THERMODYNAMIC PROPERTIES AND MOISTURE EQUILIBRIUM CHARACTERISTICS OF RAPESEED (CANOLA) DURING MULTIPLE ADSORPTION AND DESORPTION CYCLES

BY

WEIHUA YANG

A thesis
presented to the University of Manitoba
in partial fulfilment of the requirements for the
degree of
MASTER OF SCIENCE

DEPARTMENT OF AGRICULTURAL ENGINEERING
THE UNIVERSITY OF MANITOBA
WINNIPEG, MANITOBA

JUNE 1992

National Library
of Canada

Bibliothèque nationale
du Canada

Acquisitions and
Bibliographic Services Branch

Direction des acquisitions et
des services bibliographiques

395 Wellington Street
Ottawa, Ontario
K1A 0N4

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-77870-9

Canada

THERMODYNAMIC PROPERTIES AND MOISTURE EQUILIBRIUM CHARACTERISTICS OF RAPESEED (CANOLA) DURING MULTIPLE ADSORPTION AND DESORPTION CYCLES

BY

WEIHUA YANG

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

ABSTRACT

Thermodynamic properties, including the Gibb's free energy changes, isosteric heat of sorption, latent heat of vaporization, entropy of sorption, and monolayer coverage, and moisture equilibrium characteristics, including isotherm and hysteresis behaviour, hygroscopicity variations, and isotherm equations, of rapeseed (Canola) during multiple adsorption and desorption cycles have been scrutinized in this study. For ambient-air (25°C) dried canola, the Gibb's free energy, isosteric heat and entropy of sorption became, on the whole, less negative at moisture contents below 8.00 %db at the equilibrium temperatures of 3.5, 25.0 and 40.0°C with the increased number of adsorption and desorption cycles. At moisture contents above 8.00 %db, the effect of multiple adsorption and desorption cycles was not significant. For heated-air (50°C) dried canola, little effect of multiple adsorption and desorption cycles was found on the Gibb's free energy changes. Postulation was made to explain why the effect of multiple adsorption and desorption cycles on the Gibb's free energy was little for heated-air dried canola. Latent heat of vaporization of four rapeseed (canola) varieties: Westar, Tobin, Global, and Candle ranged from 44 to 152 kJ/mole at moisture contents between 4.0 and 22.0 %db, temperatures between 4 and 75°C, and multiple drying and rewetting cycles between 1 and 5. The magnitude of latent heat for these four rapeseed (canola) varieties was ranked as follows in ascensive order: Candle, Global, Tobin and Westar. The constant **a** in Eq.(11) was found to be the predominant factor to reflect the effect of multiple adsorption and desorption cycles on latent heat of vaporization of canola. The BET monolayer coverage values for canola ranged from 2.90 to 3.40 %db at the equilibration temperature of 25.0°C and on five consecutive drying and rewetting cycles. Increase in both the number of the successive moisture treatment cycles and the equilibration temperature were found to decrease the monolayer coverage of canola, as well as its hygroscopicity especially at the relative humidities below 75%. It was statistically shown that the Henderson and Chung-Pfost isotherm models were inferior to the Halsey equation. A new empirical equation was proposed based on the Halsey equation, and was proven to be better than the Halsey equation in terms of the goodness-of-fit criteria of 56 adsorption and desorption isotherms of rapeseed (canola) involving four varieties, equilibration temperatures from 4 to 75°C, relative humidity from 13 to 93%, and drying and rewetting cycles from 1 to 5. A new theory was developed in this thesis to account for the origin of sorption hysteresis. The characteristic hysteresis behaviour of canola during multiple adsorption and desorption cycles were explained in terms of the hydrophillic and hydrophobic interaction between water molecules and lipid and protein particles forming a lipid-protein complex typical of rapeseed (canola) and other oil seeds.

ACKNOWLEDGEMENTS

First of all, I wish to thank my advisor, Dr. S. Cenkowski, for his brilliant guidance, consistent encouragement, and considerateness throughout various phases of this study.

I would also like to thank Dr. W. Muir and Dr. J. A. Oleszkiewicz for the suggestions and critism they gave, and the time they spent during their serving on my thesis committee.

Thanks are also due to Mr. J. Putnam and M. McDonald for their technical suggestions and assistance during this study.

I acknowledge Natural Sciences and Engineering Research Council of Canada and The Department of Agricultural Engineering, University of Manitoba for providing financial assistance for this study.

A special thanks should go to my fiancee, Mei Tang, for her emotional support and consistent encouragement throughout the period of this study.

Finally, to colleagues, fellowmates, and friends whose contributions vary from the pertinent discussions, valuable advice, comments, and cordial encouragement, I hereby extend my sincere appreciation.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

σ - Surface tension

Θ - The angle of contact

$-$ - Denotes differential quantities when used as overhead bar

1 - Denotes the condensed phase when used as subscript

a - Denotes the sorbent phase when used as subscript, and a constant when used by itself

a_w - Water activity, decimal

A - Constant

B - Constant

b - Constant

C - Constant

d - Differential sign

∂ - Partial derivative

E - Energy of condensed phase, J

Σ - Summation

F - Free energy, J/mole

ΔF - Gibb's free energy change, J/mole

G - Denotes gaseous phase when used as subscript

H - Integral enthalpy, J

h - Molar enthalpy, J/mole

L - Latent heat of vaporization for the sorbed water, J/mole

L', Q_{vap} - Latent heat of vaporization for free water, J/mole

m - Equilibrium moisture content, % dry basis

N - number of moles

P - Hydrostatic pressure, or the vapour pressure of liquid over curved meniscus, Pa

p - Saturation vapour pressure for the water sorbed a material, Pa

p', P_0 - Saturation vapour pressure for free water, Pa

p_w - Vapour pressure of the water sorbed in a material, Pa

p_{sw}- Vapour pressure of pure supercooled water, Pa

Q_{st}- Isosteric heat of sorption, J/mole

Q_{net}- Net isosteric heat of sorption, J/mole

R - Universal gas constant

r_1, r_2 - Principal radii of curvature of the liquid-vapour interface

r_m - Mean radius of curvature of the meniscus

S - Integral entropy, J/mole K

s - Molar entropy, J/mole K

ΔS - Differential entropy of sorption, J/mole K

ΔS_{net} - Net differential entropy of sorption, J/mole K

T - Absolute temperature

Γ - N_1/N_a

V - Volume of condensed phase, m^3

v - molar volume, m^3/mole

μ_i - Chemical potential of any species in a system, $i=1, 2, \cdots, n$

1. INTRODUCTION

Over the past three decades, world production of rapeseed has been expanding by significantly increasing amounts. According to FATUS (1990), the global throughput of rapeseed in 1989 was 22 million tonnes, which amounted almost six times that in 1960. Canola, containing low levels of erucic acid and glucosinolates, is one of the major rapeseed species in the world. It is also one of the most important crops in Canada, especially from late 1960's and early 1970's when the major cash crops grown in North America, corn and wheat, faced the problem of oversupply which caused farmers to consider other alternatives like rapeseed including canola (Moysey 1973). The drying, handling, post-harvest processing, and long-term storage of canola are therefore of primary significance. A thorough knowledge of physical, chemical, mechanical and thermodynamic properties of canola is imperative to optimize the drying and processing related operations and to improve quality control during storage and handling.

There have been broad research programs conducted in many countries for rapeseed including canola. The scope of research work covers such aspects as the equilibrium moisture content - equilibrium relative humidity (EMC-ERH) relationship (Pichler 1957; Timbers and Hocking 1974; Pixton and Warburton 1977; Rao and Pfost 1980; Pixton and Henderson 1981; Sokhansanj et al. 1986; Jayas et al. 1987a; Otten et al. 1990; Yang and Cenkowski 1991), moisture sorption kinetics and drying characteristics (Sharma and Muir 1973; Singh et al. 1983; Sokhansanj et al. 1983;

Sokhansanj et al. 1984; Otten et al. 1989; Cenkowski et al. 1990d; Shatadal et al. 1990), physical properties (Moysey et al. 1977; Jayas and Sokhansanj 1985, 1986, 1989; Jayas et al. 1986, 1987b, 1989), oil composition, chlorophyll content and mineral distribution (Mills and Chong 1977; Pixton and Warburton 1977; Clear and Daun 1985; Cenkowski et al. 1989a, 1990b), microbial infestation and quality control (Mills and Sinha 1980; White and Jayas 1989), the effect of pretreatments on EMC and sorption hysteresis (Bielewicz 1991; Bielewicz et al. 1991; Yang and Cenkowski 1991), and mechanical and rheological properties (Davison et al. 1975; Cenkowski et al. 1990a, 1991; Bielewicz 1991). However, the thermodynamic properties and the moisture equilibrium characteristics of canola during various handling, processing, and storage processes are still unexplored. Especially, the thermodynamic quantities and the moisture equilibrium characteristics of canola during multiple adsorption (rewetting) and desorption (drying) (A/D) cycles are in need of considerable research and exploration.

The multiple adsorption and desorption cycles should be stressed because of its frequent encounter in the storage, processing and research stages of rapeseed. There are a number of factors in the post-harvest handling, drying, storage and research phases which can cause multiple adsorption and desorption cycles to occur. Canola in a swath can easily become wet again due to rain or dew during its field-drying. Mixing different batches of canola prior to drying and relocation of dried canola in storage bin can cause moisture migration and redistribution (Cater and Farrar 1943). This involves steadily proceeding adsorption and desorption processes. Rain, snow and humid air from a roof leak or ventilation openings could cause adsorption or even 'wet pockets' to occur (Wallace and Sinha 1962; Muir et. al 1978, 1980). On the other hand, desorption could take place in exchange of moisture with dry air. Temperature differentials have been reported to cause the movement of moisture in stored grain (Anderson et al. 1943; Ampratwum and McQuitty 1970). Also, insect infestation can cause an unbalance of moisture in a grain bulk (Christensen and Kaufmann 1969). The heat generated within a pocket of wet mouldy grain can provide a favourable environment for further growth of microorganisms (Zhang et. al 1991). As a result, the grain moisture becomes even more unbalanced. In grain drying simulation tests, researchers from time to time recycle the same batch of sample that has been repeatedly used. This is achieved by rewetting the sample after it has gone through previous drying tests.

It has been reported that successive adsorption and desorption cycles can change the thermodynamic properties of rice (Benado and Rizvi 1985), sorptive capacity of hyaluronic acid II (Block and Bettelheim 1970), and many other sorption equilibrium characteristics including isotherms and hysteresis behaviour (Kapsalis 1981, 1987). However, little is known at present about the effects of multiple adsorption and desorption cycles on the thermodynamic properties and the moisture equilibrium characteristics of canola. This information is crucial to the predictability of drying models of canola, the energetics of dehydration process of canola, the physical, chemical, and biological properties of canola, and the stability of canola during its storage. Therefore, investigation of the thermodynamic parameters, such as free energy changes, isosteric heat of sorption, and entropy of sorption, and moisture equilibrium characteristics, such as EMC-ERH relationship, hysteresis behaviour, and hygroscopicity variation, of canola during multiple adsorption and desorption cycles is of practical significance.

2. OBJECTIVES

The objectives of this study were: (i) to measure moisture sorption isotherms and to determine hysteresis magnitude and patterns for canola subjected to a cyclic drying and rewetting pretreatment; (ii) to calculate and investigate thermodynamic quantities including the Gibb's free energy change, isosteric heat, and entropy of moisture sorption of canola during multiple adsorption and desorption cycles based on the isotherms obtained in the present study and reported by other researchers; (iii) to study the effect of sequential adsorption and desorption cycles on the latent heat of vaporization for canola; (iv) to study the effect of repeated drying and rewetting cycles and temperature on monolayer coverage of canola; (v) to study the effect of successive adsorption and desorption cycles on hygroscopic equilibrium characteristics of canola; and (vi) to test the suitability of most isotherm models popular for foods and crops to the isotherms of rapeseed (canola), and to propose a versatile empirical equation that would fit the isotherms of rapeseed (canola) in a wide range of relative humidity and temperature and on each of the successive adsorption and desorption cycles.

3. LITERATURE REVIEW

3.1. Thermodynamics of Moisture Sorption

3.1.1 General Retrospect

Thermodynamic functions have been successfully related to the behaviour of water both on the surface and in the interior of a biological material by many investigators, in an attempt to account for the binding state of water, the energetics of dehydration and the rate of quality deterioration. Hill (1949, 1950, 1952), Everett (1950), Greg and Sing (1967), Ponec et al. (1974) and others had elucidated the fundamental and practical aspects of the thermodynamic relationship in sorption phenomena. These elucidations provide a criterion that enables a comparison of results from different researchers. Up-to-date reviews by Rizvi and Benado (1984) and Kapsalis (1987) have highlighted the frontier work of the hysteresis-related thermodynamics and the thermodynamics of dehydrated foods.

3.1.2 Free Energy Changes

Gibb's free energy reflects the energy level required to transfer water vapour to the surface or interior of a solid from its surroundings, or vice versa. Gibb's free energy (ΔF) can be expressed as:

$$\Delta F = \Sigma \mu_i$$

where μ_i is the chemical potential of any species in a system. Babbitt (1942) calculated the free energy and heat of adsorption of water by cellulose. Free energy changes related to the moisture sorption process of protein were calculated by Bull (1944). Furthermore, Dole and McLaren (1947) derived equations for free energy changes for sorption following a linear, Langmuir or Brunauer-Emmett-Teller (BET) isotherm. Differential free energy of adsorption, as well as the differential enthalpy and entropy of adsorption, involved in a pectic substances-water system was calculated and interpreted by Bettelheim and Volman (1957). The same thermodynamic functions of water on starch were also calculated and related to structural changes for dextrin, amylose and amylopectin by Volman et al. (1960). Chung and Pfost (1967a) reported the free energy changes and the heats of sorption for corn hull, corn gluten, corn germ and corn starch. Strasser (1969) observed that there were more pronounced difference in free energy between desorption and adsorption and smaller free energy values for the beef immediately after freeze drying than for that stored for one year. Lai et al. (1985) compared the above-mentioned thermodynamic functions between whole egg powder (WEP) and dried whole eggs with corn syrup and salt (CEP). It was found that the thermodynamic parameters for WEP were less negative than for CEP under the same conditions. This suggested that WEP had less active sites within a more random structure. Yang and Cenkowski (1991) reported that there was significant difference in free energy change existing between the first and the fifth drying and rewetting cycle for canola dried at 25°C prior to moisture equilibrium at 25.0°C. Whereas, almost no differences were observed between any two of the five consecutive A/D cycles for canola dried at 50°C prior to moisture equilibrium at the same temperature.

3.1.3 Isosteric Heat of Sorption

The isosteric heat of sorption is considered to be indicative of intermolecular attraction forces between sorbates and sorbents. It has been used in the study of the degree of irreversibility (Kingston and Smith 1964; Bettelheim et al. 1970; Iglesias et al. 1976b), in calculation of drying time and energy requirements for moisture removal (Roman et al. 1982) and in equipment design (Almasi 1978). In general, heat of desorption curves lie above those of adsorption to form a closure of lost work in a system exhibiting sorption hysteresis. The heat of sorption is low at extremely low moisture content, since water is absorbed on the most accessible sites on the external surface of a solid (Bettelheim et al. 1970). As the moisture content increases towards the monolayer coverage value, the heat of sorption increases dramatically due to the structural transitions, resultant from solubilization and swelling, of the absorbent. As the result of solubilization and swelling, new high sorptive sites for water binding are exposed (Berlin et al. 1970b; Bettelheim et al. 1970; Benado and Rizvi 1985). The heat of sorption passes its maximum around monolayer coverage as the high energy sites are covered, and declines as moisture content is extended into multiple layer adsorption region until it approaches that of free water. This phenomenon corresponds to the discontinuities in the X-ray pattern behaviour as found by Guilbot et al.(1961) with starch. More than one peak could be found in a heat of sorption curve such as the case of water adsorption on enzymatically deesterified sodium pectate and pure pectic acid (Bettelheim and Volman 1957). This indicated that new high binding sites were opened in succession to those around monolayer coverage. At very high degree of sorption, it was postulated that there might be such a region in the heat of sorption curves where the heat of adsorption will become higher than that of desorption in order to comply with the law of energy conservation (Benado and Rizvi 1985). Giacobee et al. (1971) recorded a phenomenon closely related to the above supposition. The heat of adsorption of porous glass plus preadsorbed water sorbing argon began to traverse higher than that of desorption at the argon concentration of about 6 x 10^{-3} mol/g.

The derivation of the isosteric heat of moisture sorption starts from the standard results of solution thermodynamics (Hill 1950):

$$dE = TdS - PdV + \mu_1 dN_1 + \mu_a dN_a \tag{1}$$

$$dF = -SdT + VdP + \mu_1 dN_1 + \mu_a dN_a \tag{2}$$

$$d\mu_1 = -\bar{S}_1 dT + \bar{V}_1 dP + \left(\frac{\partial \mu_1}{\partial \Gamma}\right)_{T,P} d\,\Gamma \tag{3}$$

where: E - energy of condensed phase,
S - entropy of condensed phase,
V - volume of condensed phase,
P - hydrostatic pressure,
T - absolute temperature,
μ_a,μ_1 - chemical potential of sorbent and sorbed water respectively,
N_a,N_1 - moles of sorbent and sorbed water respectively,
Γ - N_1/N_a, and

$$\bar{S}_1 = \left(\frac{\partial S}{\partial N_1}\right)_{N_a P,T}, \quad \bar{V}_1 = \left(\frac{\partial V}{\partial N_1}\right)_{N_a P,T}$$

The overhead bars indicate differential quantities. Here, the hydrostatic pressure refers to the pressure exerted by a hypothetical inert piston or by a hypothetical inert additional gas on the sorbate-sorbent system (Hill 1950). For a gas, there exists the well-known expression (Young and Crowel 1962; Hill 1952):

$$d\mu_G = -s_G dT + v_G dp$$

where the subscript G denotes gas phase, $s_G = S_G/N_G$, $v_G = V_G/N_G$, and p is the saturation vapour pressure. When the vapour is in equilibrium with the sorbed water, $d\mu_1 = d\mu_G$. Setting Γ constant, we have:

$$-\overline{S}_1 dT + \overline{V}_1 dP = -s_G dT + v_G dp \tag{4}$$

Considering only a two-component system, the hydrostatic pressure, P, is equivalent with the saturation vapour pressure, p. Thus, Eq.(4) can write as:

$$\left(\frac{dp}{dT}\right)_\Gamma = \frac{(s_G - \overline{S}_1)}{(v_G - \overline{V}_1)} \tag{5}$$

If the water vapour is treated as a perfect gas and the volume of the sorbed water is neglected, Eq.(5) becomes:

$$\left(\frac{dp}{dT}\right)_\Gamma = \frac{(s_G - \overline{S}_1)}{v_G} = \frac{(s_G - \overline{S}_1)}{(RT/p)} \tag{6}$$

where R is the universal gas constant. Since in equilibrium,

$$s_G - \overline{S}_1 = \frac{h_G - \overline{H}_1}{T}$$

Eq.(6) can accordingly be reshaped as:

$$\left[\frac{d\ln p}{d(1/T)}\right]_{\Gamma} = -\frac{(h_G - \overline{H}_1)}{R} = -\frac{Q_{st}}{R} \qquad (7)$$

where Q_{st} is the isosteric heat of sorption.

3.1.4 Latent Heat of Agricultural Products

Latent heat of vaporization is actually the transformation of isosteric heat of sorption. The predictability of drying models, the energy consumption related estimation, and the drying equipment design are highly dependent on latent heat of vaporization. These factors, therefore, stress the importance of latent heat data for agricultural materials. This is particularly important at low moisture content of agricultural materials, because it is thought that above 12 % dry basis (db) moisture content there is little difference between the latent heat of water in the materials and that of free water. Below this level the energy needed to evaporate crop moisture increases dramatically due to the altered water binding properties (Boyce 1965). The latent heat can be measured directly with a calorimetric method. However, latent heat is mostly obtained by applying the Clausius-Clapeyron equation to the sorption isotherms at different temperatures. Eq.(7) can be rearranged as:

$$\frac{d\ln p}{L} = -\frac{d\frac{1}{T}}{R} \qquad (8)$$

where the latent heat, L, is in place of the isosteric heat of sorption Q_{st}. Since the right-hand side of Eq.(8) will be the same for any substance at the same temperature, Othmer (1940) obtained the following formula to correlate latent heat data with vapour pressure:

$$\mathrm{Ln}\ P = (L/L')\ \mathrm{Ln}\ P' + C \qquad (9)$$

where P and P' are vapour pressures for the crops and the pure water, L and L' are the latent heat for the crops and the pure water, and C is a constant of integration. Thompson and Shedd (1954) used this formula to calculate the latent heat of shelled corn and wheat. Gallaher (1951) found the latent heat ratio (L/L') for wheat is of the following relationship with equilibrium moisture content (m): $L/L' = 1 + a \exp(bm)$, with the constants a and b being 23 and -0.4 respectively. This relationship applies to many other crops, such as malt with $a=0.5904$ and $b=-0.1367$ (Bala and Woods 1984), barley with $a=23$ and $b=-40$ (Boyce 1965; Ingram 1976), canola with $a=4.7$, $b=-44.2$ for $m \leq 7.5$ %db and $a=0.5$, $b=-14.5$ for $m > 7.5$ %db (Cenkowski et al. 1990d), etc. The latent heat of grain moisture was found similar for kernels of approximately the same dimensions (Boyce 1965). In fact, most of the common substances of the same nature exhibit similarity in the magnitude of condensation or vaporization heats for the same species of adsorbate (Brunauer et al. 1938). Cenkowski et al. (1990c) have calculated the latent heat of water in a variety of foods and agricultural products using the equilibrium moisture data as published in ASAE Standards (ASAE 1987). The constants, a and b, were determined for each variety. It was concluded that latent heat of vaporization of crops and foods can be predicted from moisture sorption isotherms.

3.1.5 Temperature Dependency of the Heat of Sorption

The application of Clausius-Clapeyron type equations to determine the heats of sorption necessitates consideration of the linearity of the heat of sorption with temperature. Saravacos and Stinchfield (1965) found that the linearity of the plots of 1/T versus logarithm of equilibrium vapour pressure was limited to certain temperature ranges. For example, a change of slope occurred at the temperature below 20°C in freeze-dried potato. The linearity held from -20°C to 50°C for beef and peach, but the slope (and therefore the heat of sorption) between -20°C and 20°C was low as compared with that between 20°C and 50°C. At the subfreezing temperature of -1°C to -15°C, the plots were also linear, but the slopes were considerably different from those temperature above freezing (Fennema 1978; Kapsalis 1987). Since the vapour pressure of frozen biological materials is equal to the vapour pressure of ice at the same temperature (Storey and Stainsby 1970; Mackenie 1975; Fennema 1978, 1981), different biological materials would have the same slope in the -1°C to -15°C temperature range but different line plots at temperature above freezing intersecting the -1°C to -15°C line, each at a different initial freezing point (Kapsalis 1987).

3.1.6 Entropy of Sorption

The entropy change during sorption is classically explained by the order or randomness of both sorbents and sorbates. It should be emphasized that the usual entropy discussed qualitatively or quantitatively (statistical mechanics) in terms of order-disorder, randomness of motion, etc. of the sorbed molecules is the integral entropy (Hill et al. 1951). The entropy change should be deemed as a net quantity influenced jointly by the changes of structure, state and any other related factors in sorbents and sorbates (Bettelheim and Volman 1957; Berlin et al. 1970b; Rizvi and Benado 1984). According to the second thermodynamic law, entropy production in an irreversible process is always positive. However, the entropy involved in an open system could possibly be negative (Bertlanfy 1950). The overall entropy production of water molecules in a system consisting of a hygroscopic material and water is overwhelmingly positive considering the fact that desorption usually occurs at lower relative humidity than adsorption, signifying the presence of irreversibility. However, the entropy production associated with the material itself could be positive or negative. This would appear to be supported by the finding that in some of the moisture content regions the isosteric heats associated with the bovine submaxillary mucin - water and the polygalacturonic acid - water systems were greater than the corresponding calorimetric heats, while in others, the former were smaller than the latter (Bettelheim et al. 1970). One striking feature of entropy curve is the resemblance to enthalpy curve in shape (Everett 1950; Law 1955; Bettelheim and Volman 1957; Volman et al. 1960; and others).

3.1.7 Reversibility and Irreversibility of Sorption

The presence of hysteresis indicates the irreversibility of a thermodynamic system

(Everett and Whitton 1952; Seehof et al. 1953; Kingston and Smith 1964; La Mer 1967; Watt 1980a,1980b; Kapsalis 1981,1987; Rizvi and Benado 1984; Benado and Rizvi 1985), which has violated the basic assumption of reversibility for the calculation of thermodynamic functions. However, the heat lost in an irreversible process was found to be generally small as compared with the overall energy changes (Kingston and Smith 1964; Benado and Rizvi 1985). Therefore, it could be neglected in a general qualitative description from the standpoint of applied engineering (Iglesias and Chirife 1976b; Kapsalis 1987; Benado and Rizvi 1985). Bettelheim et al. (1970) found that both the isosteric and the calorimetric functions related to the bovine submaxillary mucin - water system followed more or less the same trends up to a moisture content of about 10 %db. This seemed to indicate that in a rather broad moisture range, the isosteric heat calculated from the Clausius-Clapeyron equation could, despite hysteresis encountered, still be quite descriptive of the energetics of water binding in which the calorimetric heat was believed to bear the true meaning, even though the numerical values of the isosteric and the calorimetric heats of sorption did not correspond to each other. The heat of sorption calculated from the Clausius-Clapeyron equation also allows the calculation of the magnitude of the irreversibly created entropy and the evolution of heat. This can be done by comparing the heat calculated from the Clausius-Clapeyron equation with the differential heat of sorption that can be transformed from the integral heat measured by calorimetric method.

In most cases, moisture sorption is an irreversible process. However, reversible (hysteresis free) sorption could be effectuated under certain circumstances such as multiple drying and rewetting treatment (Rao 1941; Chung and Pfost 1967c; Benado and Rizvi 1985; Yang and Cenkowski 1991) and raised equilibrium temperature (Chung 1966).

3.2 Moisture Equilibrium Characteristics

3.2.1 Effect of Pretreatment

The pretreatment factors so far investigated include preheating, blanching, conventional drying and various special drying such as freeze drying, spray drying and electromagnetic drying, irradiation, drying and rewetting cycling, short-term compression or long-term stress, denaturation, seed soundness, growing history of crops, chemical compositions of foods, microorganism infestation, chemical reactions, etc. (Rao 1941; Bushuk and Winkler 1957; Heldman et al. 1965; Saravacos 1967; Chung et al. 1972; Iglesias and Chirife 1976c,d; San Jose et al. 1977; Hayakawa et al. 1978; Greig 1979; Bolin 1980; Chen and Morey 1989b; Ng et al. 1989; Bielewicz et al. 1991; Throne 1991; and others). Some of the factors listed above were reported to have no effect on the sorption isotherms. This included the soundness of corn kernels (Throne 1991), irradiation of canola seeds (Bielewicz 1991), compression of the flour (Bushuk and Winkler 1957). Whereas, some others had effects on a certain range or the full span of either the adsorption or the desorption isotherms or both. This included denaturation of cottage cheese whey (Greig 1979), the drying method of lactose-hydrolysed milk (San

Jose et al. 1977), etc.. However, most of them were found to have marked effects on moisture sorption characteristics of the materials tested. The impact of the pretreatment on the sorption equilibrium and, therefore, on the thermodynamic quantities derived from it, may be due to the fact that most treatments could cause changes in capillary, swelling, crystallinity, water binding groups, and other characteristics of structure (Kapsalis 1987).

Procedures for a sample preparation in multiple adsorption and desorption experiments, such as the rewetting or drying methods, are implicative. The differences among researchers in the upper and lower moisture limits, in the approaches of obtaining isotherms or isobars, and in the length of equilibration time for the preparation of samples were noticed to influence the magnitude of hysteresis. Bizot et al. (1985) found that the hysteresis magnitude is changeable for different procedures and time allowed for equilibration. Chen and Morey (1989b) examined the effect of different rewetting methods and different initial moisture contents on isotherms at 25°C and 45°C. They, on the other hand, proved statistically that no significant difference had existed between different rewetting methods and among samples prepared to different initial moisture contents.

3.2.2 Sorption Hysteresis

General Occurrence

Occurrence of sorption hysteresis could be attributed, by nature, to various irreversible thermodynamic processes (Kingston and Smith 1964; La Mer 1967; Rizvi and Benado 1984; Kapsalis 1987). Materials of different origins and compositions usually fall into different types of hysteresis as classified by Everett (1967). The hysteresis of high-sugar or high-pectin materials was more pronounced in the lower moisture content region. It was not noticeable above the water activity (a_w), 0.65. High-protein materials usually exhibited moderate hysteresis over almost the full range of relative humidity; In starchy materials, a large hysteresis loop occurred with a maximum at about a_w 0.70 (Wolf et al. 1972). There is little information available in the literature on the classification and quantization of the hysteresis related to high-oil materials. Kapsalis (1981,1987) has published comprehensive reviews on sorption hysteresis, which included the types of hysteresis, theories of hysteresis, hysteresis measurement, hysteresis related thermodynamics, and hysteresis behaviour upon multiple adsorption and desorption cycles.

Theories of Sorption Hysteresis

The theories, hypotheses, or interpretations so far proposed for sorption hysteresis include the incomplete wetting theory (Zsigmondy 1911), ink bottle theory (Kraemer

1931; McBain 1935; Rao 1941), open-pore theory (Cohan 1938, 1944), the domain theory (Everett and Whitton 1952; Everett 1955; Everett 1967). Moreover, interpretations based on the polar groups or sorptive sites of the sorbents (Seehof et al. 1953), the deformability and elastic stresses of the sorbents (Van Olphen 1965), the hydrogen-binding ability of adsorbates (Benson and Richardson 1955), difference in concentration gradient of water molecular diffusion between adsorption and desorption (Young and Nelson 1967), and the formation of cracks and fissures during adsorption which would produce an increased surface area for holding moisture during desorption (Chung and Pfost 1967c) were also proposed to account for sorption hysteresis.

According to the incomplete wetting theory, the contact angle of the receding film upon desorption is smaller than that of the advancing film upon adsorption due to the presence of impurities. This causes the capillary condensation along the adsorption branch to occur at a higher relative vapour pressure. This theory fails to explain adsorption results at low relative vapour pressure, and is not suitable for the hysteresis of closed-end loops like those originating from biological materials.

The ink bottle theory treats the pores in a sorbent as ink bottle shaped. Difference in radii exists between the neck and the cavity of the ink bottle shaped pores. Based on this theory, adsorption takes place in the large diameter cavity, while desorption occurs in the small diameter neck. Thus, for a given amount of water absorbed, the pressure is greater during adsorption than during desorption, according to Kelvin equation.

$$RT \ln P/P_0 = -2\sigma V \cos\theta / r_m \tag{10}$$

where P is the vapour pressure of liquid over the curved meniscus, P_0 the saturation vapour pressure at temperature T, σ the surface tension, Θ the angle of contact, V the molar volume of the liquid, r_m the mean radius curvature of the meniscus defined as $2/r_m = 1/r_1 + 1/r_2$, where r_1 and r_2 are the principal radii of curvature of the liquid-vapour interface, and R the universal gas constant.

The open-pore theory is an extension of the ink bottle theory by hypothesizing that the meniscus shape of the liquid in a capillary is cylindrical on adsorption, in which the Cohan (1944) equation applies, and hemispherical on desorption, in which the Kelvin equation applies. The difference in meniscus shape results in the difference in vapour pressure between adsorption and desorption, in other words, hysteresis occurs.

The domain theory explains sorption hysteresis by the domain complexion. An adsorption process may be expressed by the movement of a vertical line across the triangle in the domain complexion, while a desorption process may be described in terms of the movement of a horizontal line from the top to the bottom of the triangle. According to Everett (1967), isolated pore domain has well-defined condensation-evaporation properties involving one or more spontaneous irreversible steps. Due to the irreversibility, adsorption movement and desorption movement do not coincide, therefore exhibiting hysteresis.

The other theories or interpretations are based on the interactions of the polar groups with adsorbates (Speakman and Stott 1936; Seehof et al. 1953), mechanical constraints contributed by the elastic properties of the adsorbents (Bettelheim and Ehrlich 1963), retardation of adsorption due to the development of elastic stresses (Van Olphen 1965), and difference in hydrogen-binding ability and in the molecular sizes (steric hinderance) of the sorbates (Benson and Richardson 1955), etc. The interpretations by sorptive sites or polar groups are popular with the sorption of foods and biological materials (Berlin et al. 1970b; Bettelheim et al. 1970; Rizvi and Benado 1984; Lai et al. 1988).

