect of temperature result to that as equilibrium moisture content (EMC) increases, the temperature increases at constant low water activity, but from around 0.70 water activity, an increasing EMC as the temperature reduces was observed. The Modified BET, Modified Oswin, Modified GAB and Modified Halsey fitted well to the experimental data throughout the entire range of water activity at the three temperature ranges studied, however, Modified Bet model was found to be the best model.

For sorption thermodynamics, net Isosteric heats of adsorption, Heat of sorption (differential enthalpy) and differential entropy were found to decrease with an increase in moisture content. Monolayer moisture content and spreading pressure was found to decrease as the temperature increases. However, spreading pressure increases with increasing water activity but with a slow increment at less than  $0.5a_w$ . While Net integral enthalpy and Net integral entropy were found to decrease with increase in moisture content.

For sorption kinetics, Peleg model is the best model for describing the effect of temperature over the RH under studied which was obtained with the aid of Arrhenius equation. Activation energy of sorption process of SDP ranges between 11.29-73.28 kJ/mol at lower RH values which then decrease at higher RH values. At constant RH, the enthalpy decreases with increase in temperature with no significant difference. While entropy and free energy of activation increases with increase in temperature.

Generally, it can be concluded that particle sizes have significant effect on most of the aforementioned physical properties. Also, for good storage, Sukkari Date powder should be stored at RH of less than 50%, less than 10% d.b. moisture content and a temperature of less than 40°C.

## **5.2 Recommendations**

Since the majority of the powders produced from Sukkari Date cultivar are moderately fine particle sizes which are use majorly in this research, it is recommended to carry out the test on various particles sizes especially in the sorption isotherms, to determine its effect on particle sizes. Also, it is recommended to carry out further research on other Cultivars of Dates for below and above studied temperature.