Sorption Hysteresis upon Multiple Adsorption and Desorption Cycles

Alteration in isotherm characteristics and hysteresis size of some hygroscopic materials after exposing them to multiple adsorption and desorption cycles were reported by many researchers. McBain and Ferguson (1927) reported that hysteresis of a filter cell was still recorded at 50°C even after four successive water vapour adsorption and evacuative desorption at 200°C. Sheppard and Newsome (1929) observed that the hysteresis loop became smaller after three successive cycles of moisture adsorption and desorption for cellulose and its derivatives. Rao (1941) found that titania gel-water, silica gel-water, silica gel-carbon tetrachloride, ferric oxide gel-water, and ferric oxide gel-carbon tetrachloride systems all exhibited permanent hysteresis loops after many adsorption and desorption cycles. Rao (1941) also noticed that the activated rice grains tended to terminate the hysteresis loops upon three repeated wetting and drying cycles with distilled water, but reproduced them with carbon tetrachloride. Bushuk and Winkler (1957) reported that moisture sorption hysteresis of flour was quite reproducible. Hubbard et al. (1957) and Hart (1964) indicated that the size of hysteresis loop of wheat decreased as a result of cyclic treatment. According to Chung and Pfost (1967c), the hysteresis of hard red winter wheat (Ottawa) disappeared on the third cycle at 50°C isotherm. In addition to the cyclic treatment, the drying temperature was also responsible for the disappearance of hysteresis due to the denaturation of protoplasm (Chung 1966). Reproducible and permanent hysteresis was noticed for solid protein absorbing water vapour (Seehof et al. 1953), denatured protein absorbing polar gases (Benson and Richardson 1955) and freeze-dried beef absorbing water vapour in isobar (Strasser 1969). Berlin et al. (1970a) reported that hysteresis of moisture sorption of casein solvent-exchange dried from benzene occurred on both the first and the second cycles. The hysteresis loop on the second cycle was much larger than that on the first, indicating a difference in the sorption process in the two steps. Das et al. (1972) found a reproducible loop even after seven consecutive adsorption and desorption cycles on a soluble starch. Hysteresis similarity upon multiple cycles has been observed by Van den Berg et al. (1975) with both gelatinized and freeze-dried potato starch. Benado and Rizvi (1985) reported that the drying and rewetting treatment for dehydrated rice resulted in the disappearance of hysteresis on the second cycle equally at 10°C, 20°C and 30°C. Repeatability of hysteresis upon many adsorption and desorption cycles was especially apparent at low temperatures and over relatively short experimental durations

(Benson and Richardson 1955).

A number of postulations for the above-mentioned hysteresis behaviour in connection with pretreatment of various biological materials have been made. However, none of them are inclusive and decisive. Rao (1941) accredited the elimination of hysteresis upon multiple adsorption and desorption cycles to the loss of rigidity of organogels due to frequent shear stress of water molecules moving in and out. Van den Berg et al. (1975) stated that gelatinization hardly changed water binding ability of potato starch up to $a_w=0.94$, but it resulted in the resemblance between the hysteresis of the processed starch on first or second cycle of gelatinization and that of the native starch. Chung and Pfost (1967c) postulated that hysteresis disappearance might result from the limits of the crack formation and molecular shrinkage due to many cycles of adsorption and desorption. Other explanations such as denaturation of protoplasm (Chung 1966), surface-active substances (Rutman 1967), change in the crystalline structure when a new crystalline form persists upon subsequent cycles (Berlin et al. 1968), capillary structure change, "mixed" and "time-dependent" hysteresis when the experiment is carried out very slowly, etc, could also be found in the published literature, as briefly reviewed by Kapsalis (1987).

3.2.3 Behaviour of Sorption Isotherms

Most biological materials assume the sigmoidal Type II isotherm of the classification by Brunauer et al. (1940). Generally speaking, a specific kind of material corresponds to a specific type of isotherm. However, mutations sometimes do occur. It was found that the isotherms for apple tissues changed from a type III for the adsorption branch to a type II for the desorption branch (Wolf et al. 1972). Different types of sorption behaviour were reported by Berlin et al. (1968) for a number of dried milk products. An abrupt drop in the adsorption curve at about $a_w = 0.60$ was observed with foam spray-dried whole milk. Irregularity in the isotherms of potato starch near $a_w=0.30$ was reported by Van den Berg et al. (1975). In some rare cases, adsorption branches lay above desorption branches (Berlin and Anderson 1975; Rutman 1967). Crossing of isotherms at different temperature was reported by many researchers (Saravacos and Stinchfield 1965; Audu et al. 1978; Lee et al. 1981; Weisser et al. 1982; Silverman et al. 1983; Saravacos et al. 1986). Labuza et al. (1984) demonstrated that the a_w of saturated salt solutions should decrease with increasing temperature. The shape of the food isotherm measured by the salt solution method can be distorted if no correction is made to remedy the effect of temperature. Changes in sorption isotherms signify definite changes in the surface structure, the property of interaction, and further alterations in elasticity of micropores of the materials (Kapsalis 1981; Yang and Cenkowski 1991). Isotherms were also changed as the result of multiple adsorption and desorption cycles. Block and Bettelheim (1970) observed an increase in the sorptive capacity of hyaluronic acid II with successive isotherms. Yang and Cenkowski (1991) reported an decrease in the sorptive capacity of canola in the low to intermediate relative humidity range with sequential drying and rewetting pretreatment.

3.2.4 Temperature Effect

Equilibration temperatures and pretreatment temperatures all exhibit their own characteristic effects on sorption equilibrium.

Generally, equilibration temperature affects the isotherms in such a way that an increase in temperature causes a decrease in the amount of sorbed water at a given water activity, or an increase in water activity if the moisture content is kept constant (Kapsalis 1987). However, crossing of the isotherms at different temperatures can sometimes take place, as mentioned in the section 3.2.3. As described in the section of 3.2.3, temperature of the salt solution was also reported to distort the shape of the isotherms measured by salt solution method (Labuza et al. 1984). At subfreezing temperatures, water activity is the same for all frozen biological materials at the same temperature (Storey and Stainsby 1970; Mackenzie 1975; Fennema 1978, 1981), and can be calculated by the equation: $a_w = p_w / p_{sw}$, where a_w is water activity, p_w is the vapour pressure of water associated with the sample, and p_{sw} the vapour pressure of pure supercooled water at the same temperature (Kapsalis 1987). With respect to the effect of isotherm temperature on hysteresis magnitude and pattern, increasing temperature normally decreases the hysteresis and limits the span of the loop along the isotherm (Wolf et al. 1972; Kapsalis 1987). However, for some specific materials, such as ginger and nutmeg, the hysteresis of the whole water activity span remains constant, while for some others, such as anise, chamomile, etc., the total hysteresis even increases (Iglesias and Chirife 1976b).

Like most other pretreatment and prehistory factors, temperature, as a pretreatment parameter, affects the moisture equilibrium of a material by alteration of its characteristics. Tuite and Foster (1963) found that the hygroscopic isotherms of corn dried at temperature higher than 60°C were shifted downward as compared with those dried at ambient temperature. Chen and Morey (1989b) reported that drying temperature had a significant effect on the EMC-ERH relationship of yellow-dent corn. Several valuable conclusions have been drawn: at the same relative humidity, the higher the drying temperature, the lower the equilibrium moisture content; the higher the desorption isotherm temperature, the less the effect of drying treatment; hysteresis at 45°C equilibration temperature still existed over the entire relative humidity range for the grain dried at 50°C, but almost disappeared for that dried at 25°C; grains receiving 110°C drying treatment also exhibited hysteresis at the isotherm temperature from 5 to 45°C. The hysteresis was low at relative humidities below 60-70%, and increased strikingly as the relative humidity was extended towards 100%.

3.2.5 Isotherm Equations

More than 200 isotherm equations have been proposed for biological materials (Van den Berg and Bruin 1981). Although they might look different, many of them actually have the same form after rearrangement (Boquet et al. 1980). Van den Berg

(1985) proposed the criteria for a perfect model, but no models have so far been capable of describing the EMC-ERH relationship accurately enough for the entire range of relative humidity and for a wide span of temperatures. However, a few comparatively versatile models do exist for the isotherms of foods and other biological materials. These include the Halsey (1948), the Oswin (1946), and the Iglesias and Chirife equations (Iglesias and Chirife 1978), as well as the recently-popular Guggenheim-Anderson-de Boer (GAB) equation (Anderson 1946).

Critical reviews of the isotherm equations have been made by Chirife and Iglesias (1978), Van den Berg and Bruin (1981), and Lomauro et al. (1985). Comprehensive model applicability tests have been conducted by Boquet et al. (1978, 1979) and Chen and Morey (1989a) to a variety of foods and agricultural products. It should be pointed out that the high-oil content foods were, except for a few oil crops, excluded in the scope of their work. A lot of regional tests of the goodness of fit of some popular equations, as applied to individual foods or crops, were also reported. For example, Chen and Clayton (1971) tested different models and their temperature dependence using the EMC data of corn, and found that the empirically modified Chen's equation (Chen 1971) adequately described the temperature dependency of corn isotherms between 4.4°C and 60.0°C. Pfost et al. (1976) tested the Modified-Henderson (1952), Chung-Pfost (1967b), Day-Nelson (1965), Chen-Clayton (1971) and Strohman-Yoerger (1967) equations using isotherm data for grains. They selected the Modified-Henderson and Chung-Pfost equations to find the parameters for other grains and oilseeds. Young (1976) tested different models for Virginia-type peanuts and concluded that the Smith (1947) equation might be used to express their adsorption and desorption isotherms as long as water activities are above 0.3. Flood and White (1984) tested the Chung-Pfost and Modified-Henderson equations using the sorption data of popcorn and concluded that both equations reasonably represented the sorption data with Chung-Pfost equation having a better fit than the other. Saravacos et al. (1986) found that, although the GAB equation could give fairly good fit to the isotherms of Sultana raisins, the 5-parameter D'Arcy-Watt equation fitted the best. Ajisegiri and Sopade (1990) used the Bradley (1936), Halsey (1948), Henderson, Chung-Pfost, and Caurie (1970) equations to assess the goodness of fit to the isotherm data of Nigerian millet at the temperatures of 20, 25 and 40°C, and found that the Chung-Pfost equation gave the best fit. Recently, Jayas and Mazza (1991) modified the GAB equation and fitted this modified equation, as well as the Modified-Henderson, Modified Chung-Pfost, Modified-Halsey and Modified-Oswin equations to the EMC data of oats at the temperatures of 10, 25, 40 and 55°C. They concluded that the modified Chung and Pfost equation was the best and the modified GAB equation was the second best in describing the isotherms of oats.

The Modified-Henderson and Chung-Pfost equations were adopted as the ASAE Standard D254.4 Moisture Relationship of Grains (ASAE 1991) for cereal grains and oil seeds. However, these two equations were found to underestimate the isotherms of many crops such as lentil (Cenkowski et al. 1989b), canola (Sokhansanj et al. 1986), sunflower seeds (Mazza and Jayas 1990), etc.. This is especially true when the relative humidity ranges from 80% to 100%. Chen and Morey (1989a) compared the Modified-Halsy, Modified-Oswin, Modified-Henderson, and Chung-Pfost equations by using the isotherm data of a variety of crops. They concluded that the Modified-Henderson and the Chung-Pfost equations could serve as good models for many starchy grains and fibrous materials. These two equations were not suitable for the high protein and oil products, because they had clear patterns in the residual plots and had large values of the mean relative percentage deviation and the standard error of the estimated parameter. Thus, Chen and Morey (1989a) suggested that the part of the ASAE Standard regarding moisture relationship should be revised.

It is important to review the isotherm models hitherto tested for the isotherms of high-oil products, because this particular literature closely relates to the present study. Singh and Ojha (1974) evaluated the Henderson equation and its temperature dependency by using desorption equilibrium moisture data of groundnut at various temperatures. They reached the conclusion that Henderson equation correctly described the temperature dependency of the experimental isotherms. Nevertheless, this conclusion incurred criticism from Chirife and Iglesias (1978) who pointed out that the procedure in evaluating the constants of Henderson equation was invalid. AS mentioned above, Young (1976) tested different models for Virginia-type peanuts and concluded that the Smith equation might be used to express their adsorption and desorption isotherms as long as water activities are above 0.3. Other related work included: Osborn et al. (1989) for soybeans, and Chen and Morey (1989a) for peanut, rapeseed, soybean and sunflower seeds, Sokhansanj et al. (1986) and Otten et al. (1990) for canola. According to Chen and Morey (1989a), the best fit model for high-oil products was Modified-Halsey equation.

Among all the isotherm equations so far available, the BET, GAB, Halsey, and Caurie equations can give monolayer values, which are important in storage stability of a biological material. However, discrepancy existed between the monolayer values determined from the GAB, the Halsey and the Caurie equations and those from BET equation. The monolayer values determined by the former equations are constantly larger than those by the latter, namely, namely, BET equation.

4. EQUIPMENT

4.1 Equipment for Isotherm Measurement

The experimental set-up (Fig.1) consisted of the equilibrium moisture content (EMC) apparatus, heat exchanger and aquarium air pump (Hagen Inc., Montreal, PQ), and three-way valves. These elements were connected together by flexible plastic tubes to form a closed system.

Six EMC apparatus were used simultaneously in each experiment. Each apparatus consisted of six plastic rings (10 mm in thickness and 95 mm in inner diameter). Each ring had a wire mesh attached to its bottom. In the top section of the

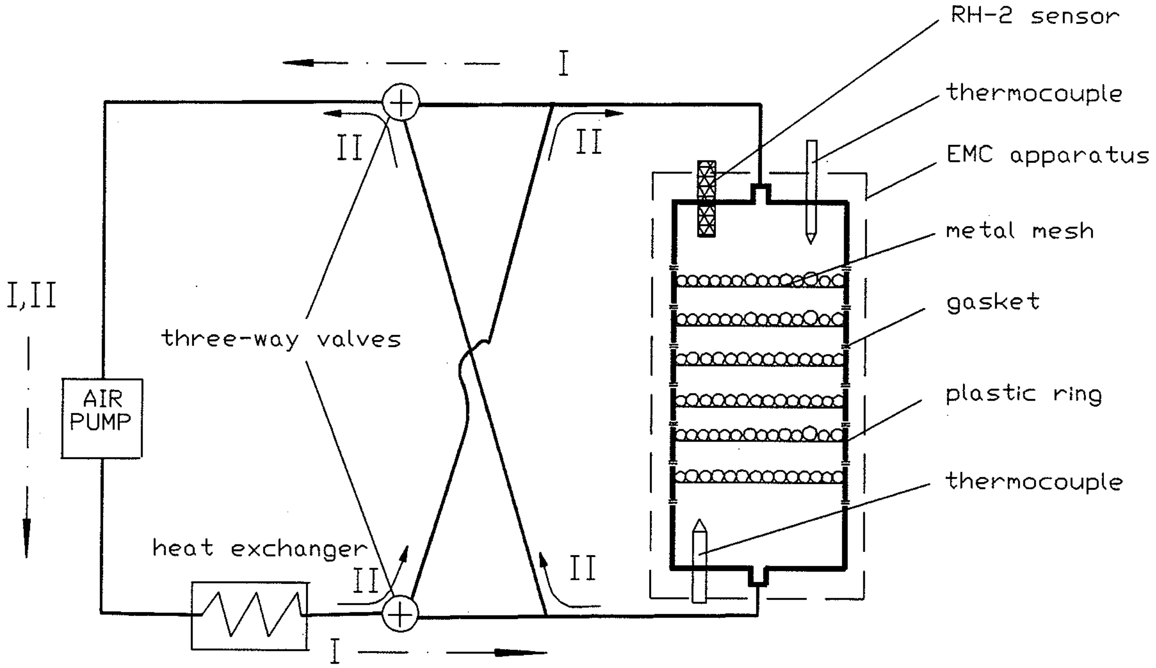

Figure 1 Diagram of experimental set-up

EMC apparatus, a bulk polymer resistance humidity sensor, RH-2 (General Eastern, Inc., Watertown, MA), was installed. The temperature of incoming and outgoing air was probed by the T-type thermocouple mounted in the top and bottom section of the EMC apparatus. The RH-2 sensors and the thermocouples were then hooked up to a Hewlett Packard data acquisition/control system (Model HP 341A), and the relative humidity and temperature data were automatically recorded.

In the preliminary experiment, the air in the head space of the system was forced to circulate in one direction, i.e., from the bottom of the EMC apparatus upward. This was the technique adopted by most researchers who experimented on EMC measurement when using the dynamic method. Results showed that the temperature gradient across the layers of canola kernels inside the EMC apparatus was approximately 0.6°C, which was undesirable for moisture equilibration. This was due to the heat generated by the Maxima air pump. To eliminate the temperature gradient, as well as any effect of it on the moisture equilibrium of canola samples, improvement was done to the tubing system. Instead of using a one-way tubing connection, a reversible tubing system was built using two three-way air valves (Fig.1). By switching these two valves, air stream from the pump could be directed to go through the EMC apparatus from the top to the bottom (indicated by II) or vice versa (indicated by I). The direction of the air stream was changed every 6 h. As a result, the top and bottom temperatures recorded by the data acquisition system showed that the temperature gradient was reduced to a negligible level.

4.2 Isothermal Chamber

The six EMC apparatus, filled with samples, were placed in a temperature controlled chamber capable of maintaining the accuracy in temperature to ±0.1°C. This chamber was 1.5 m X 1.5 m X 2 m in dimension, constructed of wood, and thermally insulated with two layers of styrofoam 100 mm in thickness.

The temperature of the chamber was maintained constant by circulating the water/ethylene glycol solution through the radiator in the chamber, the thermostat, and the compressor. The thermostat used was RMT-6 Lauda refrigerating circulator

(Brinkmann Instruments, Inc., Westbury, New York). The compressor was only used to help bring down and maintain the chamber temperature when a temperature below 15°C was desired. A mercury thermometer with 0.1°C divisions was used to verify the chamber temperature.

4.3 Equipment for Multiple Drying and Rewetting Pretreatments

Samples were rewetted by adding distilled water and then storing them in a plastic bag in a refrigerator at 8°C. Drying was conducted in a thin layer dryer where air temperature and humidity were adjustable. For drying at 25°C, ambient air (around 25°C) was forced through the samples. For drying at 50°C, the ambient air was forced through the heater in the thin layer drier before it reached the sample (Fig.2).

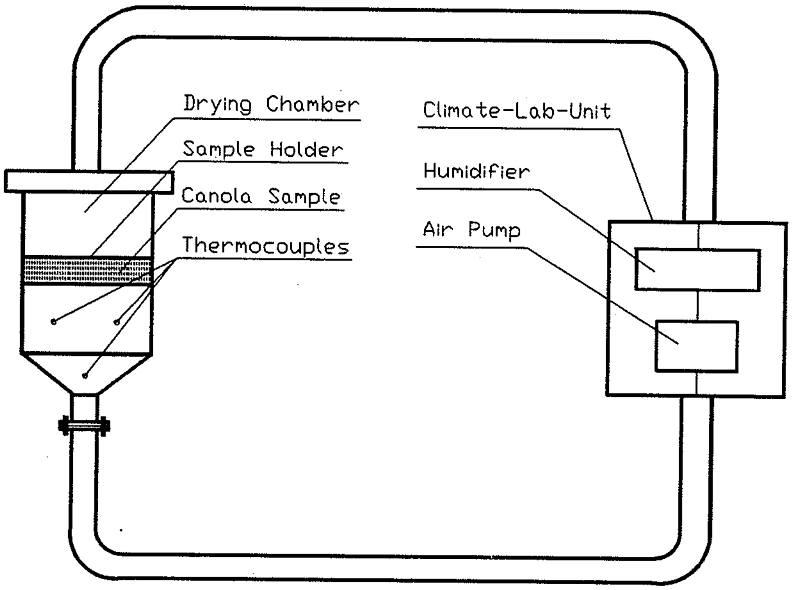

Figure 2 Thin layer dryer for drying treatment

5. MATERIALS AND METHODS

5.1 Canola Samples

Canola **Brassica napus L., cv. Westar** (1989 crop) purchased from a local supplier was used in this investigation. The initial moisture content of the canola was 6.50 %db. Kernels were in sound and clean condition. Throughout the experimental period, the sample was stored in a room at a temperature of around 25°C and at a relative humidity of approximately 50%. The room temperature and relative humidity were constant throughout the experimental period, so that moisture content fluctuations due to temperature and relative humidity changes were avoided.

5.2 Experiment Scheme

The experiments in this study were purposely designed in such a way that they would reflect the effects of drying temperature, equilibration temperature, and drying and rewetting cycles on the moisture equilibrium of canola.

It was predetermined that isotherms were to be measured in the temperature range from 3.5°C to 45.0°C. At 3.5°C, 25.0°C and 40.0°C, isotherms were measured up to the fifth drying and rewetting cycle. At other temperatures, isotherms were measured only on the first drying and rewetting cycle. The isotherms on the first cycle served for the temperature dependency test and the study of the effect of equilibration temperature on moisture equilibrium of canola. The isotherms obtained during the multiple adsorption and desorption cycles served for the study of the effect of multiple drying and rewetting cycles on the moisture sorption characteristics of canola including hysteresis, sorptive capacity, and isothermal shape and on the thermodynamic properties of water in canola.

Drying operations were conducted at two temperatures: 25°C and 50°C in a thin layer dryer. This was to prepare the sample ready for the isotherm measurement aiming at the effect of drying temperature on the moisture equilibrium of canola. Rewetting operations were carried out at low temperature (8°C) in order to avoid fungal growth.

Four sets of experiments were planned in this study. In the first set of experiments (treatment A), canola prior to the EMC tests was successively rewetted at 8°C and dried at 25°C for about 10 h. Then the EMC experiment was carried out at 25.0°C. In the second set of experiments (treatment B), canola was successively rewetted at 8°C and dried at 50°C for 6-8 h and the EMC test were conducted at 25.0°C. In the third set of experiments (treatment C) canola was five times rewetted at 8°C and dried at 25°C. After each drying and rewetting treatment, the EMC test followed at 40.0°C. For treatment D, canola was subjected to five drying (25°C) and rewetting (8°C) cycles prior to the isotherm measurement at 3.5°C. Table I gives a summary of these four treatments indicating simutaneously what objectives each treatment relates to.

Table I Summary of Treatment A, B, C and D

Treatment Category	Drying Temperature	Equilibration Temperature	Cycle Number	Objectives Related
A	25°C	25.0°C	1-5	i-vi
B	50°C	25.0°C	1-3,5	i,ii,iv-vi
C	25°C	40.0°C	1,3,5	i-vi
D	25°C	3.5°C	1,3,5	i,ii,iv-vi

5.3 Drying and Rewetting Procedure

The following procedure was used for rewetting and drying the canola samples. Five kg of canola were moistened to a moisture content in the neighbour of 20.00 %db by adding a predetermined amount of distilled water. The sample was tumbled occasionally during the addition of water to ensure uniform distribution of moisture, and was then placed in a refrigerator at 8°C for 24 h. This length of time was enough for the moisture in canola kernels to be evenly distributed (Sokhansanj et al. 1983). About 50 g of rewetted kernels were sampled. The rest of the bulk (4.6 kg) was dried in a thin layer drier at 25°C (treatment A) or 50°C (treatment B) to a moisture content of about 7.00 %db. During thin layer drying, canola was sampled, 50 g at each sampling, in predetermined time intervals so that canola samples with different moisture contents were obtained for EMC measurements. At the end of thin layer drying, the bulky canola was then transferred to a desiccator for further drying. In this step the moisture content was able to be brought down to 4.50 %db or lower. About 400 g of dried kernels were also sampled, and used in conjunction with the kernels of different

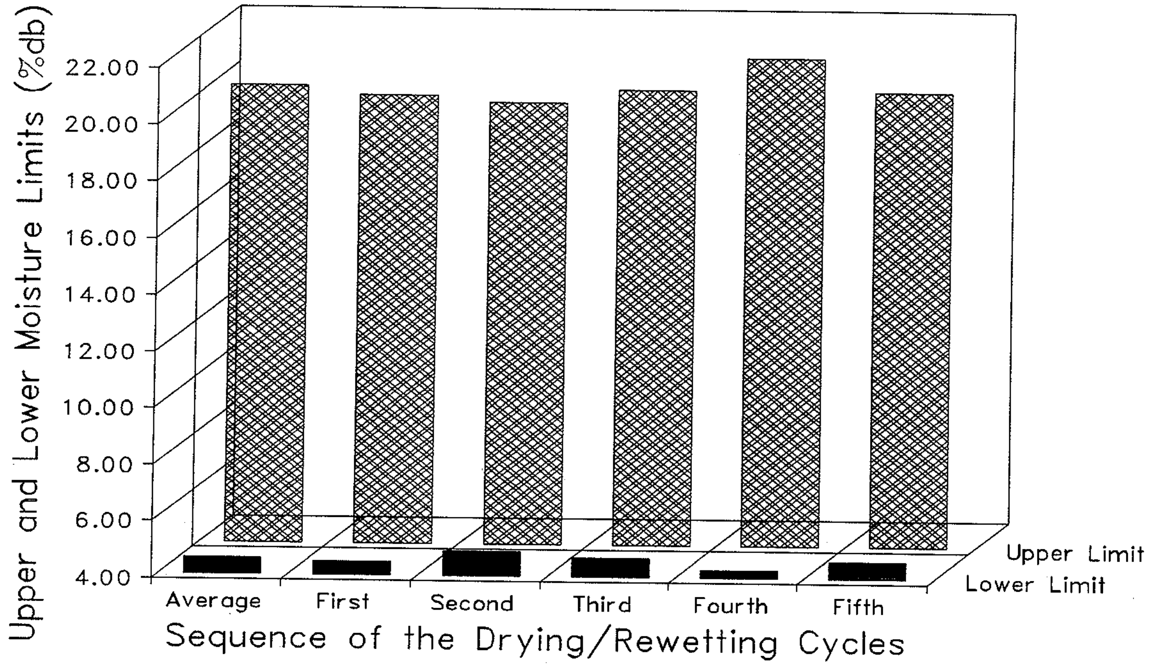

Figure 3 Drying and rewetting schedule on the first to fifth adsorption and desorption cycles for treatment A

initial moisture contents for the determination of the sorption isotherms on the first drying and rewetting cycle. The second to fifth cycles of rewetting and drying procedure followed the same schedule between the upper moisture content limit of 20.00 %db and the lower limit of 4.50 %db. Fig.3, as an example, shows the drying and rewetting scheme for the sample exposed to treatment A. The resultant moisture content limits were: 20.14 %db on an average with a standard deviation of 0.62 %db for the upper limit, and 4.55 %db on an average with a standard deviation of 0.23 %db for the lower limit. The same criteria on the drying and rewetting moisture limits were set for the treatment B, C and D. The standard deviations for their recorded moisture limits were less than 1.00 %db.

5.4 Calibration of Humidity Sensors

Secondary standard calibration was performed against a Hygro-M1 dew point humidity sensor (General Eastern Instruments Inc., Watertown, MA) for the RH-2 sensors mounted in each of the six EMC apparatus. In calibration, the six EMC apparatus were connected in series with the sensing element Model 1111L of the M1 dew point sensor, so that the six RH-2 sensors, in each individual EMC apparatus, could be calibrated simultaneously. The calibration was conducted in the isothermal chamber at 25.0°C. Two steps were taken for the calibrations in the RH ranges from 20% to 50% and from 50% to 100%, because the relative humidity of the chamber was about 50%. The procedure involved was as follows: for the calibration in the low-intermediate RH range, the six EMC apparatus in series with the sensing element Model 1111L was further connected in series with a column of desiccant until the relative humidity data collected by the data acquisition system reached as low as 20%. The desiccant column was then disconnected and the whole calibration series was kept running for 3 hours, in order for the air in the head space of the calibration series to become homogeneously distributed. Next, a syringe needle was inserted into the tubing at either end of the calibration system, and exposed to the air in the isothermal chamber. In this way, the humid air in the isothermal chamber was able to be led gradually into the calibration system to cause the relative humidity of the air inside the series to steadily go up. The relative humidity data were recorded one hour after the syringe needle was inserted. This allowed the system to become equilibrated in this duration. At first, the data were recorded every 20 s, but it was found later that the data points in one calibration were too populous to be loaded into a computer for analysis. So, the calibration was repeated collecting data in 5 min increments. For the calibration in intermediate-high relative humidity range, a water column was connected to the calibration series until the relative humidity reading for M1 sensor reached 100%. Then, the water column was taken away from the series, and the series was kept running for 3 h for homogeneity. An syringe needle was inserted into the tubing at either end of the series, and the whole system was allowed to equilibrate for 1 h before the relative humidity data were recorded in 5 min intervals. In this way, the relative humidity of the air inside the calibration system gradually went down until it reached that of the ambient air.

5.5 Procedure of Isotherm Measurement

Bringing air through layers of wet and the dry samples together in one EMC apparatus would finally result in equilibrium between the wet and the dry samples as long as they were held for a sufficient length of time. Bielewicz (1991) mentioned that after 17-20 hours (depending on the dry to moist mass ratio), the hourly-recorded relative humidity readings became constant (difference less than 0.1%). This signified that equilibrium was established. The preliminary experiments in this study showed that for most EMC measurements equilibrium was established within 8-24 hours (refer to section 6.2.1). In this study, the samples were generally allowed to stay in the EMC apparatus for more than 24 hours to ensure a complete equilibrium to be established.

There are three ways in combining the wet and dry samples to obtain the isotherms when using the method of isotherm measurement in this study. One is to rewet the sample to the same initial moisture content level (for example 20.00 %db), and then to apply predetermined mass ratios of the wet sample to dry sample (Bielewicz 1991). The second is to rewet the sample to different moisture contents, and then to apply the same amount of wet sample as the dry one in alternate layers of the EMC apparatus. The third, which was adopted in the present study, is to rewet the sample to a high moisture content, leave some of the sample for the measurement of isotherms in very high relative humidity range, and then dry the rest to different moisture levels in a thin layer dryer. The ratio of wet to dry was therefore 1:1 in this case.

The adsorption and desorption isotherms were obtained simultaneously by loading dry and wet samples, 15 g each, on the wire mesh of six plastic rings, three of them for the wet sample and the rest for the dry sample. The wet and dry samples were arranged in such a way that one wet layer was followed by one dry layer.

The relative humidities below 20 % were directly measured by a M1 dew point sensor instead of the RH-2 sensors. Moisture content measurements followed the convection oven method as specified in ASAE standard S352.1 (ASAE 1991).

6. RESULTS AND DISCUSSION

6.1 Evaluation of the EMC-ERH Measurement

The performance of the test apparatus and the certainty of the EMC-ERH measurements can be evaluated in the following four aspects: equilibration time, calibration results of the RH-2 humidity sensors, comparison of the present work with published data, and repeatability of the EMC data.

6.1.1 Equilibration Time

Preliminary experiments have been done in this study to check the length of time necessary for equilibrium to be established. Results showed that the length of time required for equilibrium to be established depended on various factors such as initial moisture contents of the wet and dry samples, equilibration temperatures, performance of the individual air pumps, and switching frequency of the three-way valves, etc.. Fig.4 and Fig.5 are constructed using the data from the preliminary experiments at the equilibration temperatures of 25.0 and 40.0°C to show the relationship between the relative humidities of the headspace in the EMC apparatus used in this study and time. The time required for the samples to reach an ensured equilibrium, i.e., when the relative humidity curves shown in Fig.4 and Fig.5 start going flat, at 40.0°C varied from 8 to 12 hours depending on the performance of individual apparatus and the initial moisture contents of the wet and dry layers (Fig.4). However, it generally took at least

15 hours for the samples at 25.0°C to reach an ensured equilibrium (Fig.5). For the EMC measurements at the temperatures below 25.0°C, equilibrium was established within 15-24 hours. In order to ensure a complete equilibrium to be established, the canola samples to be equilibrated at various temperatures involved in this study were, in practice, generally allowed to stay more than 24 hours in the EMC apparatus. However, the samples were deemed as in equilibrium with the headspace only when the hourly recorded relative humidity data were less than 0.1 % within three consecutive hours.

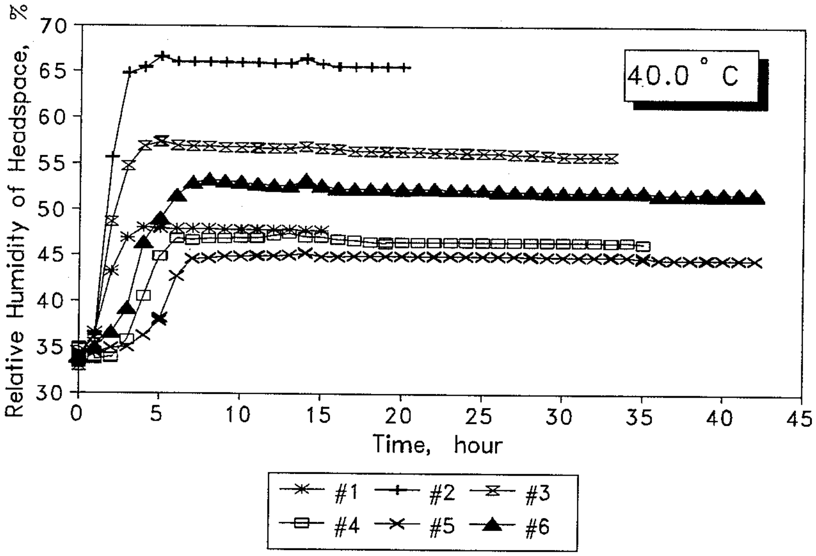

Figure 4 Relative humidities of the headspace in EMC apparatus (#1-6) as a function of time at 40.0°C. The relative humidity of ambient air was 33% at this temperature

During the experiments, it was noticed that it took a surprisingly short length of time, as compared with some cereal grains such as corn, wheat and barley, for canola

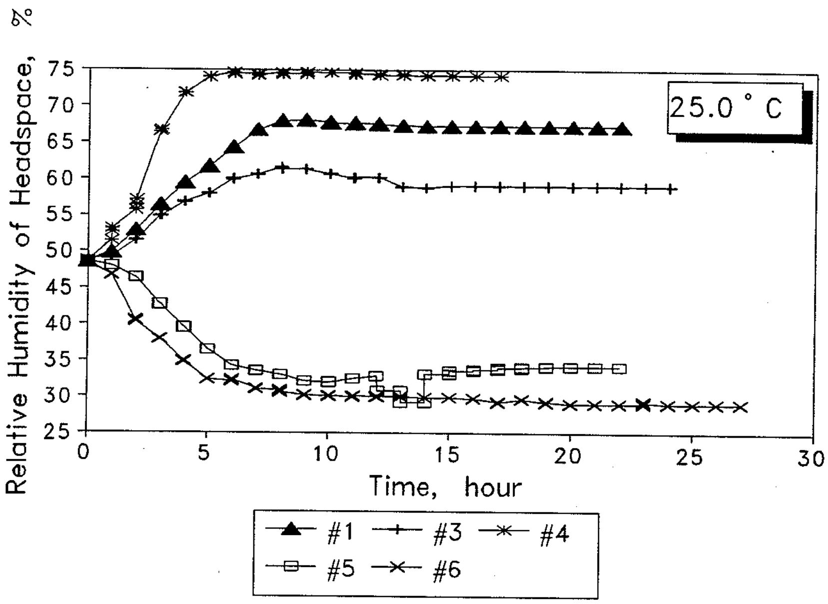

Figure 5 Relative humidities of the headspace in EMC apparatus (#1, 3-6) as a function of time at 25.0°C. The relative humidity of ambient air was 49% at this temperature

kernels to complete a drying or rewetting (tempering) process. This was reflected by the comparatively short equilibration time as shown in Fig.4 and Fig.5. Sokhansanj et al. (1983) also observed the same phenomenon. They reported that the tempering time required for the moisture of canola to be evenly distributed at 2°C is only 4 hours, while those of corn, barley and wheat are 122, 48 and 46 hours respectively. This seems to signify that canola is a crop of unique drying and rewetting characteristics, to which the comparatively short equilibration time for canola observed in this study might be due.

6.1.2 Calibration Results of the RH-2 Humidity Sensors

The calibration results for the whole range of relative humidity are shown in Fig.6, which is constructed by linking the calibration data for the low-intermediate and

intermediate-high relative humidity ranges. It can be seen from Fig.6 that in the whole span of relative humidity, the linearity between the relative humidity measured by RH-2 sensors and that by the M1 dew point sensor is poor. However, there is a well-defined linearity in each relative humidity range. Hence, separate linear regression equations were used for the calibration in the low-intermediate and intermediate-high relative humidity ranges.

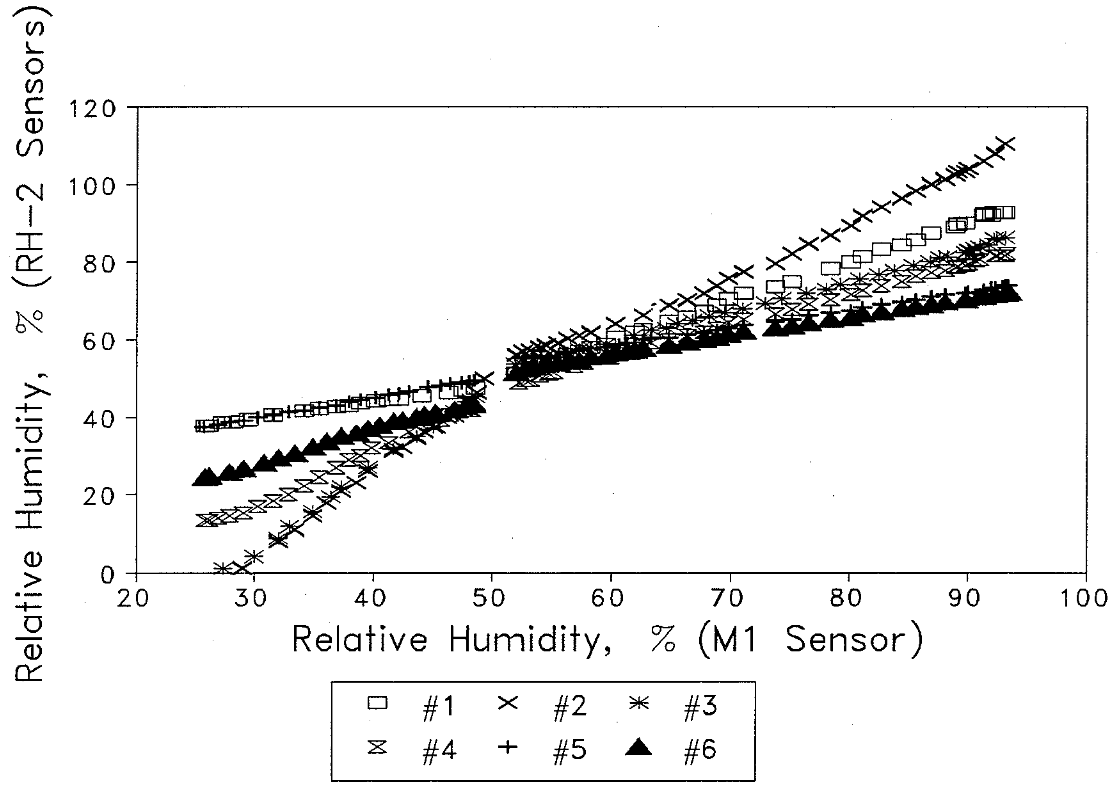

Figure 6 Calibration results showing the relationship of relative humidities between the RH-2 and M1 sensors

As the result of calibration, the output of RH-2 humidity sensors was remedied in contrast to that of M1 chilled mirror dew point sensor which has an accuracy of ±0.2°C in dew point temperature, as given in the product manual. Therefore, the RH-2

sensors were, in practice, giving the relative humidity values standardized by the M1 dew point sensor. The performance of the individual RH-2 sensor varied considerably. As can be seen in Fig.6, the relative humidity associated with each of the six RH-2 sensors deviated from one another at the relative humidities except for those around 50%. At the two extreme ends of relative humidity span, the performance of the individual RH-2 sensor deviated the most.

6.1.3 Comparison of the Present Work with Published Data

Both the adsorption and desorption EMC data at 25.0°C on the first drying and rewetting cycle for the canola dried at 25°C were plotted in Fig.7 in comparison with the published data by Pixton and Henderson (1981), Sokhansanj et al. (1986), and Otten et al. (1990). Since it was not mentioned by Sokhansanj et al. (1986) and Otten et al. (1990) whether the data collected in their studies were on adsorption or desorption processes, a search has been made through the contexts of their papers, in an attempt to make sure which process their data should belong to. To distinguish between the adsorption and desorption data is imperative, because the moisture sorption is, as reviewed in section 3.1.7, usually an irreversible process with sorption hysteresis involved. The comparison should only be made on either adsorption or desorption EMC data. It is inaccurate to use the mixed EMC data in isotherm comparison. It has been found that both EMC data collected by Sokhansanj et al. (1986) and Otten et al. (1990) were a mixture of adsorption and desorption data. In the experiments of Otten et al.

(1990), the procedure of isotherm measurement involved sealing the canola samples of 11 %db initial moisture content with salt solutions until the equilibrium was established. Thus, it is easy to infer that those EMC data which were lower than the initial seed moisture content should belong to desorption process and the reverse should belong to the adsorption process. In the experiments of Sokhansanj et al. (1986), canola samples, of about 8 %db initial moisture content, were rewetted to a predetermined moisture content in order to acquire EMC data higher than 8 %db, and dried to a moisture content below 8 %db in order to acquire EMC data lower than 8 %db. Hence, all the EMC data higher than 8 %db should belong to adsorption process, and those lower than 8 %db should belong to desorption process. According to the criterion mentioned above, adsorption and desorption data were sorted out from the mixture of isotherm data, and plotted separately with the same type of data from Pixton and Henderson (1981) and the present study. The desorption data of this study were found to be close to those of Otten et al. (1990). Both adsorption and desorption data were 5% higher than those of Pixton and Henderson (1981) in the intermediate-high relative humidity range. Most desorption EMC data reported by Sokhansanj et al. (1986), after being sorted out from the mixed data, went beyond the relative humidity range of the data obtained in this study. However, at the relative humidity of 64%, the former was lower than the latter. It is difficult to conduct a comprehensive comparison between the isotherms of this study and the published data, since most measurements were made at different temperatures. However, a qualitative comparison can be achieved by means of graph manipulation using the isotherms with temperatures as close as possible. As a result, the isotherms

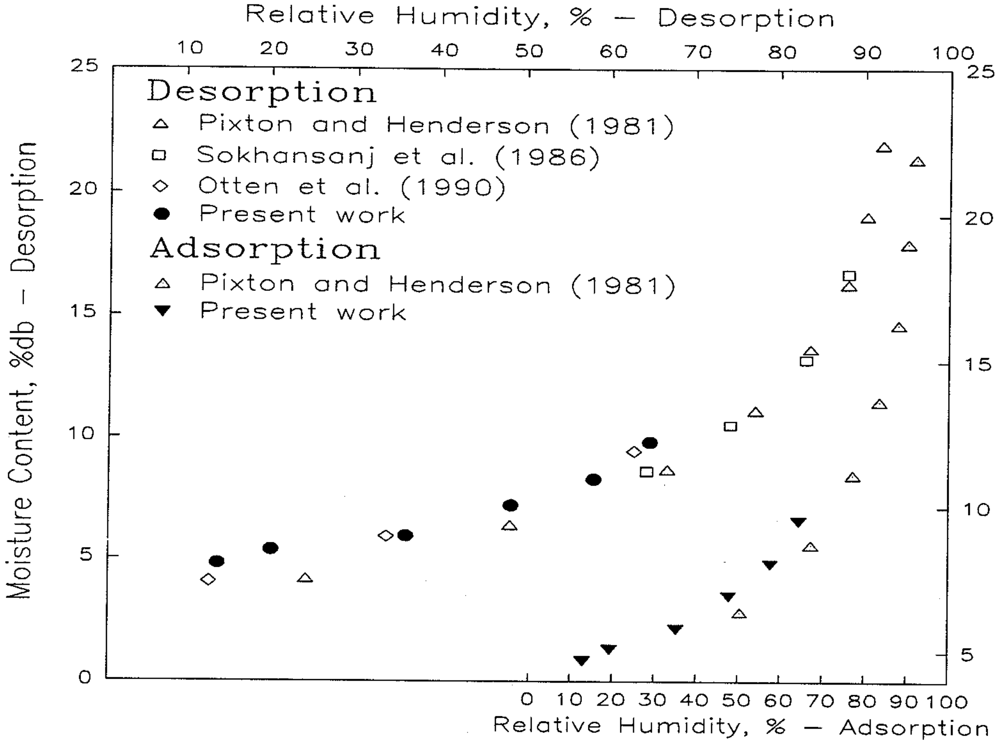

Figure 7 Comparison of the present work with published EMC data

of this study were very similar to those of Otten et al. (1990) around ambient temperatures, and were higher than the estimated isotherms reported by Pichler (1957), Pixton and Henderson (1981), and Otten et al.(1990) at temperatures higher than 30°C. The isotherms determined by Pichler (1957) were the lowest at this temperature range. The isotherms of this study at low temperature range were found to be lower than the isotherms from Sokhansanj et al. (1986), which were, in turn, lower than those from Pixton and Henderson (1981).

6.1.4 Repeatability of EMC Data

The repeatability test was performed on triplicate samples exposed to the same relative humidity at various temperatures. Ninety five percent confidence limits or standard deviations could therefore be obtained from the three parallel EMC data, which were accurate to 0.001 in the present study, at each relative humidity. Fig.8 shows both the adsorption and desorption isotherms at 25.0°C on the first to fifth drying and rewetting cycles, with vertical error bars marked at each EMC point to represent 95% confidence

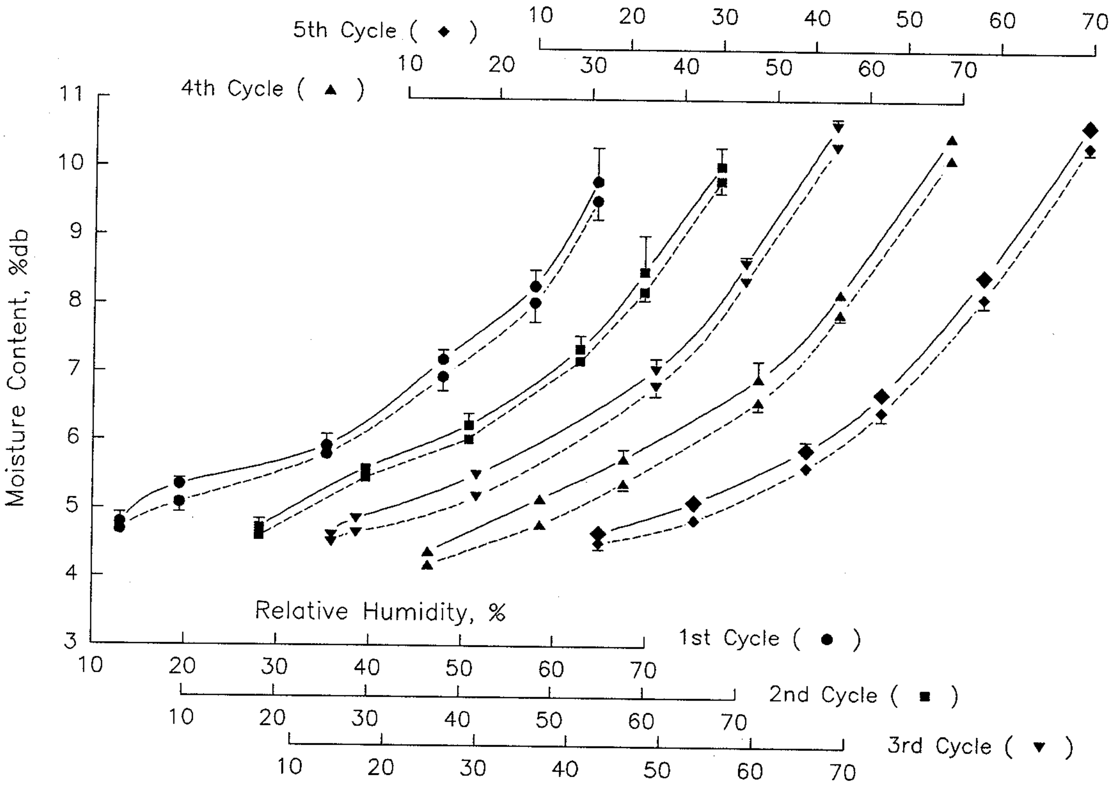

Figure 8 Adsorption (dashed line) and desorption (solid line) isotherms of Westar canola at 25.0°C on the first to fifth drying and rewetting cycles showing 95% confidence limits

limits. The error bars were positive on desorption curves and negative on the adsorption curves. As can be seen in Fig.8, most 95% confidence limits of the EMC points were so small that the error bars at the corresponding points were not able to be reflected. Only a few EMC points had relatively large 95% confidence limits. As a whole, standard deviations of most EMC measurements at various temperatures were less than 0.100 %db. Very limited number of EMC values had standard deviations up to 0.100-0.200 %db.

6.2 Isotherms of Canola at Various Temperatures during Multiple Adsorption and Desorption Cycles

The isotherms of canola measured in this study involved seven equilibrium temperatures (3.5, 6.0, 15.0, 25.0, 35.0, 40.0 and 45.0°C), two drying temperatures (25 and 50°C), and five successive adsorption and desorption cycles. Isotherms at 6.0, 15.0, 35.0 and 45.0°C were measured on only the first adsorption and desorption cycle. Most isotherms were determined at the relative humidities ranging from 30% to 80%. Some others had relative humidities between 15% and 93%. The EMC data of Westar canola collected in this study are presented in Appendix A. These isotherms, along with the EMC data reported by other researchers, have provided the basis for the calculation of thermodynamic quantities and the study of moisture equilibrium characteristics of rapeseed (canola).

6.3 Thermodynamic Properties of Moisture Sorption of Canola

6.3.1 Free Energy Changes

Free Energy Changes Related to Treatment A, B, C and D

As mentioned in the section 3.1.2, Gibb's free energy ΔF can be expressed as $\Delta F = \Sigma \mu_i$ by definition, where μ_i is the chemical potential of any species in a system. In the moisture sorption process, the free energy change with respect to water vapour is:

$$\Delta F = \mu_1 = RT \ln (a_w)$$

where μ_1 is the chemical potential of water vapour and a_w is the water activity (or alternatively, relative humidity, RH, in decimal). Using the isotherms obtained in this study, free energy changes on multiple drying and rewetting cycles for treatment A (drying at 25°C prior to moisture equilibration at 25.0°C), treatment B (drying at 50°C prior to moisture equilibration at 25.0°C), treatment C (drying at 25°C prior to moisture equilibration at 40.0°C) and treatment D (drying at 25°C prior to moisture equilibration at 3.5°C) were calculated.

As related to treatment A, B, C and D, Fig.9 to Fig.11, respectively, show the free energy changes for both adsorption and desorption branches on the first, third and fifth drying and rewetting cycles as a function of equilibrium moisture content.

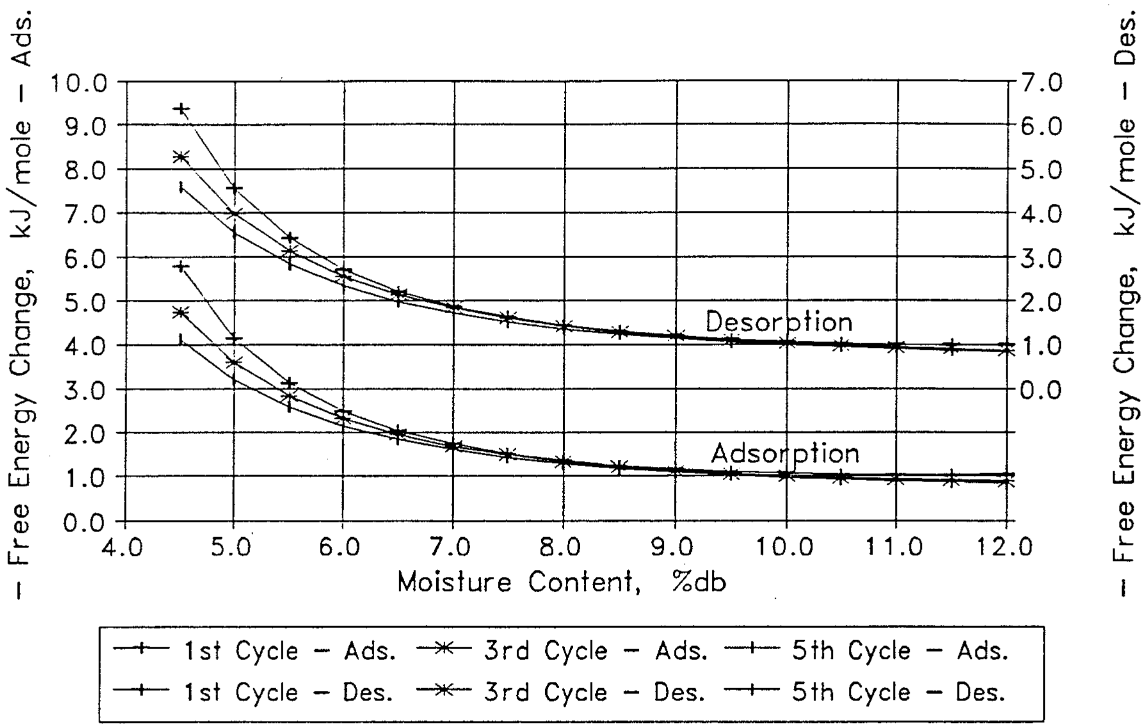

Figure 9 Free energy changes on the first, third, and fifth drying and rewetting cycles calculated from the adsorption (Ads.) and desorption (Des.) isotherms for Westar canola subjected to treatment A

Close examination of all free energy curves in this study led to the finding that above 8.0 %db moisture content in treatment D, 7.5 %db in treatment A, and 6.5 %db in treatment C, the free energy changes became more or less the same irrespective of the drying and rewetting cycles and adsorption or desorption branches. For canola samples exposed to treatment B, little difference in free energy changes between different cycles on desorption could be distinguished throughout the whole moisture content range involved (Fig.10b), and slight difference in free energy changes existed between first and fifth cycle on adsorption at moisture contents below about 9.5 %db. (Fig.10a). This difference was, however, negligible as compared with those related to treatments A and D. Thus, the comparisons of free energy changes will be made only within about 4.0 to 8.0 %db moisture range.

Free Energy Changes along Adsorption and Desorption Branches

The negative free energy values (- ΔF) in desorption branches were consistently greater than those in adsorption branches for canola samples exposed to treatment A, B and D. This was equally the case on the first, third and fifth drying and rewetting cycle. However, the negative free energy values (- ΔF) in both adsorption and desorption branches came close together for canola samples exposed to treatment C on the first and third cycle, and almost overlapped on the fifth cycle. This was due to the diminution of the hysteresis on the first and third cycle and elimination of it on the fifth cycle at 40.0°C equilibrium temperature. The results were in agreement with those reported by Chung and Pfost (1967c), Strasser (1969) and others.

Free Energy Changes as Affected by Equilibration Temperature

The negative free energy changes on either adsorption or desorption branch, at 25.0°C equilibration temperature (treatment A), were consistently larger than those on the corresponding branch at 40.0°C equilibration temperature (treatment C) on every cycle. This was because the equilibrium relative humidity was smaller at 25.0°C than that at 40.0°C for the same moisture content. It was found that the difference in free energy on

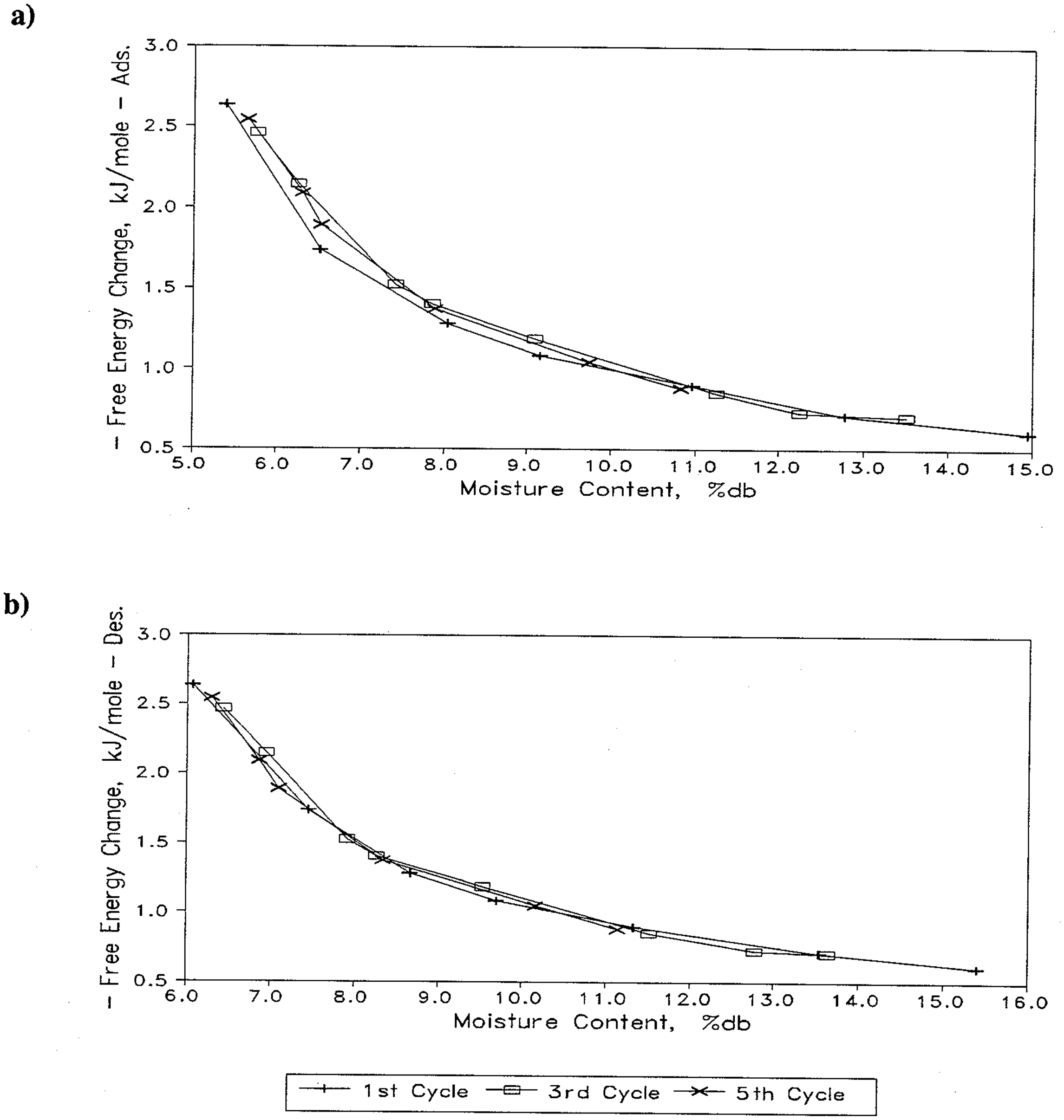

Figure 10 Free energy changes on the first, third, and fifth drying and rewetting cycles calculated from the adsorption (a) and desorption (b) isotherms of Westar canola subjected to treatment B

the same drying and rewetting cycle between 25.0°C and 40.0°C decreased with the increased number of cycles.

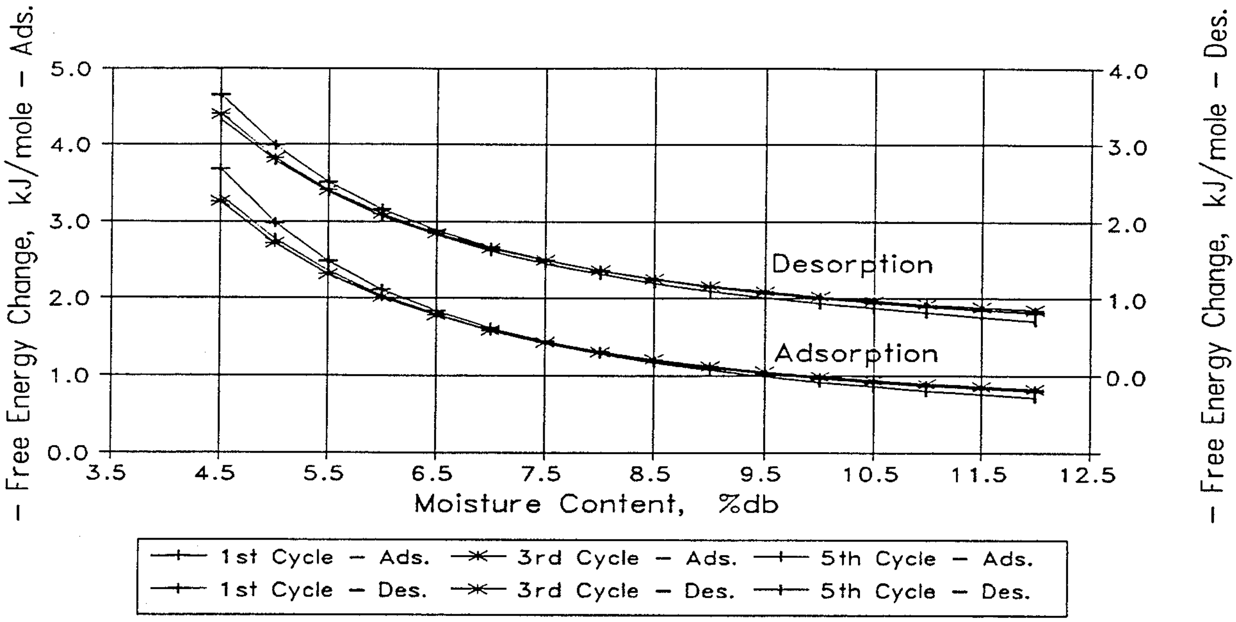

Figure 11 Free energy changes on the first, third, and fifth drying and rewetting cycles calculated from the adsorption (Ads.) and desorption (Des.) isotherms of Westar canola subjected to treatment C

Free Energy Changes for Canola as Affected by Multiple A/D Cycles

The multiple adsorption/desorption (A/D) cycles were implemented on the canola samples exposed to treatment A, B, C and D. On both adsorption and desorption branches of canola samples exposed to treatment A, C and D, the -ΔF values decreased as the number of cycles increased (Fig.9, Fig.11 and Fig.12). For treatment A, free energy decreased in a fairly constant decrement from the first to fifth cycles. As can be seen in Fig.9, the displacements in free energy curves between the first and third cycles and between the third and fifth cycles were about 0.6 kJ/mole with respect to the adsorption process and both were equally 0.4 kJ/mole with respect to the desorption process at the moisture content of 5.0 %db.

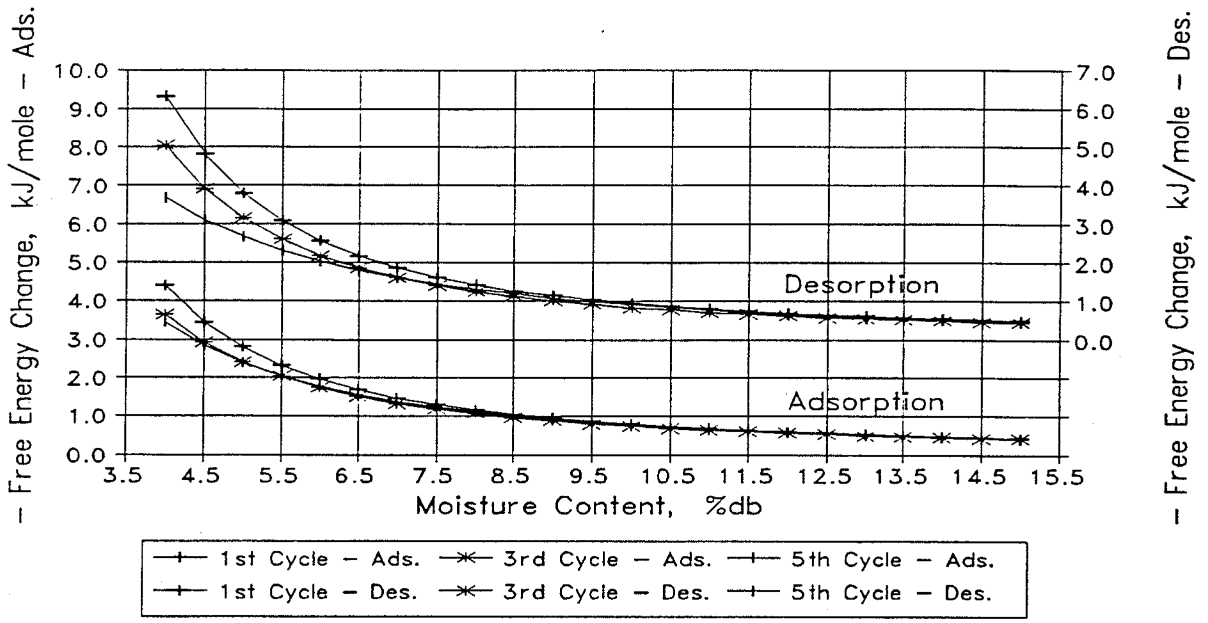

Figure 12 Free energy changes on the first, third, and fifth drying and rewetting cycles calculated from the adsorption (Ads.) and desorption (Des.) isotherms for Westar canola subjected to treatment D

For samples exposed to treatment C (Fig.11), a very little difference was found between the third and fifth drying and rewetting cycles for both adsorption and desorption processes. However, a difference remained between the first and the third cycle, although it was smaller than at 25.0°C. One of the possible explanations for this phenomenon is that in treatment C, the steric hinderance or any other resistance to water movement was not effectively eliminated by exposure of canola seeds to the first adsorption and desorption cycle under 40.0°C equilibrium temperature. It was totally eliminated after more times of exposure to adsorption and desorption cycles.

For treatment D (Fig.12), the - ΔF values also decreased as the number of cycles increased. The decrement between the first and the third cycles was almost the same as that between the third and fifth cycles in the desorption process. However, the former was much greater than the latter in the adsorption process.

On the whole, it was the trend that - ΔF values of water in canola decreased with the increased number of drying and rewetting cycles. This might index loss in the quality of canola bulk undergoing multiple cycles during its storage.

Free Energy Changes for Canola as Affected by Drying Temperature

Treatment A and B were designed to reflect the effect of drying temperature. In treatment A and B, the equilibrium temperature was 25.0°C, but the drying temperature of the former was 25°C and the latter 50°C. The absolute values of ΔF, i.e., - ΔF, for the samples exposed to treatment B decreased more on the lower than on the higher drying and rewetting cycles as compared with those for the samples exposed to treatment A. It was noticed that the pattern of free energy changes for treatment B during multiple drying and rewetting cycles was different from that for treatment A (Fig.9 and Fig.10). As can be seen in Fig.10, no difference and a slight difference in - ΔF existed respectively on desorption and adsorption as the number of drying and rewetting cycles increased to five.

The free energy changes during the multiple drying and rewetting cycles, as affected by drying temperature, suggested that for canola seeds dried at 25°C, adsorption or desorption was a much less favourable and spontaneous process on the fifth drying and rewetting cycle than on the first one. For canola seeds dried at 50°C, the favourability and spontaneity in moisture sorption was similar on each drying and rewetting cycle for desorption, and slightly increased with the number of drying and rewetting cycles for adsorption. The reason why the pattern of the free energy changes for the sample receiving treatment B was not similar to that of the sample receiving treatment A (i.e., -ΔF values decreased considerably with the increased number of drying and rewetting cycles) during multiple adsorption and desorption cycles could be postulated as follows. There probably existed a limit for the loss in moisture binding ability or the decrease in moisture sorption spontaneity and favourability of canola due to various factors such as cyclic drying and rewetting treatment, elevated drying temperature, and others. In treatment A, it was the five consecutive cycles of drying and rewetting treatment rather than the low drying temperature (25°C) that resulted in the loss in moisture binding ability or the decrease in moisture sorption spontaneity and favourability of canola, because the 25°C drying temperature was not high enough to exert measurable effect on the loss in moisture binding ability or the decrease in moisture sorption spontaneity and favourability of canola. In treatment B, however, canola was exposed to drying at an elevated temperature (50°C) before it was introduced to the isotherm apparatus for the EMC measurement on each adsorption and desorption cycle. It was quite likely that the loss in moisture binding ability or the decrease in moisture sorption spontaneity and favourability of canola might have already been brought to their limits due to the elevated temperature. As a result, there was no longer room for the multiple drying and rewetting cycles to show their effect, so that free energy along both adsorption and desorption remained almost unchanged throughout the five consecutive drying and rewetting cycles.

6.3.2 Isosteric Heat of Sorption

Temperature Dependency Test

The application of the Clausius-Clapeyron equation is based on the assumption that the heat of sorption is independent of temperature. However, as reviewed in section 3.1.5, most common substances do not exhibit linearity over a wide span of temperature. Linearity is generally found within a certain range of temperatures for a certain material. So far, little has been reported about the temperature dependency of the heat of sorption related to rapeseed (canola).

Temperature dependency test was conducted for four rapeseed varieties, i.e., Candle, Tobin, Global and Westar, using the isotherm data reported by Pixton and Henderson (1981), Sokhansanj et al. (1986) and Otten et al. (1990), and those measured in the present study. The empirical isotherm equation proposed in this study, i.e., Eq.(21), was used to express the EMC-ERH relationship of rapeseed due to its high accuracy in describing the isotherms of this agricultural product.

Fig.13 shows the relationship between ln(RH) and the reciprocal of absolute temperature, 1/T, for Westar canola investigated in this study. The lines in Fig.13, as well as in other figures in this section, are only used to distinguish between symbols, and do not necessarily indicate the trend of the ln(RH) versus 1/T relationship. It can be seen from Fig.13 that the overall linearity did not exist in the whole span of temperatures. The correlation coefficients were generally less than 0.7 if the ln(RH) was regressed against 1/T in the whole temperature range. However, regional linearity existed in the low temperature range (3.5-6.0°C), low-intermediate temperature range (6.0-25.0°C), and the intermediate temperature range (25.0-45.0°C). At low moisture contents close to 4.5 %db, the linearity was poor in the low-intermediate temperature range. From Fig.13, it is obvious that the slopes of the ln(RH) vs. 1/T lines had a different magnitude in a different temperature range. This signified different heat involvement in different temperature ranges. It is extraordinary that the slope in the low-intermediate temperature range was positive.

Fig.14 shows the result of the temperature dependency test using the EMC data of canola (rapeseed) variety Tobin reported by Sokhansanj et al. (1986). Again, overall linearity did not exist in the temperature range from 5 to 25°C. However, the different slopes in the three temperature regions were apparent. These three temperature regions were 5-10°C, 10-15°C, and 15-25°C. The relationship between ln(RH) and 1/T resembled that of this study. This would suggest that the way the solutes in a canola kernel interacted with water molecules was different in different temperature ranges. Further research is needed to verify the temperature dependency of canola varieties Westar and Tobin.

The linearity of ln(RH) versus 1/T was excellent throughout the whole temperature range (5-35°C) for rapeseed variety Candle, as shown in Fig.15, which is constructed using

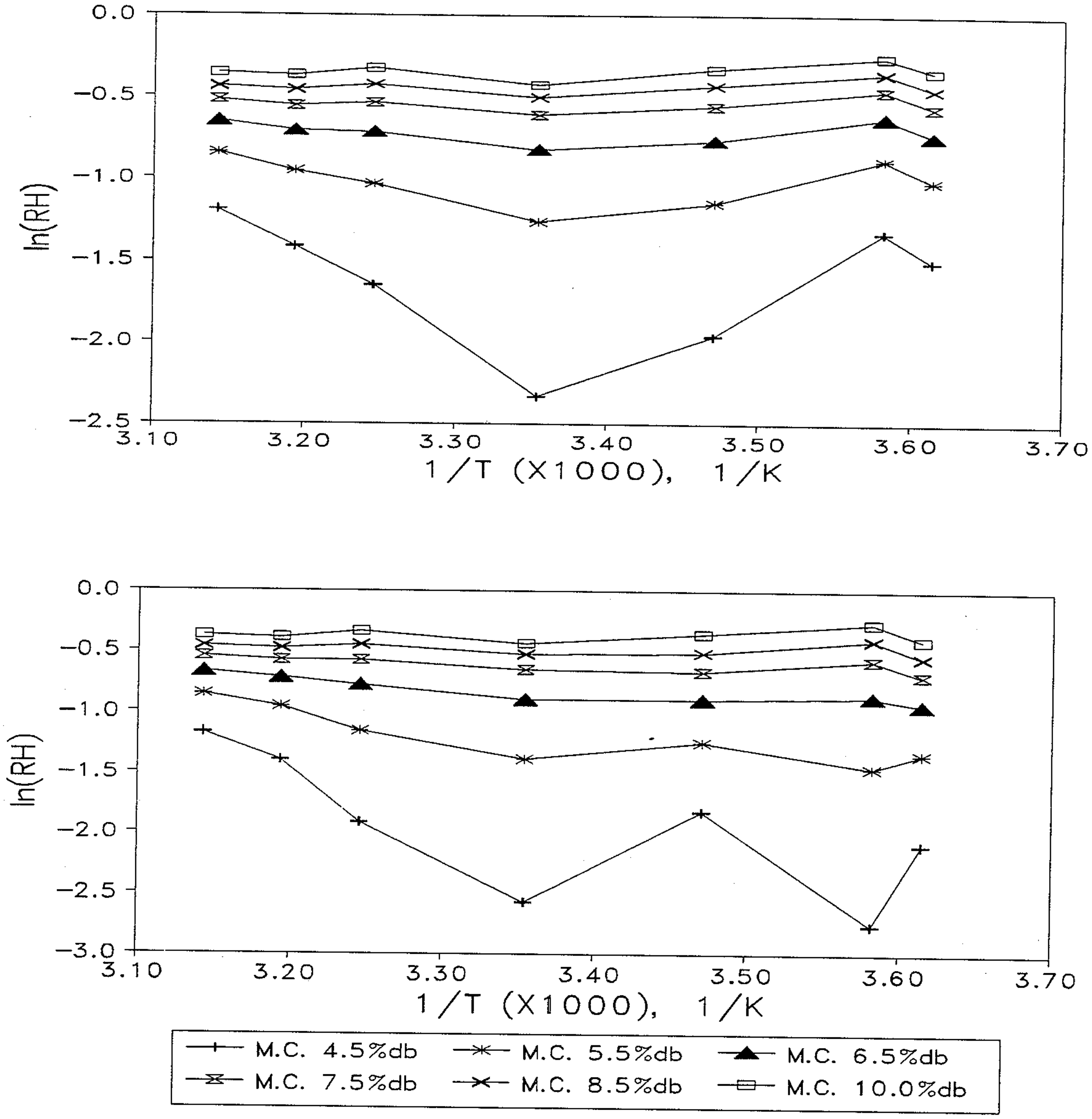

Figure 13 Relationship between ln(RH) and 1/T at temperatures from 3.5 to 45.0°C for Westar canola on adsorption (upper) and desorption (lower) respectively

the adsorption isotherms measured by Pixton and Henderson (1981). For desorption process, the linearity was equally excellent throughout the 5-35°C temperature range. No regional slope difference could be found. This suggested that the heat involvement in this

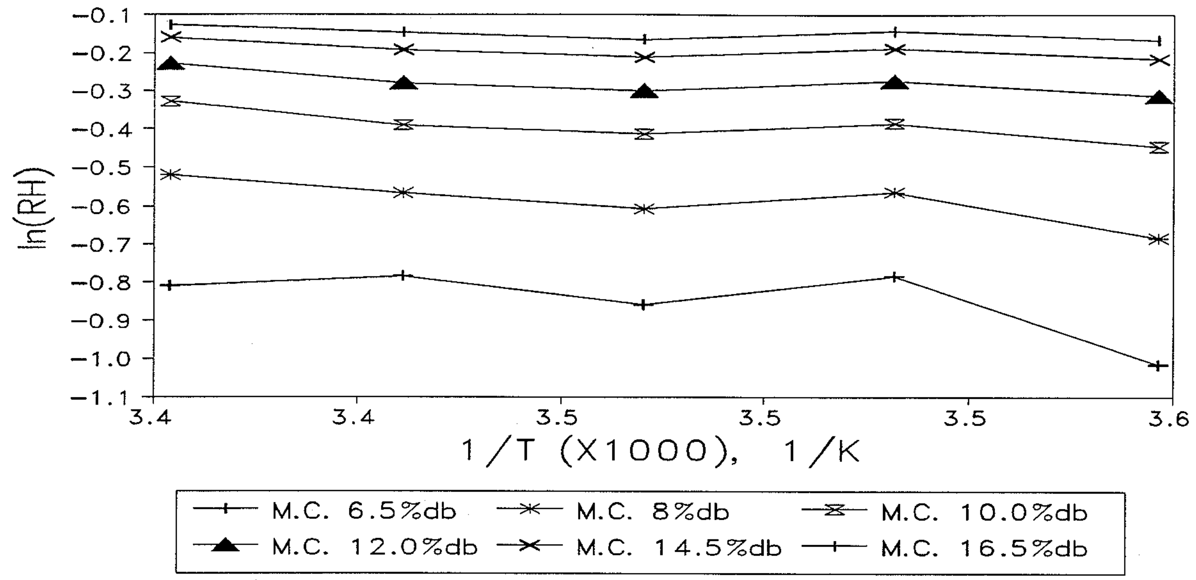

Figure 14 Relationship between ln(RH) and 1/T at temperatures from 5 to 25°C for Tobin canola investigated by Sokhansanj et al. (1986)

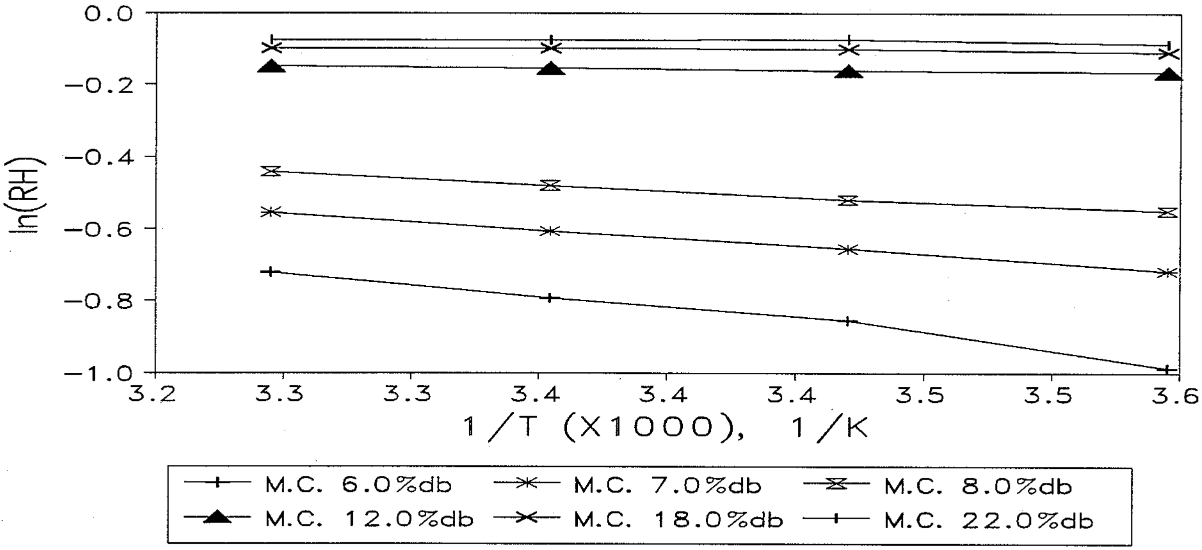

Figure 15 Relationship between ln(RH) and 1/T at temperatures from 5 to 35°C for rapeseed variety Candle investigated by Pixtion and Henderson (1981)

temperature range (5-35°C) for rapeseed variety Candle was uniform. Furthermore, this also seemed to suggest that the mechanism of water-solute interaction for candle rapeseed might be different from that for rapeseed varieties Westar or Tobin in certain temperature regions within this temperature range (5-35°C).

The temperature dependency of the isosteric heat of sorption at the intermediate to high temperature range (25-75°C) for canola variety Global is shown in

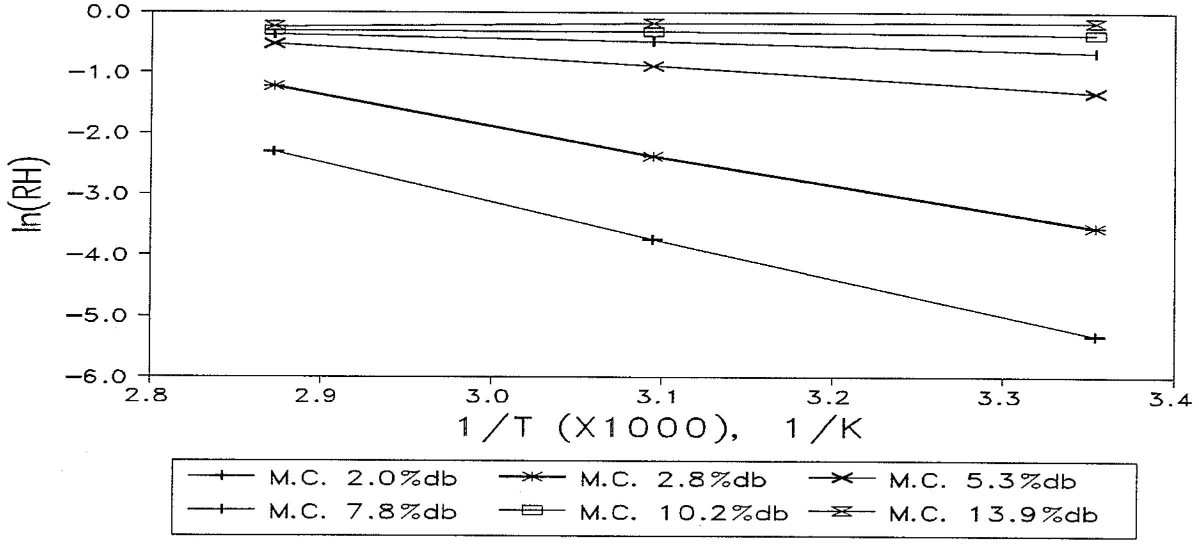

Figure 16 Relationship between ln(RH) and 1/T at temperatures from 25 to 75°C for Global canola investigated by Otten et al. (1990)

Fig.16, which is drawn using the EMC data reported by Otten et al. (1990). Excellent linearity existed, which extended from the intermediate temperature range up to the high temperature range, i.e., from 25°C to 75°C. Also, the slopes in this temperature range were comparable with the slopes in the intermediate temperature range of the present study. This suggested that the heat involvement, and therefore the water-solute binding energy, were similar in the intermediate and the intermediate-high temperature ranges for canola varieties Westar and Global.

Net Isosteric Heat of Canola during Multiple A/D cycles

As reviewed in section 3.1.3, isosteric heat of sorption can be calculated by integrating Eq.(7) between two water vapour pressures. However, it is more convenient to use the term of net isosteric heat of sorption (Q_{net}), which can be obtained by replacing the water vapour pressure with relative humidity. The Q_{net} is the difference between the isosteric heat involved in the phase transition from an adsorbed liquid to the vapour state or the reverse (Q_{st}) and the molar enthalpy of vaporization or condensation of pure water (Q_{vap}). The relationship between the total molar enthalpy change and the net isosteric heat of sorption was given by Kapsalis (1987) .

The net isosteric heats of adsorption and desorption during multiple drying and rewetting cycles were calculated using the isotherms measured in the present study. As discussed in section 6.3.2 A, the linearity between ln(RH) and 1/T was good in the temperature range of 25.0°C to 45.0°C for Westar canola. Because of this, the relative humidities at any two temperatures in this temperature range could be chosen to integrate Eq.(7) to determine Q_{net}. Thus, the resultant, Q_{net}, would not be of much difference from that determined by linear regression of ln(RH) and 1/T using relative humidities at the temperatures of 25.0, 35.0, 40.0, and 45.0°C. Hence, to simplify the calculation, the Q_{net} of water vapour on canola was calculated using only the relative humidities at the temperatures of 25.0°C and 40.0°C. In low temperature range, the net isosteric heat of sorption was only calculated on the first drying and rewetting cycle because the isotherms on the drying and rewetting cycles other than the first at 6.0°C were not available at the present time. This will be further discussed in section 6.3.3.

Fig.17 shows the absolute values Q_{net} as a function of equilibrium moisture content on the first, third, and fifth drying and rewetting cycles. The general picture

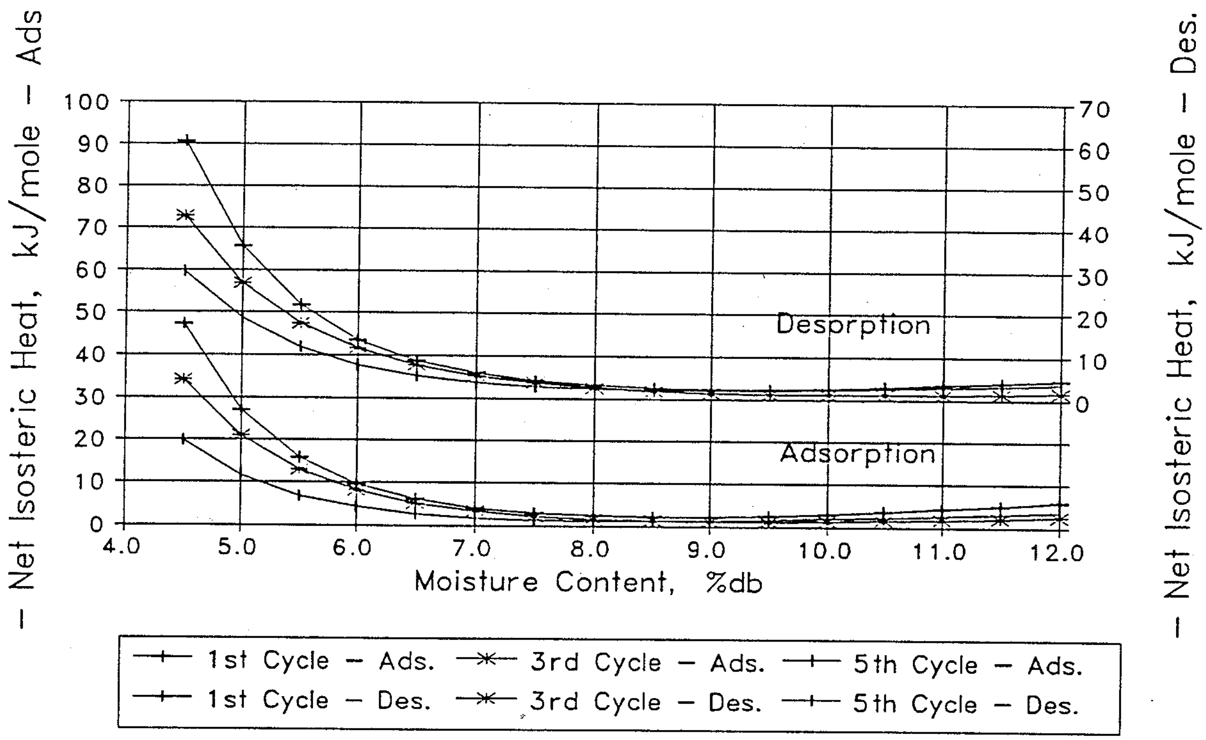

Figure 17 Net isosteric heat on the first, third, and fifth adsorption (Ads.) and desorption (Des.) cycles as a function of moisture content for Westar canola investigated in this study

of Q_{net} on the first, third and fifth drying and rewetting cycles was as follows: desorption curves always lay above the adsorption curve; the Q_{net} dropped quickly at moisture contents ranging from 4.5 to 6.0 %db; from 6.0 to 8.0 %db, it decreased slowly to its minimum (around 1 kJ/mole); from 8.0 to 12.0 %db, it lounged between 1 and 6 kJ/mole; basically, from the moisture content around 8.0 %db and up, the sorbed water behaved similar to free water.

The behaviour of Q_{net} in terms of drying and rewetting cycles is further indicated in Fig.18, which plots the absolute values of Q_{net} versus the sequence of drying and rewetting cycles. From Fig.18, as well as Fig.17, it is manifest that Q_{net}, both for adsorption or desorption, decreased as the number of drying and rewetting cycles increased. However, the decrement between the first and third cycles was less than that between the third and the fifth. This was especially true for the adsorption process. For example, the decrements from the first to third and from the third to fifth cycles, at 5.5 %db moisture content, were about 4.5 and 6.1 kJ/mole, respectively, for desorption process, while the former was about 2.5 kJ/mole and the latter was about 6.9 kJ/mole for adsorption process. This indicated that the binding strength of water to the substrate in canola seeds, or in other words, the water sorptive ability of canola seeds, decreased more and more as the number of drying and rewetting cycles increased from one to five, especially when the canola kernels underwent adsorption process. It was difficult in the present study to correlate mathematically the isosteric heat with the number of drying and rewetting cycles, since only three cycles were available. However, the relationship between the isosteric heat of sorption and the number of drying and rewetting cycles was to some extent apparent. For both adsorption and desorption processes, the relationship between the net isosteric heat and the number of cycles was more similar to that of a straight line at the two ends of the moisture content range from 4.5 to 12.0 %db than in the middle of this moisture range. In the middle of the moisture content range, the

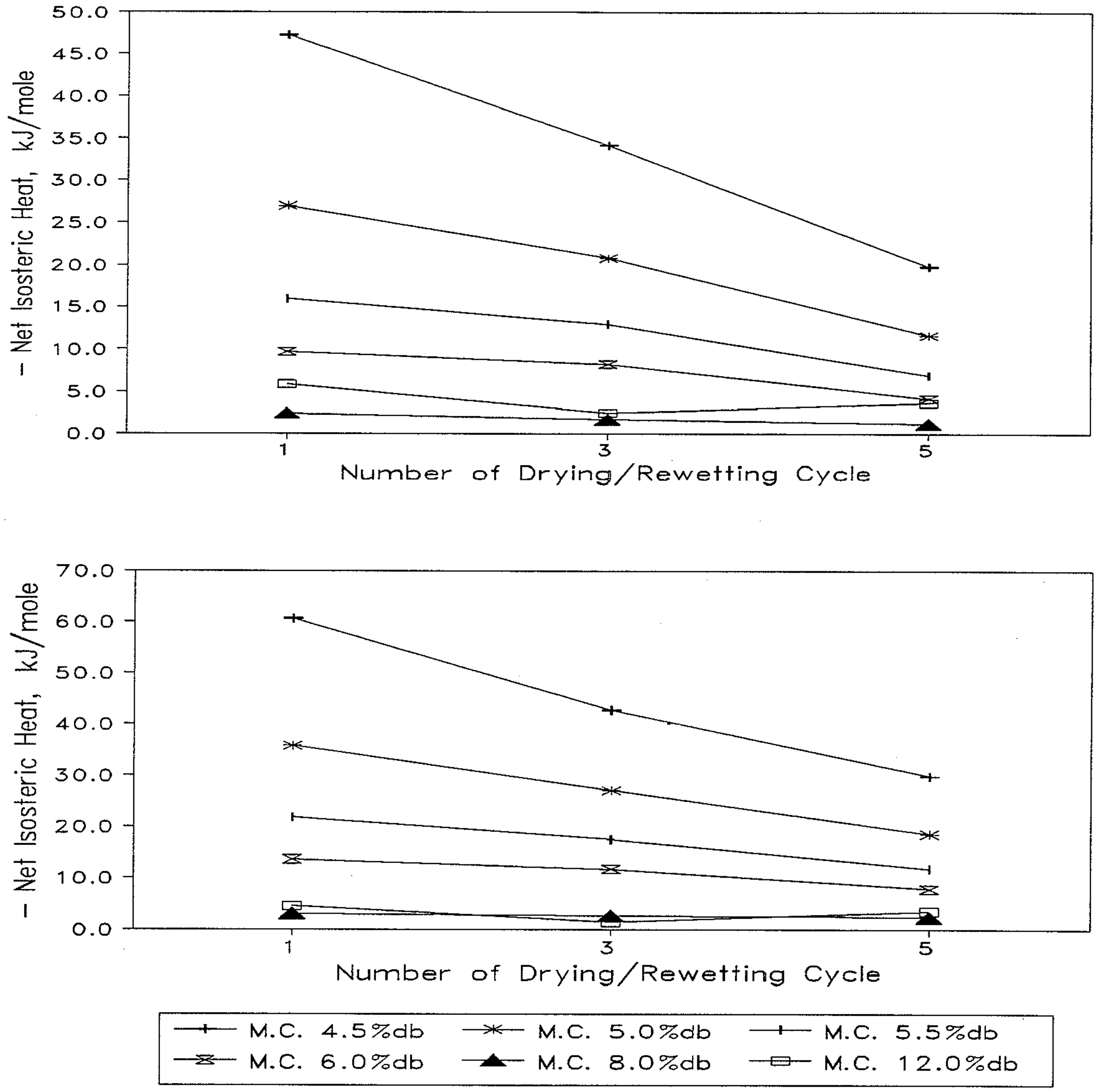

Figure 18 Net isosteric heat of adsorption (upper) and desorption (lower) as a function of the number of drying and rewetting cycles

relationship was slightly curve-shaped. The relationship between the isosteric heat, in the term of latent heat, and the number of drying and rewetting cycles will be further discussed in section 6.3.3.

From Fig.18, it can be seen that the isosteric heat changed with the number of drying and rewetting cycles primarily at moisture contents below 8.0 %db. There was little effect of drying and rewetting cycles on the isosteric heat at moisture contents higher than 8.0 %db, as indicated by the nearly slope-free lines corresponding to the moisture contents above 8.0 %db (Fig.18). This result implied that considerable changes in the water-solute interaction pattern might, although the exactly related mechanism is still unknown, have taken place at the moisture contents between the monolayer and capillary condensation regions for canola seeds undergoing multiple adsorption and desorption processes which might occur as the result of various environmental stimulators such as leakage in storage bins, weather change, temperature difference inside the bins, microorganism growth, etc..

Since a large difference in Q_{net} was observed at moisture contents below 8 %db between the first and any other drying and rewetting cycles, the empirical formula of the heat of vaporization for canola, which is an integral part of mathematical models of rapeseed (canola) drying, should be revised. The effect of drying and rewetting cycles should be taken into account, if the kernels were subjected to multiple cycles, in order to raise the prediction accuracy of the drying models.

6.3.3 Latent Heat of Vaporization for Rapeseed (Canola)

<u>Magnitude of the Latent Heat</u>

The latent heat of vaporization or condensation of water in moist rapeseed (canola)

(L_c), or alternatively, Q_{st}, was calculated using Eq.(7). The latent heat of free water was taken as 43.9 kJ/mole. This value was determined by applying the Clausius-Clapeyron equation to the vapour pressure data between 5°C and 50°C listed in appendix A of the book by Labuza (1984). Thus, the latent heat of free water used here was an average within the temperature range from 5°C to 50°C. In addition to the isotherms obtained in the present study, those by Pixton and Henderson (1981), Sokhansanj et al. (1986), and Otten et al. (1990) were also used in calculation, so that a comparison of latent heats among different rapeseed varieties could be made.

The latent heat of vaporization for moist rapeseed (canola) calculated in this study is summarized in Table II. Listed in Table II are the maximum and minimum latent heats in both adsorption and desorption processes, the temperature ranges, the equilibrium moisture content ranges, and the sources of the data used in calculation. The overall comment on the latent heat of vaporization for rapeseed (canola) is that it ranged between 44 (the latent heat of free water) and 152 kJ/mole for the moisture range from 4 to 22 %db. The latent heat of vaporization for rapeseed variety Candle was the lowest, and that for canola variety Westar was the highest among these four varieties (Candle, Tobin, Global and Westar) studied. The magnitude of latent heat for rapeseed variety Candle was generally over 50% less than that in variety Westar at the same moisture content below about 8%. The magnitude of latent heat for these four rapeseed (canola) varieties in ascensive order was: Candle, Tobin, Global and Westar. Only the latent heat of water in Global canola was found to be comparable to that in Westar canola in a certain moisture content region. For example, at the moisture content of 6 %db, the latent heats of water in both Westar and Global canola at temperatures above 25°C were around 10 kJ/mole. However, at moisture contents below 6 %db, the former increased faster than the latter. The finding indicated definite differences in the strength of sorptive sites available in different rapeseed varieties. The water sorbed in Westar canola might be bonded much more tightly than that in Candle rapeseed, as the results suggested. More energy would accordingly be required to dehydrate Westar canola than Candle rapeseed under the same conditions, if a final moisture content below 8 %db is desired.

Table II Magnitude of latent heat of vaporization for four rapeseed varieties (kJ/mole)

Data Source	Temp. Range (°C)	M.C. Range (%db)	Adsorption		Desorption	
			Max. L_c	Min. L_c	Max. L_c	Min. L_c
[1]Pixton and Henderson (1981)	5-35	6-22	46	44	50	44
[2]Sokhansanj et al. (1986)	5-25	6-19	67	44	N/A	N/A
[3]Otten et al. (1990)	25-75	2-12	96	44	N/A	N/A
[4]Present Study	3.5 | 45.0	4-20	101	45	152	44

1 Candle 2 Tobin 3 Global 4 Westar

Relationship Between Latent Heat and Equilibrium Moisture Content

The mathematical model used to describe the relationship between latent heat and equilibrium moisture content is of the following form:

$$L/L' = 1 + \mathbf{a}\exp(\mathbf{b}m) \qquad (11)$$

where L and L' denotes the latent heat of water in the material investigated and free water respectively, m denotes the equilibrium moisture content, and **a**, **b** are constants. As reviewed in section 3.1.4, the latent heats of various farm products and food materials have been calculated and correlated with equilibrium moisture contents to determine the constants **a** and **b** by many researchers. However, it was found that not all materials had a perfectly straight line relationship between ln(L/L'-1) and m over the entire moisture content range. Different linearity between ln(L/L'-1) and m was from time to time found to exist in different moisture regions for a certain material. In this case, Eq.(11) should be, as an approximation, applied to different moisture content ranges to determine the **a** and **b** constants associated with those respective ranges. This has been done by Cenkowski et al. (1990) for canola by distinguishing between the moisture contents above and below 7.5 %db.

The latent heats of water in canola variety Westar investigated in this study were also correlated with the equilibrium moisture contents to determine the constants **a** and **b**. Results are summarized in Table III, which lists the constants **a** and **b** on the first, third and fifth drying and rewetting cycles for the Westar canola samples used in the present

Table III a, b and r on different adsorption and desorption cycles for Westar canola in the moisture range from 4 to 8 %db

	Cycl #1		Cycl #3		Cycl #5	
	Ads.	Des.	Ads.	Des.	Ads.	Des.
a	48.11	59.33	38.09	34.18	17.72	17.04
b	-0.88	-0.86	-0.88	-0.80	-0.85	-0.74
r	0.993	0.996	0.999	0.999	0.989	0.993

Table IV a, b and r for Candle, Tobin and Global rapeseed (canola)

Candle (Pixton and Henderson 1981)

	m 6-16 %db		m 16-22 %db	
	Adsorption	Desorption	Adsorption	Desorption
a	0.16	0.58	0.027	0.017
b	-0.21	-0.28	-0.093	-0.053
r	0.988	0.986	0.998	0.970

Tobin (Sokhansanj et al. 1986)

	4.9-10°C Range		10-25°C Range	
	m 6.5-13 %db	m 13-18.5 %db	m 6.5-11 %db	m 11-17 %db
a	3.17	0.14		1.89
b	-0.30	-0.057	N/A	-0.20
r	0.988	0.973		0.990

Global (Otten et al. 1990)

	m 2-11 %db
a	3.45
b	-0.46
r	0.992

study in the 25.0-45.0°C temperature range. To facilitate comparison among different rapeseed varieties, the constants **a** and **b** for Global, Tobin and Candle rapeseed investigated by other researchers are also listed in Table IV. The r values in Table III and Table IV are the correlation coefficients indicating the degree of linearity between ln(L/L'-1) and m. Whenever the regional linearity occurred, Eq.(11) was applied to the specific moisture content region to determine the constants **a** and **b** for this particular moisture content region. It can be seen from Table III and Table IV, the r values are generally larger than 0.97. This means that in the moisture regions selected, Eq.(11) describes very well the relationship between the ln(L/L'-1) and m. The constants **a** and **b** are found to be quite different from one rapeseed variety to another. This is because the heat involvement was, as discussed earlier, different for the four rapeseed varieties mentioned above.

The effect of multiple drying and rewetting cycles on latent heat of water in rapeseed can also be reflected by the constants **a** and **b** in Table III. It is apparent from Table III that the constant **b** changed little as the number of cycles increased up to five, but the constant **a** decreased as the number of cycles increased. The effect is further depicted in Fig.19, where the constants **a** are plotted against the number of cycles. Constant **a** was in an approximate linear relationship with the number of cycles, although the exact relationship between them is still unknown due to insufficient data points available.

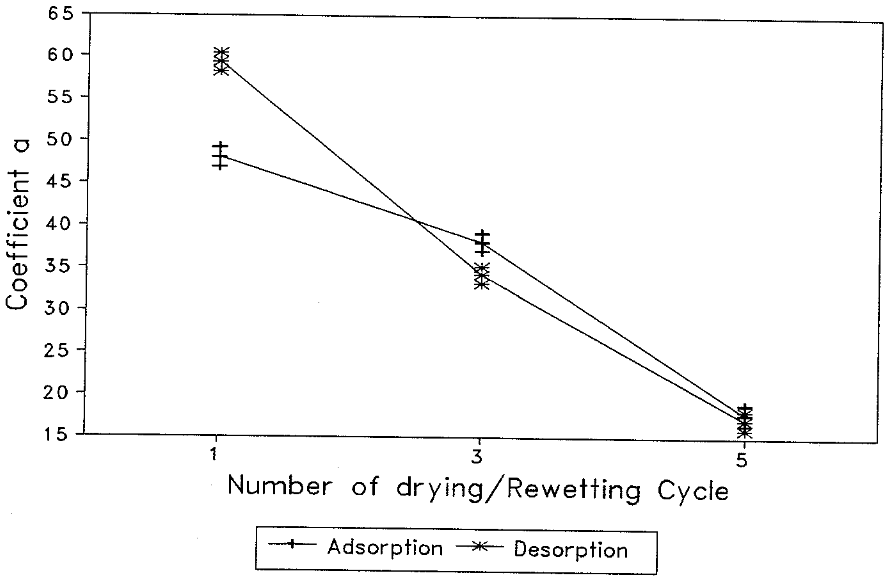

Figure 19 The relationship between the coefficient a in Eq.(11) and the number of drying and rewetting cycles with the standard error of the coefficient a being marked

6.3.4 Entropy of Sorption of Water Vapour on Canola

The differential entropy of sorption can be calculated by the following formula:

$$\Delta S = \frac{Q_{st} - \Delta F}{T} \qquad (12)$$

Because

$$Q_{st} = Q_{net} + Q_{vap} \qquad (13)$$

the entropy of sorption becomes:

$$\Delta S = \frac{Q_{net} - \Delta F}{T} + \frac{Q_{vap}}{T} \tag{14}$$

or,

$$\Delta S - \frac{Q_{vap}}{T} = \frac{Q_{net} - \Delta F}{T} \tag{15}$$

where the left-hand side denotes the net entropy of sorption (ΔS_{net}) which is the portion of entropy change over that of free water at the same temperature. Therefore,

$$\Delta S_{net} = \frac{Q_{net} - \Delta F}{T} \tag{16}$$

Considering any two isothermal temperatures (T_1 and T_2) involved in the entropy calculation, the net entropy of sorption during adsorption or desorption process at these two temperatures (ΔS_{net1} and ΔS_{net2}) will be as follows:

$$\Delta S_{net1} = \frac{Q_{net1} - \Delta F_1}{T_1} = \frac{\left(\frac{RT_1T_2}{T_2 - T_1}\ln\frac{RH_1}{RH_2} - RT_1 lnRH_1\right)}{T_1} \tag{17}$$

Simplification of the above yields:

$$\Delta S_{net1} = R\left(\frac{\ln RH_1^{T_1} - \ln RH_2^{T_2}}{T_2 - T_1}\right) \tag{18}$$

In the same way, the ΔS_{net2} can be obtained given that ΔH_{net} is constant over the temperature range as follows:

$$\Delta S_{net2}=\frac{Q_{net2}-\Delta F_2}{T_2}=\frac{(\frac{RT_1T_2}{T_2-T_1}\ln\frac{RH_1}{RH_2}-RT_2\ln RH_2)}{T_2} \tag{19}$$

Simplification of the above formula gives:

$$\Delta S_{net2}=R(\frac{\ln RH_1^{T_1}-\ln RH_2^{T_2}}{T_2-T_1}) \tag{20}$$

It can be seen from the above derivation that the net entropies of sorption at both temperatures coincide. From this step forward, it is easy to show that the entropy change will go along the same trend at any temperature within the range where the Clausius-Clapeyron equation holds. As indicated in section 6.3.2, linearity of ln(RH) versus 1/T was good in the temperature range from 25.0°C to 40.0°C for Westar canola, that is to say, the Clausius-Clapeyron equation applied fairly well to this temperature range. Thus, the entropy change could be calculated using the isotherms at any two temperatures in this temperature range without losing too much accuracy. Shown in Fig.20 are the net entropies of both adsorption and desorption calculated using Q_{net} and ΔF data at 25.0°C and 40.0°C equilibration temperatures.

Parallelism has also been found between the curves of ΔS_{net} versus moisture and the Q_{net} versus moisture, so most of the behaviour with Q_{net} curves could be found to be with ΔS_{net}. To be specific, the net entropy of desorption was invariably larger than that of adsorption. At the moisture contents above 8 %db, the entropy of sorption stayed closely to zero indicating the water sorbed in this region behaved like free water.

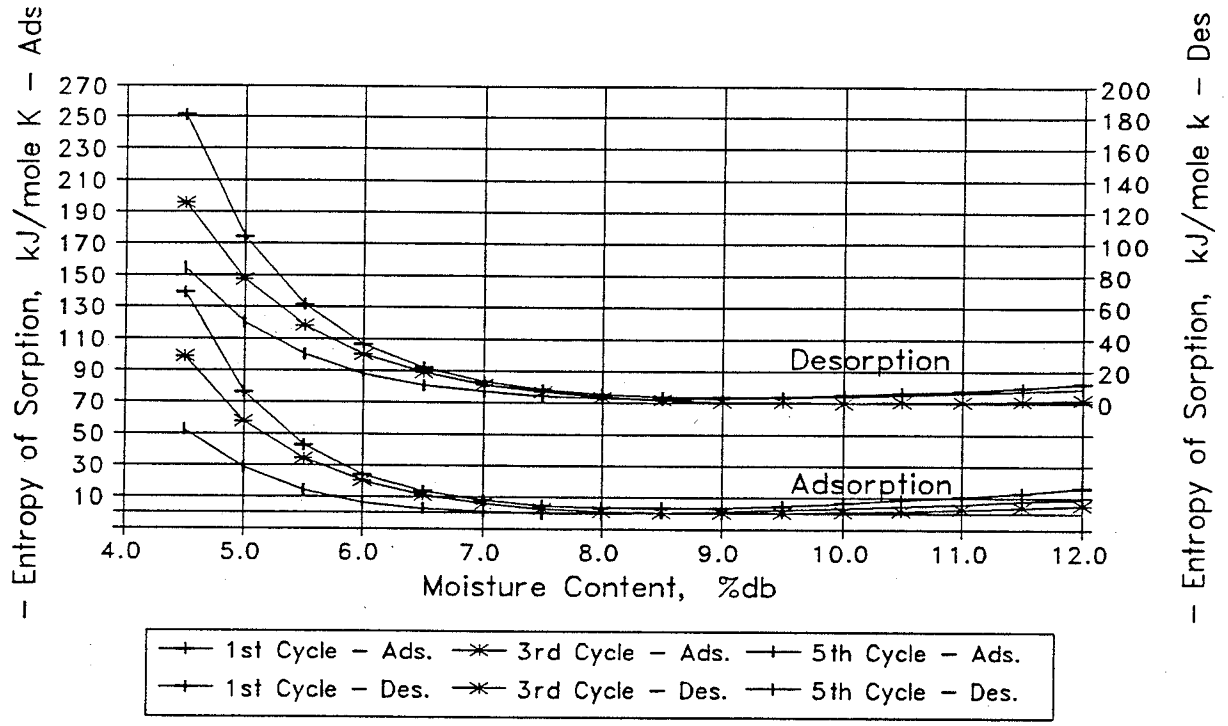

Figure 20 Net entropy of adsorption (Ads.) and desorption (Des.) as a function of moisture content in 25.0 to 40.0°C temperature range for Westar canola

The ΔS_{net}, in terms of multiple adsorption and desorption cycles, changed in the similar way as the Q_{net} did, that is, the negative values of entropy change decreased as the number of drying and rewetting cycles increased, and the decrease was faster from the third to the fifth cycle than from the first to the third cycle, especially for adsorption process. This might be a manifestation that the sorptive sites in canola seeds became less and less sorptive and more and more disorganized as the number of drying and rewetting cycles increased. This is probably due to the frequency of the stress and solubilization exerted by the water molecules moving into and out of the seeds during the multiple adsorption and desorption processes.

6.3.5 Reversibility and Irreversibility of Moisture Sorption of Canola

In most cases, moisture sorption is, as reviewed in section 3.1.7, an irreversible process. This also holds true to the moisture sorption of canola. It has been proven by the adsorption and desorption isotherms of many rapeseed varieties, such as Gulle, Hektor, Tower (Pixton and Warburton 1977), Candle (Pixton and Henderson 1981), and Westar (Bielewicz 1991; Yang and Cenkowski 1991), that moisture sorption hysteresis, which results from the existence of various irreversible processes, occurs at temperatures from 3.5°C to 45.0°C on the first adsorption and desorption cycle. However, like many other food and agricultural materials, reversible (hysteresis free) sorption isotherms have been found for canola variety Westar at 40.0°C on the fifth adsorption and desorption cycle as the result of moisture cyclic treatment (Yang and Cenkowski 1991). According to this finding, reversible isotherms of canola could be obtained by means of multiple drying and rewetting cyclic treatment up to five cycles or more at the equilibration temperature of 40°C or higher. The reversible isotherms are important in the study of water-binding characteristics of a material, since many valuable results in connection with the mechanism of irreversible sorption process, the water-solute interaction pattern during a irreversible sorption, and the state of irreversibly sorbed water, etc. can be envisaged by analyzing the differences between the thermodynamic quantities calculated from irreversible and reversible isotherms. Benado and Rizvi (1985) calculated the thermodynamic functions from the reversible and irreversible isotherms of rice. They established that for rice, the reversible thermodynamic functions corresponded to neither the adsorption nor the desorption branch of the isotherms which exhibited hysteresis, although they might look similar in shape. As mentioned earlier, it is possible to obtain reversible isotherms for canola. It is therefore possible to investigate the thermodynamic irreversibility of moisture sorption of canola by means of the reversible isotherms obtained. Unfortunately, the present research has not yet gone that far. This could become the work of the future.

6.3.6 Monolayer Coverage

Chung and Pfost (1967c) established that the monolayer coverage of desorption were consistently higher than those of adsorption, indicating stronger sorptive capacity in desorption than in adsorption. There are several isotherm equations capable of determining the monolayer coverage values, as reviewed in section 3.2.5. Among them, the BET equation is the most popular one for calculation of monolayer moisture contents.

Linearity of the BET equation, as applied to the sorption isotherms of a material, especially at low moisture content range, is the prerequisite for this equation to give good performance in monolayer value determination. Braunauer et al. (1938) reported that for most inorganic materials adsorbing organic gases, the equation could give a good fit for the isotherm data below 35% relative humidity. The BET equation was found to describe properly the sorption isotherms of some biological materials up to about 50%

relative humidity (Babbitt 1942; Pauling 1945; Mellon et al. 1947; Dole and Faller 1950; Becker 1956; Bushuk and Winkler 1957; Hall and Rodriquez-Arias 1958). The BET linearity to canola isotherms was also checked by Yang and Cenkowski (1991) using the EMC-ERH data from different sources. Linearity held up to 50% relative humidity for most isotherms of canola, with some being up to as high as 74% relative humidity.

The monolayer values for the four rapeseed varieties calculated in the present study were between 2.90 %db and 3.40 %db. The monolayer moisture contents calculated from the 25.0°C isotherms of Westar canola obtained in this study also showed the consistency of the monolayer coverage in desorption larger than those in adsorption. At 40.0°C, the monolayer coverage between adsorption and desorption were found to be close to each other. This denoted the similarity in sorptive capacity of canola on adsorption with that on desorption at this temperature, and could, to some extent, account for the cause of the reduction of hysteresis size on the lower drying and rewetting cycles and the elimination of hysteresis on the fifth drying and rewetting cycle. Cyclic treatment has been found to decrease the monolayer coverage. For example, the monolayer values for adsorption and desorption at 25.0°C on the first drying and rewetting cycle were 3.30 and 3.39 %db respectively, while those on the fifth cycle were 3.19 and 3.29 %db respectively. It has also been found in this study that increase in isothermal temperature decreased the monolayer coverage. This appeared to coincide with the results calculated from the data at different temperatures by Otten et al. (1990), namely, 3.55%, 3.09% and 2.21% at 25°C, 50°C and 75°C respectively.

The information drawn from the monolayer coverage calculated using the data obtained in this study and by other researchers, as well as the information from the thermodynamic functions discussed earlier, seemed to present the following picture of the water sorbed in canola: it was only up to moisture contents of about 3 %db that water was sorbed within the monolayer, when the strongest sorptive sites had just been covered, and the net heat of sorption and the net entropy of sorption had just come to their maximum and minimum, respectively. In the moisture range between 3-6 %db, water was sorbed in the sites of fast-decreasing sorption capacity, so the heats of sorption, which reflect the binding strength of the sorbent and sorbate, on every cycle dropped down rapidly. Water molecules remained sorbed to the solutes in a rapeseed kernel with reduced binding strength as the moisture content went up from 6 %db. Almost all the favourable sorptive sites had been occupied when moisture content reached 8 %db or so. Water that was further sorbed began to behave like free water.

6.4 Moisture Equilibrium Characteristics

6.4.1 Abnormality in Isotherms

Most isotherms obtained in this study fell into the flattened portion of the sigmoid type II classification typical of biological materials, since most EMC measurements were conducted at the relative humidities within 30-80% range. Irregularity in the isotherm shape in the approximate region of 20-45% relative humidity was observed on the first and the second adsorption and desorption cycles for the canola exposed to treatment A, as depicted in Fig.8. For the first cycle, the isotherms were abnormally concave between 20 and 45% relative humidities, while for the second cycle they became convex. The irregularity in the isotherms was reported by Van den Berg et al.(1975) for potato starch near 30% relative humidity. Since the precision of the EMC and ERH measurements was very good in our experiments, the unevenness in isotherms was not likely due to experimental errors. Such behaviour would probably indicate certain kinds of characteristic mutations, such as a transition of the isotherm process (Van den Berg et al. 1975), change in the property of water-solute interaction, and furthermore, an alteration in elasticity of micropores of the kernels. The observed irregularity in isotherms for the relative humidity around 30% corresponded to the moisture region that was between monolayer and multilayer coverage. After completion of the second rewetting and drying cycle, the isotherm curves gradually returned to regular shape on the third, fourth and fifth cycle. Above the relative humidity of about 50%, the isotherms in all cycles were almost parallel with each other (Fig.8).

6.4.2 Effect of Multiple A/D Cycles on Sorptive Capacity of Canola

The moisture sorptive capacity of canola subjected to treatment A decreased in the low to intermediate moisture range as a result of multiple adsorption and desorption cycles. This is shown in Fig.21, where the adsorption and desorption isotherms on the first and fifth drying and rewetting cycles for the canola samples subjected to

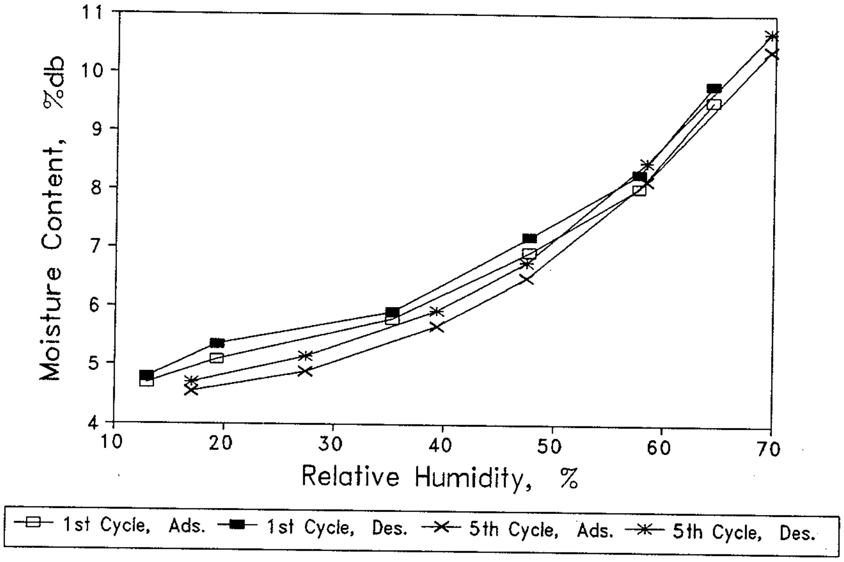

Figure 21 Comparison of adsorption and desorption isotherms of Westar canola subjected to treatment A between the first and fifth drying and rewetting cycles

treatment A are plotted together. It can be seen from Fig.21 that the isotherms on the fifth drying and rewetting cycle are quite beneath those on the first cycle at the relative humidity of 58% and lower. At the relative humidity 48%, the differences in EMC values between the first and fifth rewetting and drying cycle for desorption and adsorption curves are approximately 0.39 %db, which is about 1.5 times as much as the hysteresis size of the fifth drying and rewetting cycle at the same relative humidity and temperature. At the relative humidity of 17%, these differences are 0.43 and 0.54 %db for the adsorption and desorption curves, respectively. This is about 2-2.5 times the hysteresis magnitude of the fifth drying and rewetting cycle at the same relative humidity and temperature. This may be attributed to the sequential stress of water molecules exerted on canola tissues due to their inward and outward movement during the multiple adsorption and desorption cycles. This could, therefore, "wear away" the water holding capacity of the sorptive sites available in the canola seeds.

However, the sorptive capacity of canola seeds exposed to treatment B was constant throughout all the cycles on desorption and slightly increased on adsorption with an increased number of drying and rewetting cycles. In Fig.22, where the adsorption and desorption isotherms on the first and fifth drying and rewetting cycles for the canola samples subjected to treatment B are shown, the desorption isotherms on the first and the fifth cycles almost overlapped, and the adsorption isotherms on the first and the fifth cycle stayed close to each other, with the isotherm on the fifth cycle being slightly above that on the first cycle at the relative humidities below 68%. It is interesting to note that the effect of multiple drying and rewetting cycles on sorptive capacity of canola associated with treatment A and B were different. Unlike treatment

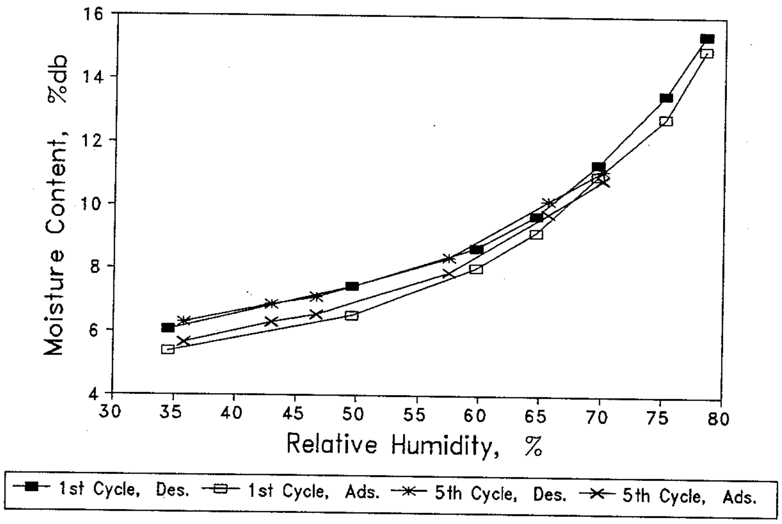

Figure 22 Comparison of adsorption and desorption isotherms of Westar canola subjected to treatment B between the first and fifth drying and rewetting cycles

A, the sorptive capacity of canola receiving treatment B stayed almost unchanged throughout the five drying and rewetting cycles. It could be expected that an elevated drying temperature must have played an important role in this regard. As discussed in section 6.3.1: Free Energy Changes for Canola as Affected by Drying Temperature, it was postulated that there probably existed a limit for the decrease in sorptive capacity due to various environmental factors such as multiple drying and rewetting cycles, elevated drying temperatures, and so on. In treatment A, it was the multiple drying and rewetting cycles rather than the ambient drying temperature (25°C) that caused the downward movement of the isotherms of canola. In treatment B, the elevated drying temperature (50°C) might have already brought the decrease in the sorptive capacity of canola to its limit. This left no room for the multiple drying and rewetting treatment to play its role, so that the isotherms related to treatment B remained hardly shifted despite five consecutive drying and rewetting cycles. The postulation presented here might, to some extent, be supported by the evidence depicted in Fig.32 in section 6.4.5: Drying Temperature Effect. As seen in Fig.32, the adsorption isotherm related to treatment B was shifted far beneath that related to treatment A at relative humidities below approximate 65% due to elevated drying temperature. This suggested that the sorptive capacity of canola decreased so considerably due to elevated drying temperature that it might have already reached its minimum limit.

The sorptive capacity of canola seeds exposed to treatment C on the fifth cycle was, as compared with that on the first cycle, also depressed at most relative humidities, except for those from 40% to 47% and those around 65% where the EMC values coincided (Fig.23).

The sorptive capacity of canola kernels subjected to treatment D exhibited the same characteristics as those subjected to treatment A, B and C. As shown in Fig.24, the isotherms on the fifth drying and rewetting cycle was shifted downwards in the whole relative humidity span, with more pronounced movement occurring at the relative humidities below 75%.

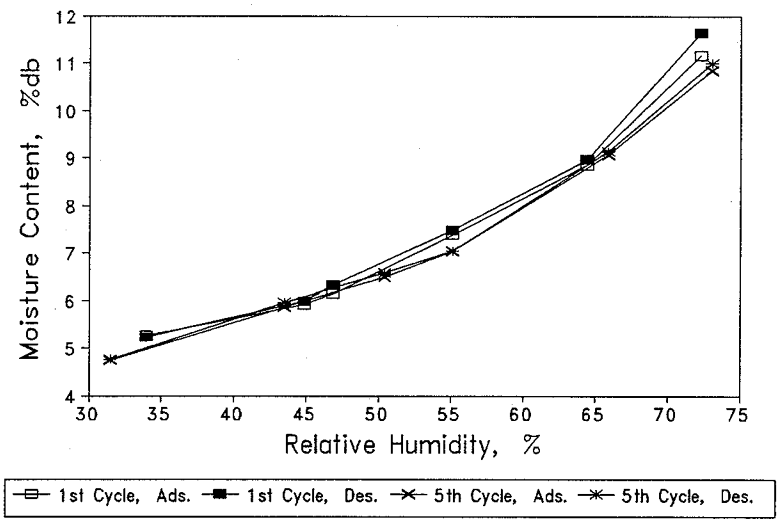

Figure 23 Comparison of adsorption and desorption isotherms of Westar canola subjected to treatment C between the first and fifth drying and rewetting cycles

The effect of multiple adsorption and desorption cycles on the sorptive capacity of canola has significant meaning on its storage stability. According to the present results, isotherms of canola tended to shift downwards as a result of both multiple A/D cycles, which are inevitable during post-harvest handling, storage and processing due to the factors elaborated in section 1, and elevated drying temperatures. As discussed

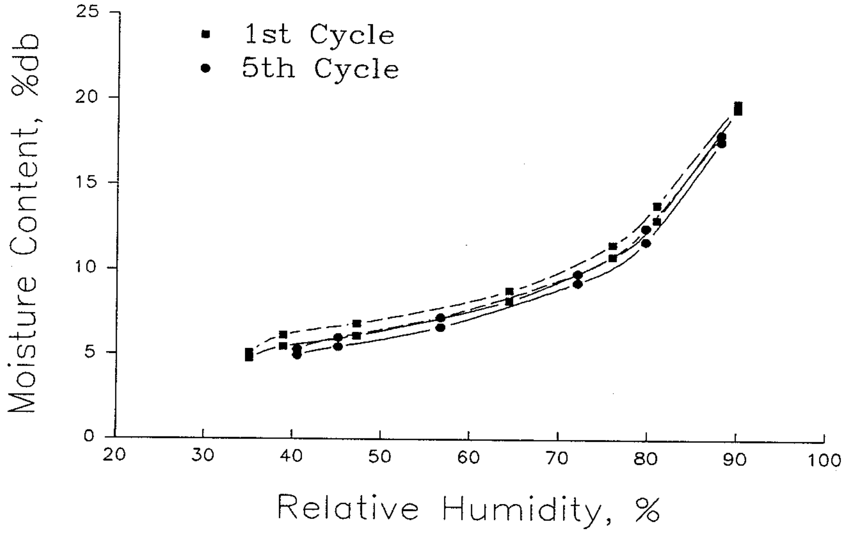

Figure 24 Comparison of adsorption (solid lines) and desorption (dashed lines) isotherms of Westar canola subjected to treatment D between the first and fifth drying and rewetting cycles

above, for the canola dried by ambient air (around 25°C), the downward shift of isotherms due to multiple cycles occurred mainly at moisture contents below 8-10 %db at 25.0°C equilibration temperature, at most moisture contents between 4 and 12 %db at 40.0°C equilibration temperature, and at almost all moisture contents between 5 and 22 %db at 3.5°C equilibration temperature. At both equilibration temperatures of 3.5 and 40.0°C, more significant downward movement of isotherms was observed at the two ends of the relative humidity range, that is, in fairly low (approximately between 20 and 40%) and fairly high (approximately between 50 and 90%) relative humidity ranges (Fig.23 and Fig.24). The downward movement of canola isotherms due to successive adsorption and desorption cycles means that for the same storage moisture the equilibrium relative humidity for canola would be higher after than before the multiple adsorption and desorption cycles. This suggested that canola would become more and more susceptible to microbial infestation as it went through multiple adsorption and desorption processes. On the contrary, the storage stability of canola dried by heated air (50°C) seemed basically not to be affected by the multiple adsorption and desorption cycles, since there was little change in sorptive capacity for the heated-air dried samples (treatment B) observed during multiple cycles. The possible reason has been explained earlier. However, the storage stability of canola was indeed affected by elevated drying temperature in such a way that the possibility of infestation increased when the moisture exchange was along adsorption path. This will be further discussed in section 6.4.5: Drying Temperature Effect. The results in the present study also suggested that the safety storage moisture content would tend to decrease as the storage length increased, since the possibility of multiple adsorption and desorption cycles would increase with the increased storage length. Therefore, as a strategy against the effect of multiple cycles, the grain should, in practice, be stored at a moisture content approximately 2-5% lower than would normally be considered safe, in order to reduce the possibility of deterioration.

6.4.3 Isotherm Equations for Rapeseed (Canola)

Preliminary Considerations

As reviewed in section 3.2.5, the Modified-Henderson and the Chung-Pfost equations were recommended as the ASAE standard to express moisture sorption isotherms of cereal grains and oilseeds (ASAE 1991). However, a certain discrepancy has been reported between the predicted values and the experimental data when these two equations were applied to the isotherms of rapeseed (Pichlor 1957; Sokhansanj et al. 1986), as well as some other agricultural products. These two equations usually underestimate the equilibrium moisture contents of rapeseed at the relative humidities above 80-85% (Sokhansanj et al. 1986), because the isotherms of rapeseed are characteristically show sharp steepness in very high relative humidity ranges. This can be manifested when the isotherm plots by Pichelor (1957) are referred to. Chen and Morey (1989a) found, after a model test, that for high oil and protein products clear patterns in the residual plots and comparatively large values of the mean relative percentage deviation (P) and the standard error (S.E.) had encountered the Modified-Henderson and Chung-Pfost equations, while these criteria were good with the Modified-Halsey and Modified-Oswin equations. Accordingly, they suggested that some parts of the ASAE Standard regarding moisture relationship of agricultural products be revised to incorporate more grains and seeds and that the Modified-Halsey and Modified-Oswin equations be considered for high oil and protein materials. However, the capability of these two equations in describing the isotherms of rapeseed, as well as other oil crops, has not yet been comprehensively proven, since limited sorption data were used by them. For example, the EMC data of rapeseed were those reported by Pixton and Warburton (1977), Pixton and Henderson (1981), and Sokhansanj et al. (1986), which only involved the first drying and rewetting cycle and the temperature range of 5-35°C. Whether these two equations can be generalized to the isotherms of rapeseed at higher temperatures and on higher drying and rewetting cycles is still in question. Thus, there is a need to test the versatility of the suggested equations in describing the isotherms of rapeseed in diversified conditions, such as in a broader temperature range, on multiple drying and rewetting cycles, etc.. More extensive and informative conclusions can expect to be made on the goodness of fit of the suggested equations to the isotherms of rapeseed, if the model test is extended to the isotherms of rapeseed in a broader span of temperatures and on more cycles of moisture treatment. The information so obtained would undoubtedly be helpful in forming an opinion on revising the ASAE standard regarding moisture relationship of farm products, as suggested by Chen and Morey (1989a). Also, the calculation of thermodynamic quantities on different cycles necessitated an analytical expression of the sorption isotherms, so that the troublesome process of taking data from graphs can be avoided. These two factors incited the following two efforts. The first was to fit most of the typical isotherm equations available in literature to the moisture sorption data of canola obtained in this study, in an attempt to check whether there existed more suitable equations specifically for canola isotherms than the Modified-Halsey and Modified-Oswin. The second was to extend the capability test of the suggested equations to the isotherms of rapeseed (canola) at higher temperatures and on more drying and rewetting cycles. The extensive curve fitting was conducted by means of the curve fit function in Sigmaplot 4.1. The isotherms involved the temperatures of 3.5, 6.0, 15.0, 25.0, 35.0, 40.0 and 45.0°C, the first to fifth drying and rewetting cycles and the relative humidity range from 15% to 80% for most isotherms except for those at 6.0°C whose relative humidity was up to 92%. Since the temperature dependency of the constants in isotherm equations was not considered at the time of the model test, most of the equations tested in this study were in their original forms. The equations used were: Guggenheim-Anderson-de Boer (GAB) (Anderson 1946), Brunauer-Emmett-Teller (BET) (Brunauer et al. 1938), Oswin (1946), Halsey (1948), Bradley (1936), Hailwood and Horronbin (1946), Smith (1947), Henderson (1952), Chung-Pfost (1967b), Caurie (1970), Harkins-Jura (1944), Mizrahi (Mizrahi et al. 1970), Kuhn (1967) and Chen (1971), as listed in the Appendix B.

Model Test Results

Summarized in Table V are the results of the extensive model applicability test to the data collected in this study. The numerals shown in the individual table box stand for the sequential numbers of the corresponding equations listed in Appendix B. Wherever the number of the Bradley equation occurs in the table box, Chung-Pfost and Chen's equations equally apply, because they are equivalent to one another (Chirife and Iglesias 1978).

The criteria set up to judge the goodness of fit were the mean relative percentage deviation (P), the standard error (S.E.) (Chen and Morey 1989a), the behaviour of the residual plot, i.e., randomly distributed (R.D.) or systematically patterned (S.P.), and the sum of residuals (Sum).

$$P = \frac{100}{N} * \Sigma \frac{|Y-Y'|}{Y}$$

$$S.E. = \sqrt{\frac{\Sigma(Y-Y')^2}{df}}$$

where, Y = the measured value

Y' = the predicted value

N = the number of observations

df = degrees of freedom of regression model.

Curve fitting results listed in Table V show that the Henderson (Appendix B, Eq.8) and Chung-Pfost (Appendix B, Eq.9) equations only gave mediocre fit to the EMC data of canola. Some other isotherm equations, such as GAB (Appendix B, Eq.1), Halsey (Appendix B, Eq.4), and Hailwood and Harrobin (Appendix B, Eq.6) have been found to give better fit than the Modified-Henderson and Chung-Pfost equations. Halsey equation has been found, despite discrepancy in some cases, to give good fit to many isotherms obtained in this study, while the Oswin equation only gave mediocre fit. Other equations than those mentioned above were not suitable for describing the isotherms of canola.

Table V: Goodness of fit of the selected isotherm equations to rapeseed

Temperature (°C)	Sequence of The Drying and Rewetting Cycles					
	The First Cycle		The Third Cycle		The Fifth Cycle	
	Adsorp.	Desorp.	Adsorp.	Desorp.	Adsorp.	Desorp.
3.5	** 4	* 4	* 4	** 4	** 4	** 4
6.0	** 4 * 5	*** 6 ** 4				
15.0	*** 4 *1,6	* 4 *1,6				
25.0	* 1,6	*1,4,6	*** 6 ** 1 * 4	*** 6 ** 1 * 4	*1,4,6	*1,4,6
35.0	**1,4,6	** 4 * 1,6				
40.0	** 4,6 *1,5,9	** 4,6 *1,5,9	**1,4,6 * 3,5	**1,4,6 * 5	***1,6 ** 4 * 5	**1,4,6 * 5
45.0	** 4	** 4				

Description: The numerals in the boxes stand for the sequential numbers of the corresponding equations listed in Appendix B.

*** denotes the excellent equations which have P values less than 2 and random or nearly random residual distributions.

** denotes the good equations which have P values between 2 and 5 and random or acceptable residual distributions.

* denotes the ordinary equations which have P values between 5 and 10.

Origination of A New Empirical Equation

Because of the potentiality of the Halsey equation to express the isotherms of rapeseed (canola), an attempt was made to empirically modify the Halsey equation in order to form a versatile equation suitable for the isotherms of most rapeseed varieties at a broad span of temperature, in a wide range of relative humidity, and for many cycles of drying and rewetting processes. This attempt was based on the consideration that a unique isotherm model that could describe accurately the EMC data of various types of materials in a extremely broad relative humidity range has been proven almost inexistent, due to the reasons given by Chirife and Iglesias (1978). Thus, it seemed more advisable and practical to develop and intensify a specific mathematical model, either theoretically or empirically, for a specific substance or a group of similar materials. Since it was found during curve fitting performed in this study that the Halsey equation overestimated, in some cases, the measured values in high relative humidity range, while underestimated them at others, the major step in modification of the Halsey equation was centred around how to insert into the Halsey equation a factor which could adjust the EMC values throughout the whole range of relative humidity. As a result of hundreds of curve fitting operations, a empirical equation, based on the Halsey formula, was developed and shown in Eq.(21).

$$RH = \exp(C\, A^{m}/m^{B}) \qquad (21)$$

where m is equilibrium moisture content in percent dry basis, $_{RH}$ is relative humidity in decimal (interchangeable with a_w), and A, B and C are constants.

Performance of the New Empirical Equation

Eq.(21) has been found to express very well almost all the isotherms of the rapeseed variety Candle obtained by Pixton and Henderson (1981), the variety Tobin by Sokhansanj et al. (1986), the variety Global by Otten et al. (1990), and the variety Westar both by Bielewicz (1991) and in this study, with the involved relative humidity, temperature and drying and rewetting cycle ranges being from 15 to 94%, 4 to 75°C and 1 to 5 cycles. The estimated parameters and goodness-of-fit criteria associated with this equation are listed in Appendix C: Section I-A and Section I-B. The only exception is for the isotherm of Global canola at 75°C by Otten et al. (1990). The best-fit model for this case was, after a model search using the equations listed in Appendix B, the GAB equation, instead of the proposed empirical equation. Nevertheless, the EMC data at 75°C, as pointed out by Otten et al. (1990), were not final and needed to be verified. The capability of Eq.(21) in describing the isotherm of Global canola at this temperature is accordingly reserved for future confirmation despite the existing discrepancy.

As a summary of the performance of the new empirical equation, Table VI lists the percentage of the P values which fell into each of the four categories: $P < 2$, P between 2 (inclusive) and 5, P between 5 (inclusive) and 10, and $P > 10$ (inclusive), the ratio of the number of randomly distributed residual plots over the total of the residual plots involved, i.e., 56, the maximum S.E., and the maximum sum of residuals for the new empirical equation, as well as the Halsey equation. As can be seen in Table VI, for the new empirical equation, about 95% P values were below 5, and the ratio of the randomly distributed residual plots over the total is about 0.71 (40/56). This indicated that the new empirical equation was quite capable of describing the isotherms of rapeseed.

Table VI Summary of the performance of Eq.(21) and the Halsey equation as equally applied to 56 isotherms from different sources

	P<2	P:2-5	P:5-10	P>10	R.D. Ratio*	S.E.	Sum
Halsey	31%	44%	24%	0%	26/56	≤2.21%	≤0.087
Eq.(21)	52%	43%	4%	2%	40/56	≤0.97%	≤0.053

* The number of the isotherms whose residual plots were randomly distributed over the total of the isotherms tested

Comparison between the Halsey and the New Empirical Equation

Because of the similar performance of the Halsey equation and Eq.(21) proposed in this study for the moisture sorption isotherms of rapeseed, much work has been done in goodness-of-fit comparison between these two equations as they were fitted to all the isotherms used in this study. Curve fitting results, as listed in Appendix C and summarized in Table VI, showed that Eq.(21) is better than the Halsey equation in terms of the criteria of P, S.E., sum of residual, and the behaviour of residual plot. By replacing the Halsey equation with Eq.(21), both the number of the P values below 5 and the number of randomly distributed residual plots increased by about 20% (Table VI). The only disadvantage of Eq(21) over the Halsey equation is that it is a three-parameter model, while the Halsey is a two-parameter model. In many cases, the constant A in Eq. (21) was close to unity. This made the new model resemble the Halsey equation in performance, since the new equation looks like the combination of the Bradley and the Halsey in appearance. However, in quite a few other cases, the constant A was not close to unity. This deviation in the constant A from unity functioned in adjusting the Halsey equation to a better applicability to the measured data. For example, the constant A was 1.633 for the isotherm measured in the present study at 25.0°C on the first drying and rewetting cycle (Table VII). It made much difference in goodness of fit as compared with that of the Halsey equation. From Table VII, the mean relative percentage deviation (P), the standard error (S.E.) and the sum of residuals (Sum) for Eq.(21) were 2.36, 0.45 (%) and 0.025 respectively, while those for the Halsey equation were 8.86, 1.34 (%) and 0.066, respectively.

Table VII Performance of the Halsey equation and Eq.(21) as applied to the adsorption isotherm of Westar canola obtained in this study at 25.0°C on the first drying and rewetting cycle

Equations	A	B	C	P	S.E.(%)	Sum	Residual
Halsey		2.2097	51.213	8.86	1.34	0.066	S.P.
Eq.(21)	1.6327	5.4961	999.88	2.36	0.45	0.025	R.D.

This was further depicted in Fig.25. The predicted curve by Eq.(21) was very close to the experimental data, while the predicted curve by the Halsey equation was not. Systematically patterned residual plots existed for the Halsey equation. The residuals for Eq.(21) were, however, basically randomized, and the residual magnitude at each points was much smaller than that of the Halsey equation (Fig.25).

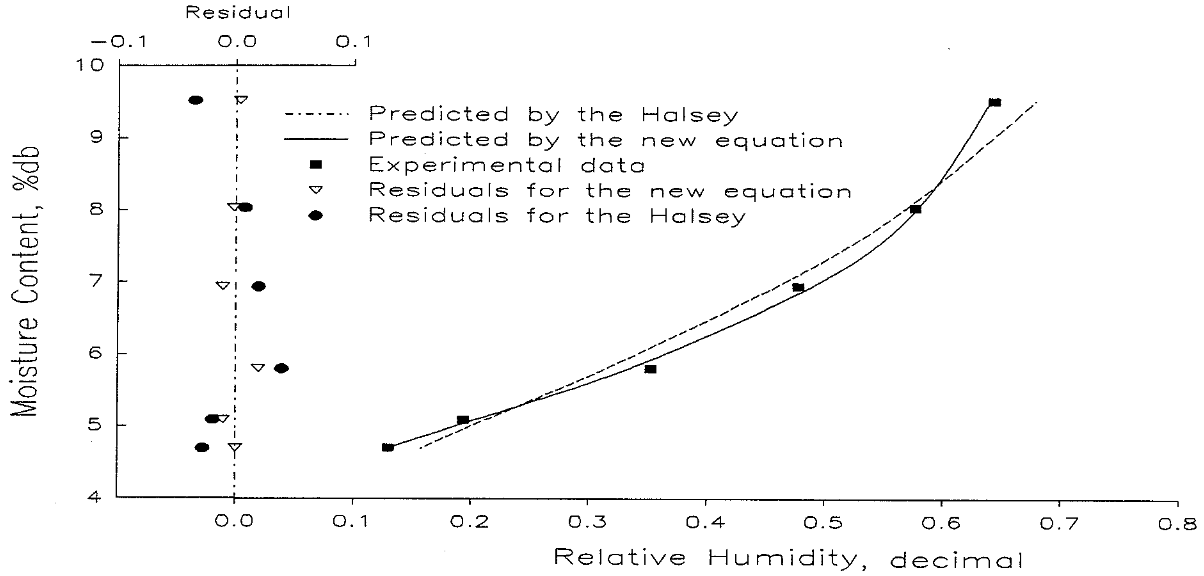

Figure 25 Performance of the Halsey and Eq.(21) as applied to the adsorption isotherm of Westar canola measured in the present investigation at 25.0°C on the first drying and rewetting cycle

Comparison among the Henderson, Chung-Pfost, Halsey and Eq.(21)

In order to compare the performance among the Henderson, Chung-Pfost, Halsey, and the proposed empirical equation, the desorption isotherm at 15°C reported by Pixton and Henderson (1981) was used in the model test. This isotherm was selected due to its broad relative humidity range (21.5 to 91.7%). The curve fitting results are listed in Table VIII. Fig.26 is also constructed based on the regression results of these models to facilitate the comparison. From both Table VIII and Fig.26, it is manifest that the Henderson and Chung-Pfost equations did not give a good fit to the isotherm.

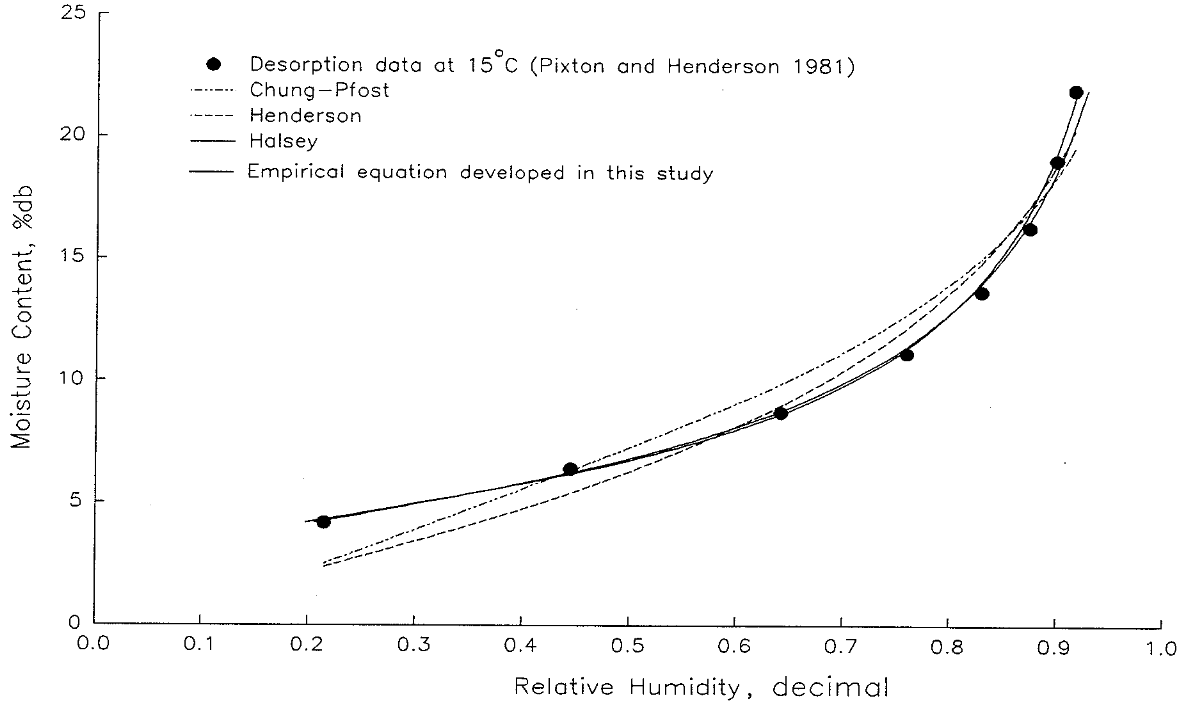

Figure 26 Goodness-of-fit comparison among the Henderson, Chung-Pfost, Halsey and Eq.(21) using the desorption isotherm at 15°C reported by Pixton and Henderson (1981)

They all underestimated the isotherm at the relative humidities above about 80% and below 40%, whereas, they all overestimated the isotherm between 40% and 80% relative humidities. Both the Halsey equation and Eq.(21) described the experimental data very

Table VIII Curve fitting results for the Chung-Pfost, Halsey, Henderson and Eq.(21) with respect to the desorption isotherm of rapeseed variety Candle at 15°C reported by Pixton and Henderson (1981)

Equations	A	B	C	P	S.E.(%)	Sum	Residual
Chung-Pfost	3.2990	0.2143		6.06	1.280	0.102	S.P.
Halsey		1.7828	20.666	2.12	0.42	0.032	S.P.
Henderson	0.0411	1.4330		6.40	1.34	0.104	S.P.

well throughout the whole relative humidity range tested. The residual plots for the four models are shown in Fig.27. The residual plots for the Henderson and Chung-Pfost equations were alike and of clear patterns. The residual plots for the Halsey equation and Eq.(21) were also similar to each other and slightly patterned. However, they had a much smaller residual magnitude than the Henderson and Chung-Post equations.

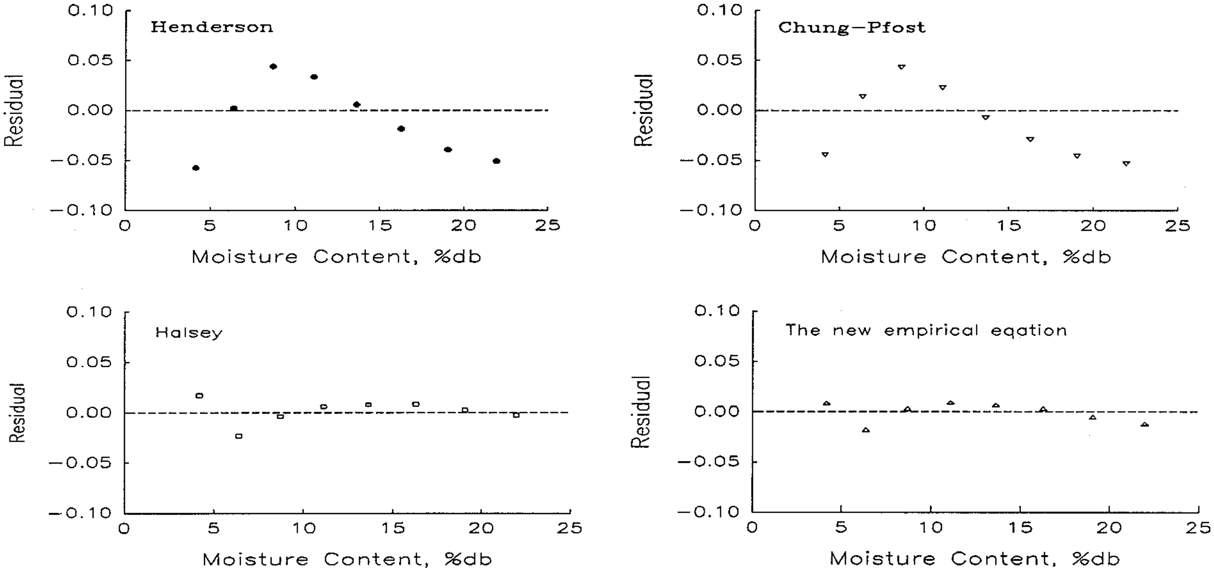

Figure 27 Residual plots for the Henderson, Chung-Pfost, Halsey, and Eq.(21) as applied to the desorption isotherm at 15°C reported by Pixton and Henderson (1981)

Results from the model test conducted in this study confirmed that the two standardized equations, the Henderson and the Chung-Pfost equations, are not capable of describing the isotherms of rapeseed (canola) well. The ASAE standard regarding moisture relationship of agricultural products should be revised specifying one or more new equations for expressing the EMC-ERH relationships of high-oil farm products

including rapeseed (canola). The Halsey equation and the new empirical equation proposed in this study are two potential equations to be recommended to describe the isotherms of rapeseed, with the latter being more suitable than the former.

6.4.4 Hysteresis Effect upon Multiple Adsorption and Desorption Cycles

As described in section 5.2: Experimental Scheme, four multiple adsorption and desorption treatments (A, B, C and D) were conducted. In each treatment, samples were equally exposed to five successive drying and rewetting cycles. Hysteresis effect upon multiple drying and rewetting cycles for the four different treatments had some common features, but was largely different from one another.

For treatment A (canola samples were five times dried at 25°C, rewetted to a moisture content in the vicinity of 20.00 %db, and exposed to isotherms at 25.0°C), the hysteresis of Westar canola was considerably reproducible throughout the five adsorption/desorption cycles. This has already been shown in Fig.8. Fig.28 depicts the hysteresis magnitude and pattern for the first to fifth drying and rewetting cycles for Westar canola exposed to treatment A. The hysteresis gaps on each cycle were between 0.1 to 0.4 %db for the 10% to 70% relative humidity range. The hysteresis patterns on the first and the second cycles were irregular as compared with those on the rest. In the lower relative humidity range (below 45%), the hysteresis magnitude on the 3rd and 4th drying and rewetting cycles increased when compared to the first two cycles. On the

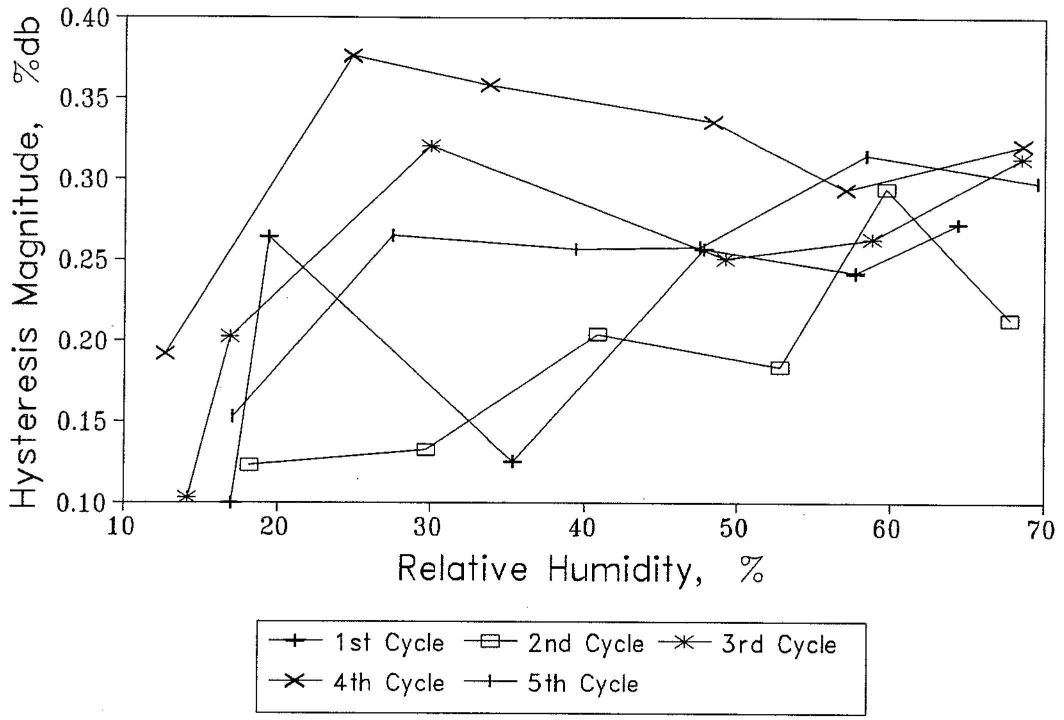

Figure 28 Hysteresis magnitude and pattern on the first to fifth drying and rewetting cycles for Westar canola subjected to treatment A

fifth cycle, hysteresis size dropped down to about the average level of the first and the last cycles. For relative humidity above 45%, the hysteresis magnitude became more or less equal as the number of the drying and rewetting cycles increased.

For treatment B (canola samples were five times dried at 50°C, rewetted to a moisture content in the neighbourhood of 20.00 %db, and equilibrated at 25.0°C), the hysteresis of Westar canola was, as can be seen in Fig.29, also remarkably reproducible upon the first to fifth adsorption and desorption cycles. Somewhat like the hysteresis behaviour related to treatment A, the hysteresis for treatment B also increased from the first cycle, reached its peak value on the second cycle, and then decreased as the number

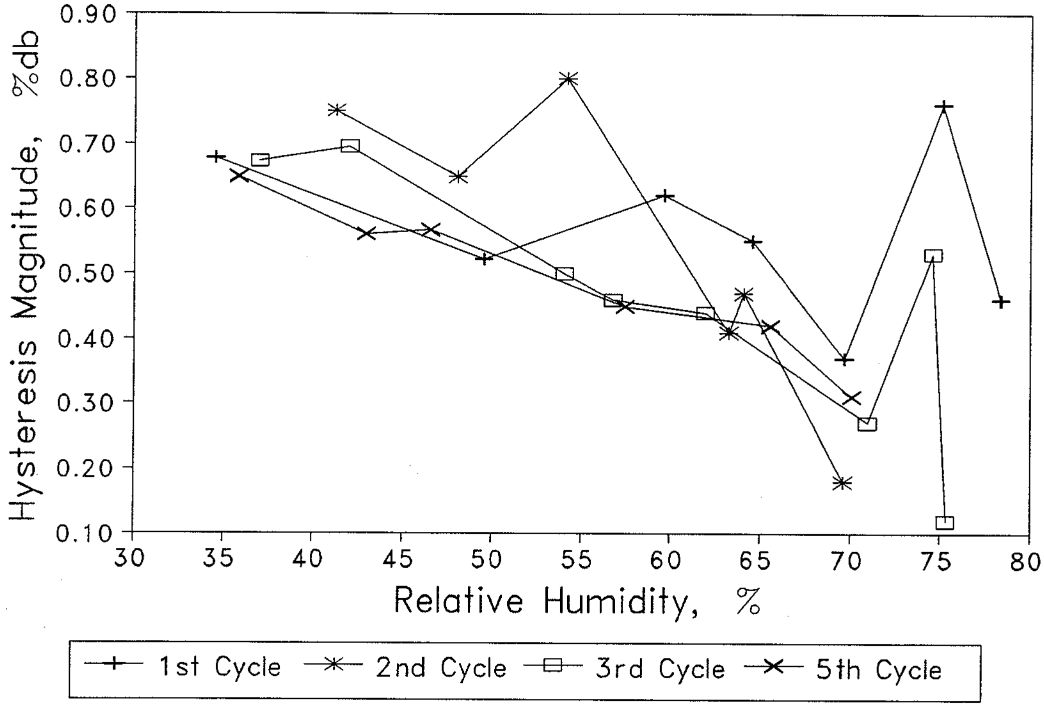

Figure 29 Hysteresis magnitude and pattern on the first, second, third and fifth drying and rewetting cycles for Westar canola exposed to treatment B

of cycles further increased to five. However, the hysteresis pattern was quite different from that for treatment A. The number one difference was that the hysteresis gap at the relative humidities lower than 45% was enlarged and gradually narrowed down as relative humidity increased from 45% (Fig.29). The number two difference was that the hysteresis magnitude for treatment B ranged from 0.1 to 0.8 %db at the relative humidities between 30% and 80% (Fig.29), which was, as a whole, more than double that for the samples subjected to treatment A. At the relative humidity around 48%, the hysteresis sizes for all the cycles were in the neighbourhood of 0.6 %db. At approximately 70% relative humidity, the hysteresis decreased to about 0.3 %db. Fluctuation in hysteresis was encountered on the first and the third cycles at relative humidities between 70% and 80% (Fig.29).

For treatment C (five times drying at 25°C, rewetting to a moisture content in the vicinity of 20.00 %db, and equilibrating at 40.0°C), the hysteresis (Fig.30) once again showed the same pattern the samples exposed to treatment A and B exhibited, that is, the hysteresis magnitude increased from the first cycle, reached its maximum on the third cycle, and declined on the fifth cycle. However, the hysteresis size was greatly reduced on the first and third rewetting and drying cycles as compared with the hysteresis magnitude of the samples that either received treatment A or B, and diminished to a negligible level on the fifth cycle.

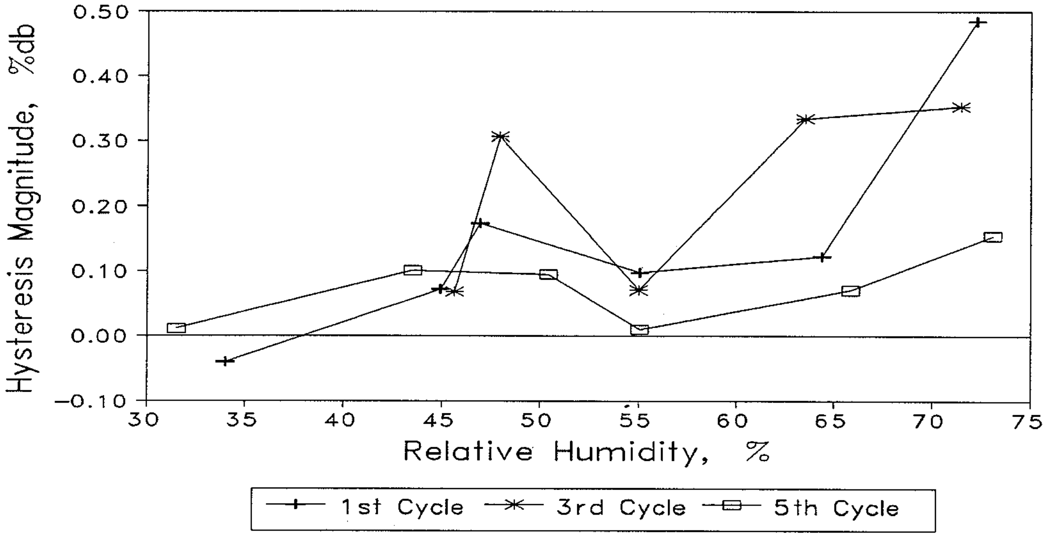

Figure 30 Hysteresis magnitude and pattern on the first, third and fifth drying and rewetting cycles for Westar canola subjected to treatment C

For treatment D (five times drying at 25°C, rewetting to a moisture content in the vicinity of 20.00 %db, and equilibrating at 3.5°C), hysteresis was also pronouncedly

reproducible upon the sequential adsorption/desorption cycles, as shown in Fig.31. Hysteresis values related to treatment D were from 0.1 to

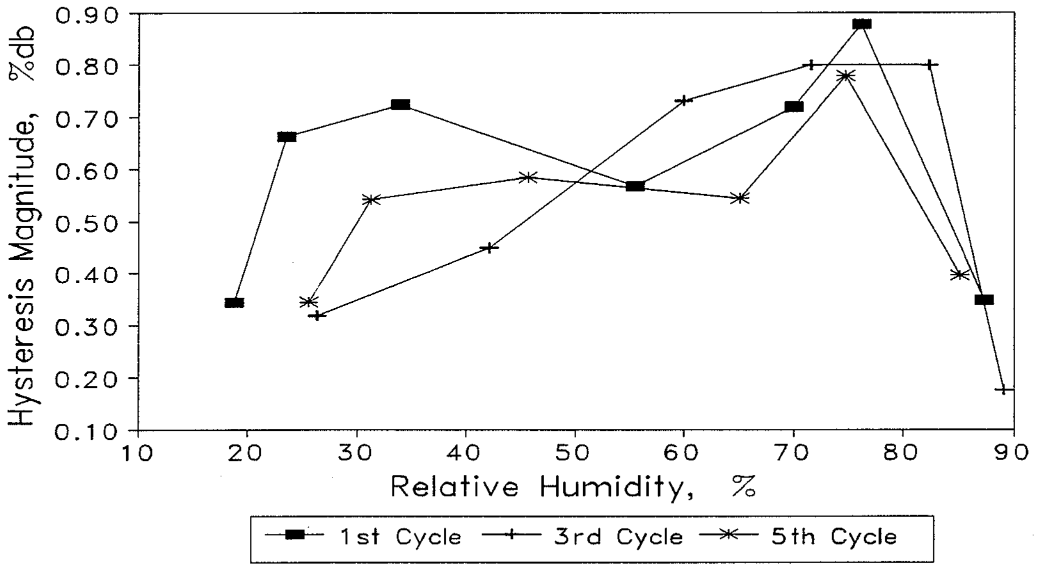

Figure 31 Hysteresis magnitude and pattern on the first, third and fifth drying and rewetting cycles for Westar canola subjected to treatment D

0.9 %db within the relative humidity between 18% and 90%. This magnitude was much higher than that related to treatment A and C at the same relative humidities, and marginally comparable with that related to treatment B. The hysteresis was small at both ends of the relative humidity range, and large at the relative humidities between the two ends. The hysteresis size was the largest for the first cycle, and the smallest for the fifth cycle.

6.4.5 Temperature Effect on Hysteresis upon Multiple A/D Cycles

Drying Temperature Effect

As described in section 6.3.5, 6-8 hour drying at 50°C (treatment B) did not change the reproducibility of the hysteresis in the 25.0°C isotherm (Fig.31). After each 50°C drying cycle the entire hysteresis gap was enlarged, especially at relative humidities below 45%, as compared with the samples that received treatment A. The hysteresis magnitude for Westar canola exposed to treatment B was more than double that for the samples exposed to treatment A. It was also noticed that the enlargement in hysteresis magnitude for the samples subjected to treatment B was predominantly caused by the downward shift of the adsorption isotherms for treatment A. This can be manifested from Fig.32, where only the adsorption and desorption isotherms on the first drying and rewetting cycle for the Westar canola subjected to treatment A and B are plotted. As can be seen in Fig.32, the adsorption isotherm related to treatment B lay below that of treatment A, but the desorption isotherms for both treatments remained almost in breast of each other. This might suggest that the steric hinderance or any other types of resistance to the inward movement of water molecules might have been strengthened due to heat penetration, so water molecules had more difficulty in getting into the sorptive sites of canola kernels exposed to treatment B than those to treatment A. As a result, the canola kernels subjected to treatment B entrapped less water than those subjected to treatment A on an adsorption process. Similar alteration in the hygroscopic characteristics of corn dried at a temperature higher than 60°C was also reported by

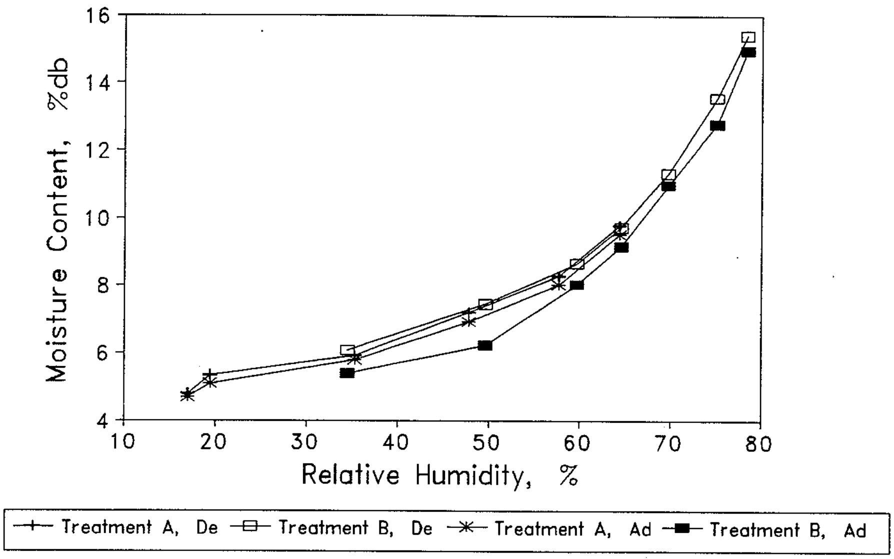

Figure 32 Comparison of the adsorption and desorption isotherms on the first drying and rewetting cycle between Westar canola samples exposed to treatment A and B

Tuite and Foster (1963). Nevertheless, the sorptive capacity of canola kernels might, as suggested by the similarity of the desorption isotherms for both treatments (Fig.32), have remained intact in spite of drying at 50°C despite the heated air drying. Thus, the kernels maintained the same amount of water at the same relative humidity and equilibrium temperature. Alteration in hygroscopic characteristics due to drying at a raised temperature would further suggest that canola seeds dried by heated air might induce more changes in their physical, chemical and biological properties, or rather, in their quality, than those dried by ambient air, according to the research results about the interrelations of variables in stored agricultural products (Sinha 1973).

Another significant effect of drying temperature was the marked difference in free energy changes between the samples exposed to treatment A and B. In both adsorption

and desorption processes, there was a significant difference between the differential free energy on the first and the fifth cycle at equilibrium moisture contents below approximately 7.5 %db for samples exposed to treatment A, while the differential free energy related to the samples exposed to treatment B on the first and the fifth cycle was close together throughout the entire tested moisture range. This has been discussed in detail earlier in section 6.2.1: Free Energy Changes for Canola as Affected by Drying Temperature. An explanation to this observation has been given in that section.

Equilibrium Temperature Effect

The temperature at which the equilibrium was reached affected the hysteresis behaviour of canola seeds upon multiple adsorption and desorption cycles. So far, most literature about the equilibrium temperature effect on sorption hysteresis was centred around a single cycle, i.e., the first drying and rewetting cycle. Little was reported regarding the effect of equilibrium temperature on hysteresis behaviour during multiple adsorption and desorption cycles.

With respect to the effect of equilibrium temperature on the hysteresis of canola on the first adsorption and desorption cycle, it followed the trend that hysteresis magnitude decreased with the increase of temperature. Fig.33 shows the hysteresis sizes on the first adsorption and desorption cycle at the temperatures of 3.5, 6.0, 25.0, 35.0, 40.0, and 45.0°C. It can be seen that the lines that connected a specific legend to

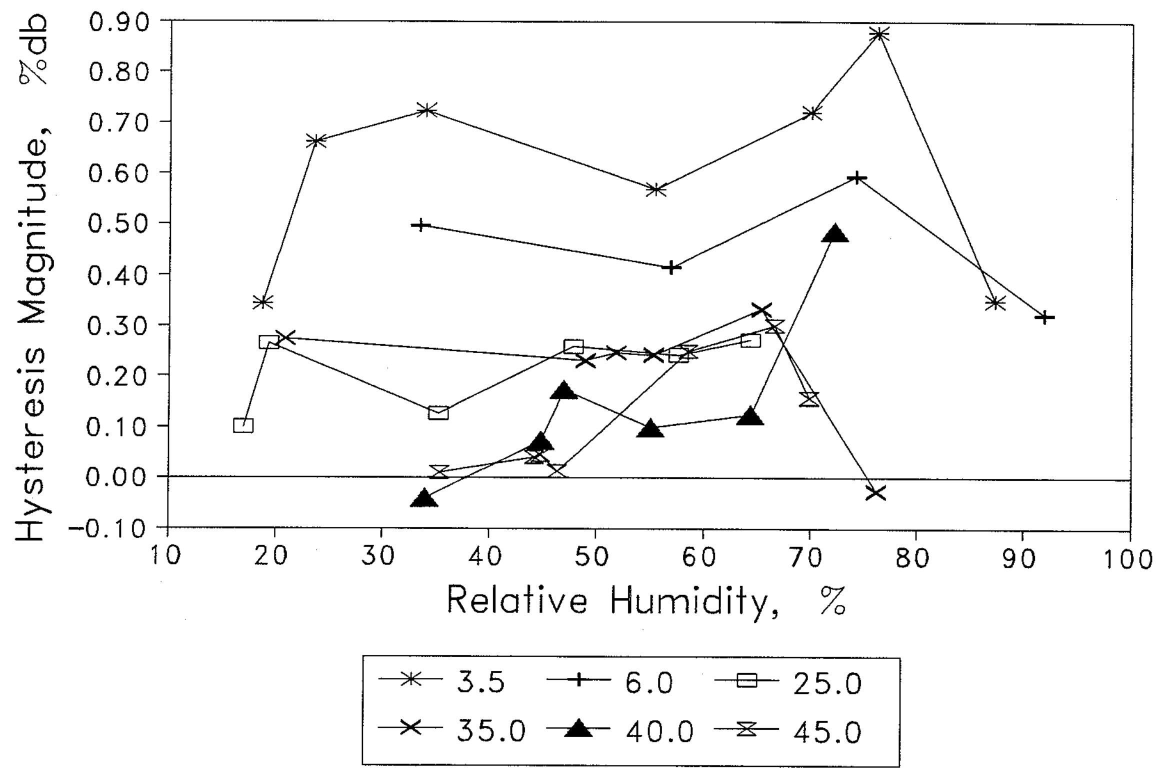

Figure 33 Hysteresis magnitude of Westar canola on the first drying and rewetting cycle at the equilibration temperatures of 3.5, 6.0, 25.0, 35.0, 40.0 and 45.0°C

indicate hysteresis magnitude and pattern at a specific temperature move up as the equilibrium temperature decreases.

With respect to the effect of equilibrium temperature on the hysteresis behaviour of canloa upon multiple adsorption and desorption cycles, hysteresis was, as discussed in section 6.3.5, persistent throughout the five consecutive adsorption and desorption cycles at 3.5°C (exemplified by treatment D) and 25.0°C (exemplified by treatment A and B) equilibrium temperatures in spite of different drying temperatures (e.g., drying at 25°C for treatment A and D, and drying at 50°C for treatment B). However, it diminished considerably on the first and third cycle and basically was eliminated on the fifth cycle at 40.0°C equilibrium temperature (exemplified by treatment C). This agrees with the conclusion by Benson and Richardson (1955) that the repeatability of hysteresis on successive adsorption and desorption cycles was especially apparent at low equilibrium temperatures.

6.4.6 Postulation of the Origin of Sorption Hysteresis Phenomenon

A Hypothesis to Explain the Origin of Sorption Hysteresis Phenomenon

There are many theories and hypotheses proposed to explain sorption hysteresis phenomenon, as reviewed earlier in section 3.2.2: Theories of Sorption Hysteresis. However, none of the hypotheses and theories are extensive and conclusive. An inclusive explanation to the hysteresis phenomenon should be one which is able to account for a general sorption process rather than for the sorption process limited to a particular kind of substance.

In this study, an attempt was made to account for the sorption hysteresis phenomenon in a general sense. A new hypothesis has been developed to serve this purpose, which will be described in detail below.

The new hypothesis initiated from the common behaviour of sorption isotherms as affected by temperature. The characteristics of such behaviour is that the isotherms are always shifted downward in response to the increase of temperature. Careful examination of this kind of characteristics led to the finding that many adsorption branches came close to, or even overlapped the desorption branches at a certain higher temperature than that under which the adsorption occurred, provided that the temperature was not so high as to cause composition degradation and structure alteration of the sample. This finding seemed to indicate that the temperature under which an adsorption process occurred was equivalent to the temperature of a particular desorption process which proceeded at a higher temperature than the counterpart desorption branch of this very adsorption process. In other words, an adsorption process might have occurred, by virtue, at a higher temperature than did its counterpart. Taking the fact that a majority of the adsorption processes are exothermal under consideration, it is reasonable to meditate that the heat evolved in an adsorption process might be responsible for the above-mentioned conjecture that an adsorption process was actually carried out at a higher temperature than its counterpart desorption process.

Let us take moisture sorption process as an example to get into the hypothesis proposed in this study. Fig.34 shows a diagram of a sorbate environment with constant temperature, T_g, during a isothermal process of moisture sorption. To reach an equilibrium between the sorbed water within the sorbent with water vapour in the sorbate environment, moisture would be transferred in either directions shown in Fig.34

depending on whether adsorption or desorption was carried on, as governed by the chemical potential law. The sorption process, or more specifically, the condensation of water molecules in vapour to the matrix of the sorbent or the vaporization of the sorbed water in the sorbent into sorbate environment, could happen among numerous microregions, exemplified by microregion A, all over the sorbent.

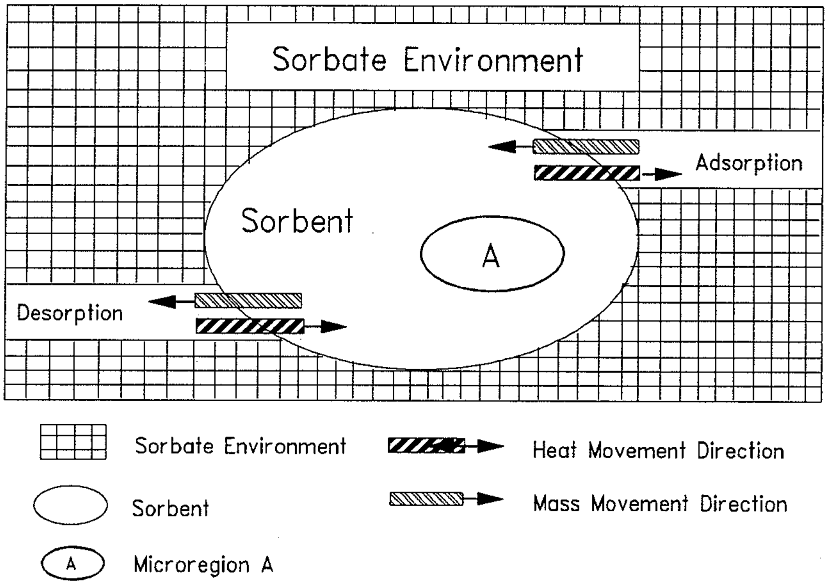

Figure 34 A diagram showing the sorbent, the sorbate environment, the directions of heat and mass movement, and a microregion (A) during a sorption process

The microregion A contained, as indicated in Table IX, N_s moles of sorbent and N_1 moles of sorbed water which had chemical potential μ_1. Microregion A was at the temperature of T_1. The water vapour in the sorbate environment was of the following parameters: relative humidity (water activity) a_{wg}, chemical potential μ_g, and temperature T_g. It is exothermal during an adsorption process, and endothermal during a desorption process. It was hypothesized that the heat evolved during a adsorption process which occurred

Table IX List and description of the thermodynamic parameters related to the sorbate and the sorbent

Parameters	Description
Sorbate Environment	
a_{wg}	Relative humidity (water activity) of water vapour in sorbate environment
T_g	Temperature of the sorbate environment
μ_g	Chemical potential of water vapour in sorbate environment
Microregion A (Sorbent)	
a_{w1}	Water activity of the condensed water in microregion A
T_1	Temperature of microgegion A
μ_1	Chemical potential of the condensed water in microregion A
N_1	The number of moles of the condensed water in microregion A
N_s	The number of moles of the sorbent contained in microregion A
The Hypothesized Phase B	
a_{w1g}	Relative humidity (water activity) of the water vapour in the hypothesized phase B, which is equal to a_{w1}
T_1	Temperature of the hypothesized phase B, which is equal to the temperature of microregion A
μ_{1g}	Chemical potential of the water vapour in the hypothesized phase B

in microregion A could not get out of the sorbent instantly because of the heat resistance of the common materials, or in other words, the imperfection of the common substance in heat dissipation ability, so two possible outcomes could result. Firstly, heat accumulation would occur within microregion A as soon as the heat was released, and the temperature of microregion A (T_1) would accordingly go up, i.e., $T_1 > T_g$. Secondly, the heat released in microregion A would force the temperature of its neighbouring microregions to rise. As a result, the adsorption processes in either microregion A or its adjacent microregions would be caused to proceed at a raised temperature. For desorption, the heat necessary for the sorbed molecules to evaporate would be gradually transported from the environment of constant temperature T_g to the molecules of sorbed water. The heat transported from outside the sorbent would go to the most accessible molecules of sorbed water, which were generally least bonded to a sorptive site in the sorbent and were closest to or even remained as free water in the mass transfer passages or the gaseous micropores within the sorbent. As the most accessible sorbed water molecules evaporated, the heat would reach the second most accessible sorbed water molecules, and so on. In such a way, the heat transported would reach more and more bond water molecules as the sorbed water molecules evaporated and moved out of the sorbent according to their heat accessibility and binding strength. The amount of heat needed for the sorbed water molecules of different heat accessibility and binding strength to evaporate was different, but no factors in connection with the vaporization of water molecules during a desorption process would, unlike the heat accumulation in a adsorption process, give rise to variation in T_1, namely, $T_1 = T_g$ in this case. Hence, the desorption occurred at the same temperature as that of the sorbate environment. This probably might be why the adsorption isotherms always lie below the desorption isotherms to give hysteresis. Based on this point of view, the desorption isotherms might represent the true equilibrium state.

As hypothesized above, the heat released when the state of water changed from vapour to liquid in a microregion of a common sorbent during an adsorption process would accumulate in this microregion (and accordingly rise in the temperature of this microregion) and diffuse to the adjacent microregions to cause the increase of the temperature of the adjacent microregions. If the sorbent had not given any necessary response to adjust itself under this extremity, the microregional temperature would have kept going up as the adsorption proceeded. However, this is not the case for a real adsorption process where there is no temperature rise observed. It is further hypothesized that a rise in the temperature of a microregion would not last long, because the sorbent had to give up some of the water molecules that had just become sorbed in it after they released the heat of condensation as the response to the extremity of the microregional temperature increase. As a result, some of the sorbed water molecules went back to the vapour phase converting into their kinetic energy the amount of heat that was not dissipated. This adjustment left the microregional temperature unchanged. Such a self-adjusting process is thermodynamically a must for the system to protect itself from being distorted due to the extremity of microregional temperature rise. The Le Chatelier law (Emery 1969) governed at this point.

In order to explain this hypothesis thermodynamically, a pretended three-phase model (Fig.35) is set up. It is assumed that there existed a small volume of water vapour (shown by the dashed layer B) between the predominating vapour phase (e.g., the vapour in sorbate environment, mass transfer passages of the sorbent, gaseous micropores of the sorbent, and any other spaces within the sorbent which would allow the vapour) and the sorbed water. This third phase came into prominence immediately after the state change of water molecules during an adsorption process and was in equilibrium with the condensed water in this very microregion of elevated temperature. So, its temperature was the same as T_1, its chemical potential was μ_{1g}, which was

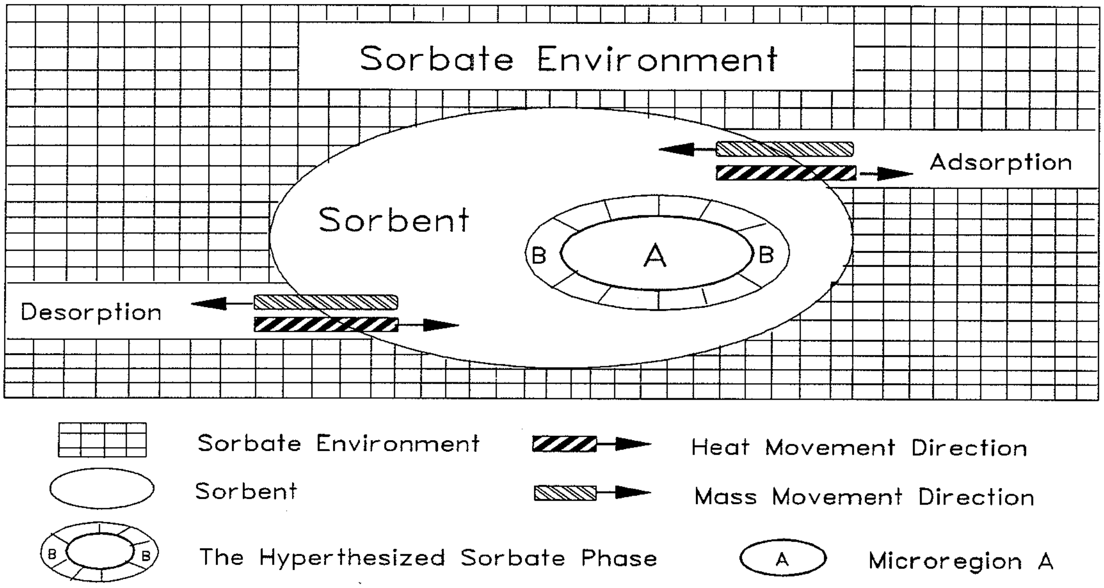

Figure 35 A hypothesized three-phase model of a sorption process for explaining the origin of sorption hysteresis

equal to the chemical potential of the condensed water, μ_1, and the relative humidity (water activity) of the water vapour in this phase was a_{w1g}, which was equal to the water activity of the condensed water in the microregion, a_{w1}. This portion of water vapour was also in connection with the predominating water vapour source, which was of chemical potential μ_g. These two volumes of vapour would behave in the way that any two sources of gas with different state parameters would do when joined together. Exchange of mass and energy would happen in order to reach an equilibrium between them. According to the chemical potential principle, when the gas state reaches equilibrium with sorbed state, the chemical potential of the gas state (μ_g) must equal to the chemical potential of the sorbed state (μ_1), i.e.,

$$\mu_g = \mu_1$$

or,

$$\mu_g = \mu_{1g}$$

that is,

$$R\ T_g \ln(a_{wg}) = R\ T_1 \ln(a_{w1g})$$

It is generally thought under the present theoretical system that T_1 is equal to T_g. Thus, when equilibrium is established, $a_{w1g} = a_{wg}$. However, this is only true for an ideal system where there are no factors causing the variation of T_1. In a real system, T_1 was higher than T_g due to the latent heat of condensation which was not able to totally get out of the sorbent immediately after its release during an adsorption process occurring in a microregion because of the imperfection of the heat dissipation ability of the sorbent, just as hypothesized earlier. Thus, a_{w1g} tended to be forced higher than a_{wg} in order to maintain $\mu_1 = \mu_g$. Nevertheless, the outcome of the exchange of the two volumes of water vapour would be that a_{w1g} became equal to a_{wg}. As the response to such a circumstance, the microregional desorption had to occur in order to bring a_{w1g} down. This meant the decrease of the equilibrium moisture content of the sorbent at the same vapour partial pressure (or water activity). In the same manner, depress in moisture uptake would happen in numerous microregions scattered all over the sorbent as adsorption proceeded. It added up together to form the macroscopic phenomenon of sorption hysteresis.

The same conclusion would be reached if we look at Eq.(22) (Hill 1952) below:

$$\phi = \mu_{pa} - \mu_a = (\frac{\partial E_s}{\partial N_a})_{S,,V,,N_1} = R\ T \int_0^P \Gamma d\ln P \tag{22}$$

where $\Gamma = N_1/N_a$.

The ϕ, called surface potential or spreading pressure, is the difference between the chemical potential of the sorbent with sorbed water and that of the pure sorbent. As long as equilibrium is established between the sorbed water and the predominating water vapour after the sorbent has gone through an adsorption process, i.e., the state parameters such as P and T are stable, the ϕ is kept at a certain constant value until the oncoming adsorption process which will occur in the same microregion or the heat transferred from its neighbouring microregions strikes in. According to the Le Chatelier law (Emery 1969), any factors causing change on a system would simultaneously cause the system to respond in such a way that the changes would be reduced to minimum. In this case, the factor causing change was the increase in the microregional temperature. The response would be the decrease in N_1 (the moles of sorbed water), according to Eq.(22), since the system pressure P and the moles of the adsorbent N_a are invariable.

With respect to the energy balance, the water molecules desorbed due to microregional temperature rise reverted to the predominating vapour phase carrying the amount of energy which corresponded to part of the latent heat of condensation released during an adsorption process and would otherwise have totally dissipated into the environment if the heat dissipation ability of the sorbent had been perfect. The total energy was still conserved, but the energy distribution had been different from that in the case of no microregional temperature rise. In other words, part of the heat released from the kinetic energy of water vapour due to its 'immobilization' during an adsorption was fedback to the original form of kinematic energy of water vapour by inducing some of the adsorbed water molecules to evaporate.

As a summary, this hypothesis attributed the mechanism of sorption hysteresis to the imperfection of the common materials in heat dissipation. As a result, the adsorption processes tended to take place at an elevated temperature. To release some of the sorbed molecules was a must in order to maintain a consistent chemical potential among different phases in equilibrium. During desorption, there were no factors which would cause variations in the microregional temperature to occur, so the temperature at which the desorption process took place was the same as that of a sorbate environment. In this sense, desorption represented the true equilibrium. Based on this hypothesis, it could be expected that a desorption branch that occurred at a certain higher temperature than the counterpart desorption branch of a particular adsorption process would overlap this very adsorption branch.

According to this hypothesis, any materials which were not perfect heat dissipators are bound to show sorption hysteresis. Any factors that made difference in heat dissipation ability would make a difference in hysteresis magnitude. At low temperatures, the heat dissipative characteristics of common materials is usually poor, so the hysteresis sizes are generally large. Increase in temperature would normally cause the heat dissipation ability of a material to be improved, so the hysteresis loop minimizes or even disappears. There are reports that multiple drying and rewetting cycles have caused disappearance of some kinds of materials (Rao 1941; Chung and Pfost 1967; Benado Rizvi 1985; and others). It could also be explained, according to the discussion in section 6.3.2: Net Isosteric Heat of Canola during Multiple A/D Cycles, 6.3.4, 6.4.1, 6.4.2 and 6.4.5 of this thesis, that an increase in the number of multiple drying and rewetting cycles greatly reduced the heat involvement in a sorption process and changed the structure of the sorbent which might possibly be in favour of the improvement of the heat dissipative ability of the sorbent, so adsorption and desorption paths were brought close together.

The hypothesis on the origin of sorption hysteresis proposed in this study can also explain the shape of a hysteresis loop. Most materials show very narrow or even no hysteresis at extremely low or high relative humidities and comparatively large hysteresis in the middle range of relative humidities. From the point of view of the hypothesis proposed in this study, the following double-faceted explanation could be given. On one hand, the water molecules are, according to Bettelheim et al. (1970), sorbed in the most accessible locations on the external surfaces of the sorbent or any possible locations very close to the predominant vapour phase within the sorbent at extremely low relative humidities. The sorptive sites in these locations are normally of low binding strength. At extremely high relative humidities, most condensed moisture remains as free water in the capillaries, micropores, and any other possible mass transfer passages as the least favourable locations are covered. Thus, the heat involved in a sorption process at the two ends of the relative humidity span is little, while it peaks in the middle range, especially around the monolayer region (Bettelheim et al. 1970; Rizvi and Benado 1984). The microregional temperature rise would therefore be little during an adsorption process, or in other words, adsorption would occur at about the same temperature as desorption, at the two extreme ends of the relative humidity range. This enabled adsorption and desorption branches to come close or even overlap at these two ends of the relative humidity range. On the contrary, microregional temperature rise could be expected to occur during the adsorption processes which took place at the relative humidities in the middle region. This would contribute to the formation of hysteresis in the middle of relative humidity range, according to this hypothesis. On the other hand, the water sorbed at the two ends of the relative humidity range stayed, as mentioned above, in the locations close to the predominant vapour phase. The heat released due to the state change of water molecules would, if any, be easily dissipated into the environment. Little microregional temperature rise occurred under such circumstances. Neither did the sorption hysteresis. As water became sorbed in more powerful sorptive sites, it would be farther from the predominant vapour phase and more surrounded by other microregions. It would be more difficult for the heat released during an adsorption process to get out of the sorbent into the environment. A more severe microregional temperature rise, and accordingly larger hysteresis magnitude could be expected. The effect of either or both of these two factors described above, i.e., the heat involvement difference at different relative humidities and the distance of the sorptive sites in a microregion from the predominant vapour phase, or rather, environment, resulted in the typical shape of sorption hysteresis. Mutations in hysteresis shape sometimes happen. This might be attributed to the changes in the above-mentioned two factors due to the changes in compositions of sorbent, state of solutes, structure of sorbent, etc. For example, the hysteresis of moisture sorption of dried apple slices is extraordinarily large and does not have a close end at very low relative humidity (Wolf et al. 1972). This might be because the heat involvement at extremely low relative humidities during the moisture adsorption process of dried apple slices increased greatly as compared with a normal case, since the sugar exposed on the exterior of the dried apple slices exerted strong hydrogen binding on the water molecules coming to the dried apple slices even at the relative humidities (or moisture contents) next to zero. The heat released was probably too intense to instantly and totally dissipate into the environment, although the locations where adsorption occurred was close to the predominant vapour phase. This was why the moisture sorption hysteresis of dried apple slices is, according to the proposed hypothesis, extraordinarily large and without a close end at extremely low relative humidities.

Explanation on the Hysteresis of Canola upon Multiple A/D Cycles

A variety of explanations have been advanced to account for the hysteresis phenomenon upon multiple adsorption and desorption cycles, as reviewed in section 3.2.2: Sorption Hysteresis during Multiple Adsorption and Desorption Cycles. In the present thesis, it is attempted to explain the hysteresis behaviour of canola upon multiple moisture sorption cycles, based on the recent developments on the electronic microscopy of oilseeds. The functional role of the oilseed hulls in the moisture sorption is not considered here, because most water is absorbed by the cotyledon. In oilseeds, lipids and proteins are the two main components. Both of them play very important roles in interactions with water. Arnott et al. (1983) found, when examining Cercis Canadensis under a TEM (Transmission Electron Microscopy), that in the cytoplasm, protein bodies are surrounded by a good number of lipid droplets. Such a configuration is very extensive with oilseeds. Canola is also of the same type of structure (Mills and Chong 1977). When water molecules enter the cytoplasm in the adsorption process, the most probable outcome of the hydrophobic repulsion of lipids against water molecules would be that water stayed with protein by hydrogen bonding. In such a configuration, the entropy of this system could be maintained at the minimum. When the process is reversed to desorption, this configuration would make it difficult for water molecules to exudate because of the double effects of the hydrophillic attraction of proteins and the hydrophobic repulsion of lipids. Thus, the equilibrium moisture content on desorption could not coincide with that on adsorption given the same relative humidity. As a result, the hysteresis was left over. Coincidence could not be possible unless the equilibrium temperature was increased or the vapour pressure in the surrounding was reduced, in order to provide more driving force for the water molecules to get out of the traps. Besides, for such protein-lipid configurations, protection mechanisms are built into oilseeds. This protection is probably due to the cell wall folding phenomenon (Arnott 1983; Swift and Buttrose 1972; Lott 1974) widely occurring in most of the oilseeds. Since the wall folding allows for the cell wall to undergo the drying and rewetting treatment without stretching the walls to the breaking point, the wall is well protected under the extremity. The integrity of the cell and the protein-lipid complex are also well protected. As a consequence, the hysteresis persists upon multiple adsorption and desorption cycles. It is still unknown whether a raised temperature would eliminate the cell wall folding phenomenon, but the protein-lipid complex was reported considerably distorted due to heat penetration (Mills and Chong 1977). They found that apparent gradual disruption of the regular pattern and coalescence of tightly packed lipid droplets appeared in severely heat-damaged canola. Protein bodies also appeared abnormal, with more irregular outlines than those of undamaged cells, according to these authors. Such findings could, to a large extent, explain the diminution of hysteresis magnitude of canola on the first and third drying and rewetting cycles at 40.0°C equilibrium temperature as compared with those at 25.0°C equilibrium temperature, and the elimination of hysteresis of canola on the fifth drying and rewetting cycle at 40.0°C.

7. SUMMARY AND CONCLUSIONS

Moisture sorption isotherms of canola variety Westar have been measured at the temperatures of 3.5, 25.0, and 40.0°C up to five consecutive adsorption and desorption cycles, and at temperatures of 6.0, 15.0, 35.0, and 45.0°C on the first adsorption and desorption cycle. Based on the isotherms measured, the following conclusions could be made:

1. Irregularity was found in the isotherms of canola at 25.0°C on the first and second adsorption and desorption cycles in the approximate relative humidity region of 20 to 45%, as compared with the isotherms on higher cycles. Isotherms of canola were, on the whole, shifted downwards, especially at relative humidities below 60%, as the result of the cyclic adsorption and desorption treatment and drying at elevated temperature, though the decrements were different at different equilibration temperatures. This indicated decrease in hygroscopicity of canola undergoing multiple adsorption and desorption cycles. A reversible (or hysteresis free) isotherm was available for canola through repeated drying and rewetting treatment up to the fifth cycle at 40.0°C.

2. Moisture sorption hysteresis of canola was persistent throughout five successive adsorption and desorption cycles at the equilibration temperatures of 3.5 and 25.0°C. However, it basically disappeared as the number of adsorption and desorption cycles increased up to five at the equilibration temperature of 40.0°C. Drying by heated air

at 50°C was found to enlarge the hysteresis magnitude of canola at relative humidities below 45%. Like many other materials, the hysteresis size of canola decreased with the increased equilibration temperature.

3. For the canola dried at 25°C, the Gibb's free energy became less and less negative at moisture contents below 8 %db at the equilibration temperatures of 3.5, 25.0 and 40.0°C with the increased number of adsorption and desorption cycles. This indicated that moisture sorption became a less favourable process for canola as it went through drying and rewetting cycles more often. At moisture contents above 8 %db, the effect of multiple adsorption and desorption cycles on the Gibb's free energy changes was not significant. For the canola dried at 50°C, little effect of multiple drying and rewetting cycles was found on the Gibb's free energy as calculated along both adsorption and desorption isotherms at 25.0° (treatment B), as compared with A and D.

4. The isosteric heat of moisture sorption of canola decreased considerably with the increased number of adsorption and desorption cycles at moisture contents below 8 %db. This indicated definite loss in moisture affinity of canola undergoing multiple adsorption and desorption cycles. Above 7.5 %db moisture content, the effect of multiple adsorption and desorption cycles on the isosteric heat was not significant.

5. Latent heat of vaporization of four rapeseed (canola) varieties, i.e., Westar, Tobin, Global and Candle, ranged from about 44 to 152 kJ/mole for moisture contents between

4.0 and 22.0 %db, temperatures between 4 and 75°C, and multiple drying and rewetting cycles between 1 and 5. The latent heat magnitude of Westar canola was found to be the largest among the four varieties, and those of Tobin and Global canola were placed the second and third. The latent heat magnitude of Candle rapeseed was the lowest of all. This finding indicated difference in the binding strength of sorptive sites available in different rapeseed (canola) varieties. The constant a in Eq.(11) was found to be the predominant factor to reflect the effect of multiple adsorption and desorption cycles on latent heat of vaporization of canola.

6. The entropy of moisture sorption of canola became less negative with the increased number of drying and rewetting cycles at moisture contents below about 8 %db. Like most other materials, the shape of entropy curves for canola resembled that of isosteric heat curves. It was mathematically shown in this study that entropy would assume the same magnitude and trend at any temperature within the temperature range in which the Clausius-Clapeyron equation held.

7. The BET monolayer coverage values for canola ranged from 2.90 to 3.40 %db at the equilibration temperature of 25.0°C and on five consecutive drying and rewetting cycles. It has been further confirmed by this study that the monolayer coverage in desorption were consistently larger than those in adsorption for sorption processes showing hysteresis. Both cyclic treatment of moisture and increase in equilibration temperature were found to decrease the monolayer coverage of canola.

8. It was statistically confirmed that the Henderson and Chung-Pfost isotherm equations are not suitable for expressing the moisture sorption isotherms of rapeseed (canola). The Halsey equation is a good model for describing the EMC-ERH relationship of rapeseed (canola). The new empirical equation proposed in this study showed better performance than the Halsey equation towards the moisture isotherms of rapeseed (canola) based on the goodness-of-fit criteria including the mean relative percentage deviation, the standard error, the behaviour of residual plot, and the sum of residuals of a total of 56 adsorption and desorption isotherms involving four rapeseed (canola) varieties, equilibration temperatures from 4 to 75°C, relative humidities from 13 to 93%, and drying and rewetting cycles from 1 to 5.

9. A new theory was proposed to account for the origin of sorption hysteresis. It was based on the hypothesis that adsorption tended to occur at a higher temperature than that at which its counterpart desorption occurred due to the inherent potential of microregional temperature rise, which resulted from the accumulation of the heat released during an adsorption process, for a common sorbent. The hysteresis behaviour of canola during multiple adsorption and desorption cycles was explained in terms of the hydrophillic and hydrophobic interaction between water and the lipid droplets and protein particles coexisting in a lipid-protein configuration and the cell wall folding phenomenon of canola.

8. LIMITATIONS AND SUGGESTIONS

It is one of the limitations related to this study that EMC measurement did not reach extremely low moisture content regions. Thus, it was not possible to calculate the equilibrium heat of sorption. Another limitation was that in explaining the mechanism of hysteresis occurrence of canola during multiple adsorption and desorption cycles the electron microscopic structure of canola was cited from elsewhere instead of being obtained in this study, although the electron microscopy of canola cited was very relevant. Since the hysteresis has been found eliminated at 40°C on the fifth drying and rewetting cycle, this makes it possible to calculate the thermodynamic functions from reversible isotherms at temperatures of 40°C or higher and to compare them with those calculated from irreversible isotherms. It would be constructive if the new empirical isotherm equation proposed for rapeseed (canola) in this study could be applied to the isotherms of other oilseeds and high-oil products to test its goodness-of-fit to these isotherms. More investigations should, in the future, go to the storage stability of canola during multiple adsorption and desorption cycles.

9. REFERENCES

Ajisegiri, E.S. and Sopade, P.A. 1990. Moisture sorption isotherms of Nigerian millet at varying temperatures. J. Food Eng. 12:283-292.

Almasi, E. 1978. Binding energy of bound water in foodstuffs. Acta Alimentaria 7:213.

ASAE. 1987. ASAE Standards D254.4: Moisture Relationship of Grains. Am. Soc. Agric. Eng., St. Joseph.

ASAE. 1991. ASAE Standards D254.4: Moisture Relationship of Grains. Am. Soc. Agric. Eng., St. Joseph.

ASAE. 1991. ASAE standard S352.1. Am. Soc. Agric. Eng., St. Joseph.

Ampratwum, D.B. and McQuitty, J.B. 1970. Moisture changes in dry and tough wheat in unventilated storage subjected to a cooling-warming cycle. Can. Agric. Eng. 12:18-20.

Angold, R.E. 1979. Cereals and bakery products. In: Food Microscopy. Vaughan, J.G. (Ed.). Academic Press, New York. pp.75-138.

Anderson, R.B. 1946. Modifications of the Brunauer, Emmet and Teller equation. J. Am. Chem. Sco. 68:686-691.

Anderson, J.A., Babbitt, J.D. and Meredith, W.O.S. 1943. The effect of temperature differential on the moisture content of stored wheat. Can. J. Res. 21C:297-306.

Arnell, J.C. and McDermot, H.L. 1957. Sorption hysteresis. In: Surface Activity. Vol.2. Schulman, J.H. (Ed.). Butterworth, London. p.113.

Arnott, H.J. and Webb, M.A. 1983. Scanning electron microscopy and histochemistry of oilseeds. In: New Frontiers in Food Microstructure. Bechtel, D.B. (Ed.). Am. Asso. Cereal Chem., Inc., St. Paul. pp.149-198.

Audu, T.O.K., Loncin, M. and Weisser, H. 1978. Sorption isotherms of sugars. Lebensm. Wiss. U.-Technol. 11:31.

Babbitt, J.D. 1942. On the adsorption of water vapor by cellulose. Can. J. Res. 20A:143-172.

Babbitt, J.D. 1945. Hysteresis in the adsorption of water vapor by wheat. Nature. 156:265-266.

Babbitt, J.D. 1949. Observations on the adsorption of water vapor by wheat. Can. J. Res. 27F:55-72.

Bala, B.K. and Woods, J.L. 1984. Simulated Malt Drying. J. Agric. Eng. Res. 30:235-244.

Bechtel, D.B., Gaines, R.L. and Pomeranz, Y. 1982. Protein secretion in wheat endosperm - Formation of the matrix protein. Cereal Chem. 59:336-343.

Becker, H.A. and Sallans, H.R. 1956. A study of the desorption isotherms of wheat at 25°C and 50°C. Cereal Chem. 33:79-91.

Bell, A.E. 1989. Gel structure and food biopolymers. In: Water and Food Quality. Hardman, T. (Ed.). Elsevier Applied Science. pp.251-276.

Benado, A.L. and Rizvi, S.S.H. 1985. Thermodynamic properties of water on rice as calculated from reversible and irreversible isotherms. J. Food Sci. 50:101-105.

Benson, S.W. and Richardson, R.L. 1955. A study of hysteresis in the sorption of polar gasses by native and denatured proteins. J. Am. Chem. Soc. 77:2585-2590.

Berlin, E. and Anderson, B.A. 1975. Reversibility of water vapor sorption by cottage cheese whey solids. J. Dairy Sci. 58:25-29.

Berlin, E., Anderson, B.A., and Pallansch, M.J. 1968. Water vapor sorption properties of various dried milks and wheys. J. Dairy Sci. 51:1339-1344.

Berlin, E., Anderson, B.A. and Pallansch, M.J. 1970a. Contraction of dried casein particles surfaces effected by sequential H_2O vapor sorption and desorption cycles. J. Coll. Int. Sci. 33:312-316.

Berlin, E., Kliman, P.G. and Pallansch, M.J. 1970b. Changes in state of water in proteinaceous systems. J. Coll. Int. Sci. 34:488-494.

Bertalanffy, L.V. 1950. The theory of open systems in physics and biology. Science. 111:23-29.

Bettelheim, F.A., Block, A. and Kaufman, L.J. 1970. Heats of water vapor sorption in swelling biopolymers. Biopolymers. 9:1531-1538.

Bettelheim, F.A. and Ehrlich, S.H. 1963. Water vapor sorption of mucopolysaccharides. J. Phys. Chem. 67:1948-1953.

Bettelheim, F.A. and Volman, D.H. 1957. Pectic substances - water. II. Thermodynamics of water vapor sorption. J. Polymer Sci. 24:445-453.

Bielewicz, J. 1991. Effects of canola pretreatments on sorption hysteresis and rheological behavior of single kernels. M.Sc. thesis, University of Manitoba, Winnipeg.

Bielewicz, J., Cenkowski, S. and Muir, W.E. 1991. Effects of growing history and selected pretreatments on equilibrium moisture content of canola seeds and its hysteresis. Submitted for publication in J. Stored Prod. Res.

Bizot, H., Buleon, A., Mouhous-riou, N. and Multon, J.L. 1985. Some facts concerning water vapor sorption hysteresis on potato starch. In: Properties of Water in Foods. Simatos, D. and Multon, J.L. (Ed.). Martinus Nijhoff Publishers, Dordrecht. pp.83-93.

Block, A. and Bettelheim, F.A. 1970. Water vapor sorption of hyaluronic acid. Biochim. Biophys. Acta. 201:69.

Bolin, H.R. 1980. Relation of moisture to water activity in prumes and raisins. J. Food Sci. 45:1190-1192.

Boquet, R., Chirife, J. and Iglesias, H.A. 1978. Equations for fitting water sorption isotherms of foods. II. Evaluation of various two-parameter models. J. Food Technol. 13:319-327.

Boquet, R., Chirife, J. and Iglesias, H.A. 1979. Equations for fitting water sorption isotherms of foods. III. Evaluation of various three-parameter models. J. Food Technol. 14:527-534.

Boquet, R., Chirife, J. and Iglesias, H.A. 1980. Technical note: of the equivalence of isotherm equations. J. Food Technol. 15:345-349.

Boyce, D.S. 1965. Moisture and temperature changes with position and time during drying. J. Agric. Eng. Res. 10:333-341.

Bradley, R.S. 1936. Polymolecular adsorbed films. Part 1. The adsorption of argon on salt crystals at low temperature and the determinations of surface fields. J. Chem. Soc. 58:1467-1474.

Breese, M.H. 1959. Hysteresis in the hygroscopic equilibria of rough rice at 25°C. Cereal Chem. 32:481-487.

Brunauer, S., Deming, L.S., Deming, W.E. and Teller, E. 1940. On a theory of the van der waals adsorption of gases. J. Am. Chem. Soc. 62:1723-1732.

Brunauer, S., Emmett, P.H. and Teller, E. 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60:309-319.

Bull, H.B. 1944. Adsorption of water vapor by proteins. J. Am. Chem. Soc. 66:1499-1507.

Bushuk, W. and Winkler, C.A. 1957. Sorption of water vapor on wheat flour, starch and gluten. Cereal Chem. 34:73-86.

Carter, D.G. and Farrar, M.D. 1943. Redistribution of moisture in soyabean bins. Agric. Eng. 24:296.

Caurie, M. 1970. A new model equation for predicting safe storage moisture levels for optimum stability of dehydrated foods. J. Food Technol. 5:301-307.

Cenkowski, S., Bielewicz, J. and Britton, M.G. 1990a. A single kernel creep and recovery test. ASAE Paper No. NC90-102, Am. Soc. Agric. Eng., St. Joseph.

Cenkowski, S., Jayas, D.S., Daun, J.K. and Shatadal, P. 1990b. Chlorophyll contents at different stages of maturity. CSAE Paper 90-409, Can. Soc. Agric. Eng., Ottawa.

Cenkowski, S., Jayas, D.S. and Hao, D. 1990c. Latent heat of vaporization for main crops and selected foods. CSAE Paper No.90-408, Can. Soc. Agric. Eng., Ottawa.

Cenkowski, S., Muir, W.E. and Jayas, D.S. 1990d. Simulation of canola and barley drying in a deep bed. J. Food Process Eng. 12:171-190.

Cenkowski, S., Sokhansanj, S. and Solsuski, F.W. 1989a. The effect of drying temperature on green color and chlorophyll content of canola seed. Can. Inst. Food Sci. Technol. J. 22:383-386.

Cenkowski, S., Sokhansanj, S. and Sosulski, F.W. 1989b. Equilibrium moisture content of lentils. Can. Agric. Eng. 31:159-162.

Cenkowski, S., Zhang, Q, Bielewicz, J. and Britton, M.G. 1991. Effect of maturity stage on mechanical properties of canola seeds. ASAE Paper No. 91-6054, Am. Soc. Agric. Eng., St. Joseph.

Chen, C.S. 1971. Equilibrium moisture curves for biological materials. Trans. of the ASAE. 14:924-926.

Chen, C.S. and Clayton, J.T. 1971. The effect of temperature on sorption isotherms of biological materials. Trans. of the ASAE. 14:927-929.

Chen, C.C. and Morey, V. 1989a. Comparison of four EMC/ERH equations. Trans. of the ASAE. 32:983-990.

Chen, C.C. and Morey, V. 1989b. Equilibrium relativity humidity (ERH) relationships for yellow-dent corn. Trans. of the ASAE. 32:999-1006.

Chirife, J. and Iglesias, H.A. 1978. Equations for fitting water sorption isotherms of foods: Part 1 - a review. J. Food Technol. 13:159-174.

Christensen, C.M. and Kaufmann, H.H. 1969. Grain storage - the role of fungi in quality loss. Chapter 2. University of Minnesota Press, Minneapolis.

Chung, D.S. 1966. Thermodynamic factors influencing moisture equilibrium of cereal grains and their products. Ph.D. dissertation, Kansas State Univ., Manhattan.

Chung, D.S., Park, S.W., Hoover, W.J. and Watson, C.A. 1972. Sorption kinetics of water vapor by yellow dent corn. Part I. Analysis of kinetic data for damage corn. Cereal Chem. 49:598-604.

Chung, D.S. and Pfost, H.B. 1967a. Adsorption and desorption of water vapor by cereal grains and their products. Part I. Heat and free energy changes of adsorption and desorption. Trans. of the ASAE. 10:549-555.

Chung, D.S. and Pfost, H.B. 1967b. Adsorption and desorption of water vapor by cereal grains and their products. Part II. Development of the general isotherm equation. Trans. of the ASAE. 10:552-555.

Chung, D.S. and Pfost, H.B. 1967c. Adsorption and desorption of water vapor by cereal grains and their products. Part III: A hypothesis for explaining the hysteresis effect. Trans. of the ASAE. 10:556-557.

Clear, K.M. and Daun, J.K. 1985. Chlorophyll of canola seed and oil. CUAP project #81-4. Can. Grain Commission, Grain Research Laboratory. Sept 16, 1985.

Cohan, L.H. 1938. Sorption hysteresis and the vapor pressure of concave surfaces. J. Am. Chem. Soc. 60:433-435.

Cohan, L.H. 1944. Hysteresis and the capillary theory of adsorption of vapors. J. Am. Chem. Soc. 66:98-105.

Das, B., Sethi, R.K. and Chopra, S.L. 1972. Sorption and desorption of water vapor on starch. Israel J. Chem. 10:963-965.

Davison, E., Middendorf, F.J. and Bilanski, W.K. 1975. Mechanical properties of rapeseed. Can. Agric. Eng. 17:50-54.

Day, D.L. and Nelson, G.L. 1965. Desorption isotherms for wheat. Trans. of the ASAE. 8:293-297.

Dole, M. and Faller, I.L. 1950. Water sorption by synthetic high polymers. J. Am. Chem. Soc. 72:414-419.

Dole, M. and Mclaren, A.D. 1947. The free energy, heat and entropy of sorption of water by proteins and high polymers. J. Am. Chem. Soc. 69:651-657.

Emery, F.E. 1969. Systems Thinking. Penguin Books. p.8.

Everett, D.H. 1950. Thermodynamics of Adsorption. Part 1. General considerations. Trans. of the Faraday Soc. 46:453-459.

Everett, D.H. 1955. A general approach to hysteresis. Part 4. An alternative formation of the domain model. Trans. Farady Soc. 51:1551-1557.

Everett, D.H. 1967. Adsorption hysteresis. In: The Solid-Gas Interface. Flood, E.A. (Ed.). Marcel Dekker, Inc., New York. pp.1055-1113.

Everett, D.H. and Whitton, W.I. 1952. A general approach to hysteresis. Trans. of the Faraday Soc. 48:749-757.

FATUS. 1990. Foreign Agricultural Trade of the United States. The United States Government Publication, New York.

Fennema, O. 1978. Enzyme kinetics at low temperature and reduced water activity. In: Dry Biological Systems. Crow, J.H. and Clegg, J.S. (Ed.). Academic Press, New York. pp.297-322.

Fennema, O. 1981. Water activity at subfreezing temperatures. In: Water Activity:

Influence on Food Quality. Rockland, L.B. and Stewart, G.F. (Ed.). Academic Press, New York. pp.713-732.

Fish, B.P. 1958. Diffusion and thermodynamics of water in potato starch gel. In: Fundamental Aspects of the Dehydration of Foodstuffs. Soc. Chem. Ind., London. p.143.

Flood, C.A., Jr. and White, G.M. 1984. Desorption equilibrium moisture relationship for popcorn. Trans. of the ASAE. 27:561-571.

Gallaher, G.L. 1951. A method of determining the latent heat of agricultural crops. Agric. Eng. 32:34,38.

Giacobee, F., Aylmore, L.A.G. and Steele, W.A. 1972. Thermodynamic properties of argon adsorbed on porous glass plus preadsorbed water. J. Coll. Int. Sci. 38:277-284.

Greg, S.J. and Sing, K.S.W. 1967. Adsorption, Surface Area and Porosity. Academic Press, New York.

Greig, R.I.W. 1979. Sorption properties of heat denatured cheese whey protein. Part. II. Unfreezable water content. Dairy Ind. Int. June:15.

Guibot, A., Charbonniere, R., Abadie, P. and Drapron, R. 1961. The contribution of water to the fine structure of macromolecular starch chains. Staerke 13:204.

Hailwood, A.J. and Horrobin, S. 1946. Absorption of water by polymers: Analysis in terms of a simple model. Trans. Faraday Soc. 42B:84-92.

Hall, C.W. and Rodriquez-Arias, J.H. 1958. Equilibrium moisture content of shelled corn. Agric. Eng. 39:466-470.

Halsey, G. 1948. Physical adsorption in non-uniform surfaces. J. Chem. Phys. 16:931-937.

Harkins, W.D. and Jura, G. 1944. Surfaces of solids. XIII. A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surfaces of a solid. J. Am. Chem. Soc., 66:1366-1373.

Hart, J.R. 1964. Hysteresis effects in mixture of wheats taken from the same sample but having different moisture content. Cereal Chem. 41:340-350.

Heldman, D.R., Hall, C.W. and Hedrick, T.I. 1965. Vapor equilibrium relationships of dry milk. J. Dairy Sci. 48:845-852.

Hayakawa, K.I., Matas, J. and Hwang, P. 1978. Moisture sorption isotherms of coffee products. J. Food Sci. 43:1026-1027.

Henderson, S.M. 1952. A basic concept of equilibrium moisture. Agric. Eng. 33:29-32.

Hill, T.L. 1949. Statistical mechanics of adsorption. 5. Thermodynamics and heat of adsorption. J. Chem. Phys. 17:520-535.

Hill, T.L. 1950. Statistical mechanics of adsorption. 9. Adsorption thermodynamics and solution thermodynamics. J. Chem. Phys. 18:246-256.

Hill, T.L. 1952. Theory of physical adsorption. Adv. in Catalysis. 4:211-258.

Hill, T.L., Emmett, P.H. and Joyner, L.G. 1951. Calculation of thermodynamic function sof adsorbed molecules from adsorption isotherms measurements: Nitrogen on graphon. J. Am. Chem. Soc., 75:5102-5107.

Hubbard, J.E., Earle, F.R. and Senti, E.R. 1957. Moisture relations in wheat and corn.

Cereal Chem. 34:422-433.

Iglesias, H.A. and Chirife, J. 1976a. Isosteric heats of water sorption on dehydrated foods. Part I. Analysis of the differential heat curves. Lebensm.- Wiss. U.-Technol. 9:116.

Iglesias, H.A. and Chirife, J. 1976b. Isosteric heats of water vapor sorption on dehydrated foods. Part II. Hysteresis and heat of sorption comparison with BET theory. Lebensm.-Wiss. U.-Technol. 9:123.

Iglesias, H.A. and Chirife, J. 1976c. Prediction of the effect of temperature on water sorption isotherms of food material. J. Food Technol. 11:109-116.

Iglesias, H.A. and Chirife, J. 1976d. Equilibrium moisture content of air-dired beef. Dependence on drying temperature. J. Food Technol. 11:565-573.

Iglesias, H.A. and Chirife, J. 1978. An empirical equation for fitting water sorption sothems of fruits and related products. Can. Inst. Food Sci. & Technol. J. 11:12-15.

Iglesias, H.A., Chirife, J. and Viollaz, P. 1976. Thermodynamics of water sorption by sugar beet root. J. Food Technol. 11:91-101.

Ingram, G.W. 1976. Deep bed drier simulation with intra-particle moisture diffusion. J. Agric. Eng. Res. 21:263-272.

Jayas, D.S., Kukelko, D.A. and White, N.D.G. 1987a. Equilibrium moisture-equilibrium relative humidity relationship for canola meal. ASAE Paper No. 87-6534, Am. Soc. Agric. Eng., St. Joseph.

Jayas, D.S. and Mazza, J. 1991. Comparison of modified GAB equation with four other three-parameter equations for the description of sorption data of oats. ASAE Paper No. MNSK91-115. Am. Soc. Agric. Eng., St. Joseph.

Jayas, D.S. and Sokhansanj, S. 1985. Resistance to airflow of rapeseed (canola). ASAE Paper No. 85-3516, Am. Soc. Agric. Eng., St. Joseph.

Jayas, D.S. and Sokhansanj, S. 1986. Effect of foreign material on resistnace to airflow of canola (rapeseed). ASAE Paper No. 86-6572, Am. Soc. Agric. Eng., St. Joseph.

Jayas, D.S. and Sokhansanj, S. 1989. Design data on resistance of airflow through canola (rapeseed). Trans. of the ASAE. 32:295-296.

Jayas, D.S., Sokhansanj, S., Moysey, E.B. and Barber, E.M. 1987b. Effect of airflow distribution on the resistnace of canola (rapeseed) to airflow. Can. Agric. Eng. 29:189-192.

Jayas, D.S. and Sokhansanj, S, and White, N.D.G. 1989. Bulk density and porosity of two canola species. Trans. of the ASAE. 32:291-294.

Jayas, D.S. and Sokhansanj, S, Moysey, E.B. and Barber, E.M. 1986. Resistance to airflow of canola as affected by direction of airflow. CSAE paper No. 86-409. Can. Soc. Agric. Eng., Ottawa.

Kapsalis, J.G. 1981. Moisture sorption hysteresis. In: Water Activity: Influences on Food Quality. Rockland, L.B. and Stewart, G.F. (Ed.). Academic Press, New York. pp.143-177.

Kapsalis, J.G. 1987. Influence of hysteresis and temperature on moisture sorption isotherms. In: Water Activity: Theory and Applications to Food. Rockland, L.B. and Beuchat, L.R. (Ed.). Marcel Dekker, Inc., New York. pp.173-213.

Kingston, G.L. and Smith, P.S. 1964. Thermodynamics of adsorption in capillary systems. Part I. Origin of irreversibility. Trans. of the Faraday Soc. 60:705-720.

Kraemer, E.O. 1931. Chapter XX. In: A Treatise on Physical Chemistry. Taylor, H.S. (Ed.). D. Van Nostrand Co., New York.

Kuhn, I. 1964. A new theoretical analysis of adsorption phenomena. Introductory part: the characteristic expression of the main regular types of adsorption isotherms by a single simple equation. J. Colloid Sci. 19:685-698.

Labuza, T.P. 1984. Moisture Sorption: Practical Aspects of Isotherm Measurement and Use. Am. Assoc. Cereal Chem., St. Paul. p.77.

Labuza, T.P., Kaane, A. and Chen, J.Y. 1984. Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. J. Food Sci. 50:385-391.

Lai, C.C., Gilbert, S.G. and Mannheim, C.H. 1985. Thermodynamics of water-egg powders interaction. J. Food Sci. 50:1615-1617.

La Mer, V.K. 1967. The calculation of thermodynamic quantities from hysteresis data. J. Coll. Int. Sci. 23:297-301.

Law, J.L. 1955. The adsorption of water vapor on germanium and germanium dioxide. J. Phys. Chem. 59:67-71.

Lee, R.Y., Silverman, G.J. and Munsey, D.T. 1981. Growth and enterotoxin A production by Staphylococcus aureus in precooked bacon in the intermediate moisture range. J. Food Sci. 46:1687-1692, 1700.

Lomauro, C.J., Bakshi, A.S. and Labuza, T.P. 1985. Evaluation of food moisture sorption isotherm equations. Parts I and II. Lebensm.-Wiss. U.Technol. 18:110.

Lott, J.N.A. 1974. Cell walls in cucurbita maxima cotyledons in relation to imbibition. Can. J. Bot. 52:1465-1468.

Mackenzie, A.P. 1975. The physico-chemical environment during freezing and thawing of biological materials. In: Water Relations of Foods. Duckworth, R.B. (Ed.). Academic Press, New York. pp.477-504.

Mazza, G. and Jayas, D.S. 1990. Equilibrium moisture content - equilibrium relative humidity relationships of sunflower seeds, hulls and kernels. CSAE Paper No.90-406, Can. Soc. Agric. Eng., Ottawa.

McBain, J.W. 1935. An explanation of hysteresis in the hydration and dehydration of gels. J. Am. Chem. Soc. 57:699-700.

McBain, J.W. and Ferguson, J. 1927. On the nature of the influence of humidity changes upon the composition of building materials. J. Phy. Chem. 31:564-590.

Mellon, E.F., Korn, A.H. and Hoover, S.R. 1947. Water adsorption of proteins. I. J. Am. Chem. Soc. 69:827-831.

Mills, J.T. and Chong, J. 1977. Ultrastructure and mineral distribution in heat-damaged rapeseed. Can. J. Plant Sci. 57:21-30.

Mills, J.T. and Sinha, R.N. 1980. Safe storage periods for farm-stored rapeseed based on mycological and biochemical assessment. Phytopathology 70:541-547.

Mizrahi, S., Labuza, T.P. and Karel, M. 1970. Computer-aided predictions of extent of growning in dehydrated cabbage. J. Food sci. 35:799-803.

Moysey, E.B. 1973. Storage and drying of oilseeds. In: Grain Storage:Part of a System.

Sinha, R.N. and Muir, W.E. (Ed.). The Avi Publishing Copany, Westport. pp229-250.

Moysey, E.B., Shaw, J.T. and Lampman, W.P. 1977. The effect of temperature and moisture on the thermal properties of rapeseed. Trans. of the ASAE 20:768-771.

Muir, W.E., Kumar, A., Fraser, B.M. and Britton, M.G. 1978. Development of emergency structures for grain storage. Can. Agric. Eng. 20:30-33.

Muir, W.E., Sinha, R.N., Wallace, H.A.H. and Sholberg, P.L. 1980. Emergency farm structures for storing grain - a multidisciplinary evaluation. Trans. of the ASAE, 23:208-213.

Ng, P.K.W., Bushuk, W. and Borsa, J. 1989. Effect of gamma high-energy electron irradiations on breadmaking of two canadian wheat cultivars. Can. Inst. food Sci. 2:173-176.

Osborn, G.S., White, G.M., Sulaiman, A.H. and Walton, L.R. 1989. Predicting equilibrium moisture properties of soybeans. Trans. of the ASAE, 32:2109-2113.

Oswin, C.R. 1946. The kinetics of package life III isotherm. J. Chem. Ind. 65:419-421.

Othmer, D.F. 1940. Correlating vapor pressure and latent heat data. A new plot. Ind. Eng. Chem. 32:841-856.

Otten, L., Brown, R.B. and Vogel, K.F. 1989. Thin layer drying of canola. ASAE Paper No. 89-6100, Am. Soc. Agric. Eng., St. Joseph.

Otten, L., Brown, R. and Vogel, K. 1990. Equilibrium moisture content of canola. CSAE Paper No. 90-407, Can. Soc. Agric. Eng., Ottawa.

Pauling, L. 1945. The adsorption of water by proteins. J. Am. Chem. Soc. 67:555-557.

Pfost, H.B., Mourer, S.G., Chung, D.S. and Milliken, G.A. 1976. Summarizing and reporting equlibrium moisture data for grains. ASAE Paper No. 76-3520. Am. Soc. Agric. Eng., St. Joseph.

Pichler, H.J. 1957. Sorption isotherms for grain and rape. J. Agric. Eng. Res. 2:159-165.

Pixton, S.W. and Henderson, S. 1981. The moisture content-equilibrium relative humidity relationships of five varieties of Canadian wheat and of candle rapeseed at different temperatures. J. Stored Prod. Res. 17:187-190.

Pixton, S.W. and Warburton, S. 1977. The moisture content/equilibrium relative humidity relationship and oil composition of rapeseed. J. Stored Prod. Res. 13:77-81.

Ponec, V., Knor, Z. and Cerny, V. 1974. Adsorption on Solids. Butterworth and Co., London.

Rao, K.S. 1941. Hysteresis in sorption. I-VI. J. Phys. Chem. 45:500-539.

Rao, V.G. and Pfost, H.B. 1980. Physical properties related to drying 20 food grains. ASAE Paper No.80-3539, Am. Soc. Agric. Eng., St. Joseph.

Rizvi, S.S.H. and Benado, A.L. 1984. Thermodynamic properties of dehydrated foods. Food Technol. 38:83-92.

Rodriquez-Arias, J.H., Hall, C.W. and Bakker-Arkema, F.W. 1963. Heat of vaporization for shelled corn. Cereal Chem. 40:676-683.

Roman, N., Urbicain, M.J. and Rotstein, E. 1982. Moisture equilibrium in apples at several temperatures: experimental data and theoretical considerations. J. Food Sci. 47:1484-1488

Rutman, M. 1967. The effect of surface active agents on sorption isotherms of models systems. M.Sc. thesis, Massachusetts Institute of Technology, Cambridge.

San Jose, C., Asp, N.G., Burvall, A. and Dahlgvist, A. 1977. Water sorption in lactose hydrolyzed milk. J. Dairy Sci. 60:1539-1543.

Saravacos, G.D. 1967. Effect of the drying method on the water sorption of dehydrated apple and potato. J. Food Sci. 32:81-84.

Saravacos, G.D. and stinchfield, R.M. 1965. Effect of temperature and pressure on the sorption of water vapor by freeze-dried food materials. J. Food sci. 30:779-786.

Saravacos, G.D., Tsiourvas, D.A. and Tsami, E. 1986. Effect of temperature on the water adsorption isotherms of sultana raisins. J. Food Sci. 51:381- 383,387.

Seehof, J.M., Keilin, B. and Benson, S.W. 1953. The surface areas of proteins. V. The mechanism of water sorption. J.Am. Chem. Soc. 75:2427-2430.

Sharma, S.C. and Muir, W.E. 1973. Simulation of heat and mass transfer during ventilation of wheat and rapeseed bulks. Can. Agric. Eng. 16:41-44.

Shatadal, P., Jayas, D.S. and White, N.D.G. 1990. Thin-layer rewetting characteristics of canola. Trans. of the ASAE. 33:871-876.

Sheppard and Newsome. 1929. The sorption of water vapor by cellulose and its derivatives. J. Phys. Chem. 33:1817-1835.

Silverman, G.J., Munsey, D.T., Lee, C. and Ebert, E. 1983. Interrelationship between water activity, temperature and 5.5 percent oxygen on growth and enterotoxin A secretion by Staphylococcus aureus in precooked bacon. J. Food Sci., 48:1783-1786,1795.

Singh, R.S. and Ojha, T.P. 1974. Equilibrium moisture content of groundnut and chillies. J. Sci. Food Agric. 25:451-459.

Singh, D., Sokhansanj, S. and Middleton, B. 1983. Drying characteristics of wheat, barley and canola at low temperatures. ASAE Paper No. NCR83-207, Am. Soc. Agric. Eng., St. Joseph.

Sinha, R.N. 1973. Interrelations of physical, chemical, and biological variables in the deterioration of stored grains. In: Grain Storage: Part of a System. Sinha, R.N. and Muir, W.E. (Ed.). The Avi Publishing Co., Inc., Westport. pp.15-47.

Smith, P.R. 1947. The sorption of water vapor by high polymers. J. Am. Chem. Soc. 69:646-651.

Sokhansanj, S., Lampman, W.P. and MacAulay, J.D. 1983. Investigation of grain tempering on drying tests. Transactions of the ASAE. 26:293-296.

Sokhansanj, S., Singh, D. and Wasserman, J.D. 1984. Drying characteristics of wheat, barley and canola subjected to repetitive wetting and drying cycles. Trans. of the ASAE. 27:903-906, 914.

Sokhansanj, S., Zhijie, W., Jayas, D. and Kameoka, T. 1986. Equilibrium relative humidity-moisture content of rapeseed (canola) from 5°C to 25°C. Transactions of the ASAE. 29:837-939.

Speakman, J.B. and Stott, E. 1936. The adsorption of water by wool. Part II. The influence of drying conditions on the affinity of wool for water. J. Text. Inst. 27:T186-T190.

Storey, R.M. and Stainsby, G. 1970. The equilibrium water vapor pressure of frozen cod. J. Food Technol. 5:157-163.

Strasser, J. 1969. Detection of quality changes in freeze-dried beef by measurement of the sorption isobar hysteresis. J.Food Sci. 34:18-21.

Strohman, R.D. and Yoerger, R.R. 1967. A new equilibrium moisture - content equation. Trans. of the ASAE, 10:675-677.

Swift, J.G. and Buttrose, M.S. 1972. Freeze etch studies of protein bodies in wheat scutellum. J. Ultrast. Res. 40:378-390.

Thompson, H.J. and Shedd, C.K. 1954. Equilibrium moisture and heat vaporization of shelled corn and wheat. Agric. Eng. 35:786-789.

Throne, J.E. 1991. Equilibrium moisture content of cracked and whole corn (maze). J. Stored Prod. Res. 27:129-130.

Timbers, G.E. and Hocking, R.P. 1974. Vapour pressure and moisture equilibrium in rapeseed. Engineering Research Service Report No.7142-2. Agriculture Canada, Ottawa.

Tuite, J. and Foster, G.H. 1963. Effect of artificial drying on the hygroscopic properties of corn. Cereal Chem. 40:630-637.

Van den Berg, C. 1985. Water Activity. In: Concentration and Drying of Foods. McCarthy, Q. (Ed.). Elsevier Applied Science Publisher, London. pp.11-36.

Van den Berg, C and Bruin, S. 1981. Water activity and its estimation in food systems: theoretical aspects. In: Water Activity: Influence on Food Quality. Rockland, L.B. and Stewart, G.F. (Ed.). Academic Press, New York. pp.1-43.

Van den Berg, C., Kaper, F.s., Weldring, A.G., and Wolters, I. 1975. Water binding by potato starch. J. food. Technol. 10:589-602.

Van Olphen, H. 1965. Thermodynamics of interlayer adsorption of water in clay. I. Sodium vermiculite. J. Colloid Sci. 20:822-837.

Volman, D.H., Simons, J.W., Seed, J.R. and Sterling, C. 1960. Sorption of water vapor by starch. Thermodynamics and structural changes for dextrin, amylose, and amylopectin. J. Polymer Sci. 36:355-364.

Wallace, H.A.H. and Sinha, R.N. 1962. Fungi associated with hotspots in farm stored grain. Can. J. Plant Sci. 42:130-141.

Watt, I.C. 1980a. Adsorption-desorption hysteresis in polymers. J. Macromol. Sci.-Chem. A14:245-255.

Watt, I.C. 1980b. Sorption of water vapor by keratin. J. Macromol. Sci.-Rev. Macromol. Chem. C18:169-245

Weisser, H, Wever, J. and Loncin, M. 1982. Water vapor sorption isotherms of sugar substitutes in the temperature range 25 to 80°C. Inter. Zeits. Lebens. Technol. Verfahrenstechnik. 33:89.

White, N.D.G. and Jayas, D.S. 1989. Safe storage conditions and infestation potential of canola meal by fungi and insects. J. Stored Prod. Res. 25:105-114.

Wolf, M., Walker, J.E. and Kapsalis, J.G. 1972. Water vapor sorption hysteresis in dehydrated foods. J. Agric. Food Chem. 20:1073-1077.

Yang, W.H. and Cenkowski, S. 1991. Moisture sorption hysteresis of canola upon multiple drying and rewetting cycles. ASAE Paper No. MNSK91-116, Am. Soc. Agric. Eng., St. Joseph.

Young, J.H. 1976. Evaluation of models to describe sorption and desorption equilibrium moisture content isotherms of Virginia-type peanuts. Trans. of the ASAE, 19:146-150,155.

Young, D.M. and Crowell, A.D. 1962. Physical Adsorption of Gases. Butterworth and Co., Washington, D.C..

Young, J.H. and Nelson, G.L. 1967. Theory of hysteresis between sorption and desorption isotherms in biological materials. Trans. of the ASAE. 10:260-263.

Zhang, Q., Muir, W.E., Sinha, R.N. and Cenkowski, S. 1991. Heat production in wet wheat under adiabatic conditions. Can. Agric. Eng. (in press).

Zsigmondy, R. 1911. Structure of gelatious silicic acid. Theory of dehydration. Z. Anorg. Chem. 71:356.

APPENDIX A

Table A1 Isotherm data for treatment A (drying of Westar canola at 25°C prior to moisture equilibration at 25.0°C)

1st Drying and Rewetting Cycle

RH, %	64.4	57.7	47.8	35.3	19.4	13.0
Adsorption						
Mean, %db	9.517	8.028	6.932	5.793	5.086	4.691
Std. Dev.	0.110	0.117	0.081	0.022	0.057	0.027
95% Conf.	0.273	0.290	0.201	0.054	0.140	0.066
Desorption						
Mean, %db	9.798	8.270	7.189	5.918	5.350	4.791
Std. Dev.	0.200	0.095	0.057	0.069	0.036	0.057
95% Conf.	0.497	0.236	0.140	0.172	0.089	0.140

2nd Drying and Rewetting Cycle

RH, %	67.8	59.7	52.8	40.8	29.7	18.2
Adsorption						
Mean, %db	10.060	8.515	7.390	6.260	5.621	4.760
Std. Dev.	0.111	0.212	0.077	0.069	0.021	0.048
95% Conf.	0.275	0.525	0.192	0.172	0.053	0.119
Desorption						
Mean, %db	9.847	8.221	7.206	6.056	5.488	4.637
Std. Dev.	0.175	0.128	0.071	0.059	0.022	0.024
95% Conf.	0.433	0.318	0.177	0.145	0.053	0.060

3rd Drying and Rewetting Cycle

RH, %	68.5	58.8	49.2	29.9	16.9	14.2
Adsorption						
Mean, %db	10.354	8.382	6.840	5.213	4.682	4.541
Std. Dev.	0.026	0.026	0.056	0.005	0.013	0.003
95% Conf.	0.065	0.065	0.140	0.011	0.033	0.008
Desorption						
Mean, %db	10.667	8.645	7.091	5.533	4.885	4.644
Std. Dev.	0.042	0.038	0.064	0.027	0.010	0.016
95% Conf.	0.105	0.095	0.158	0.066	0.024	0.038

4th Drying and Rewetting Cycle

RH, %	68.8	57.0	48.3	33.8	24.8	12.7
Adsorption						
Mean, %db	10.195	7.924	6.626	5.419	4.813	4.215
Std. Dev.	0.024	0.039	0.052	0.036	0.029	0.028
95% Conf.	0.061	0.096	0.130	0.090	0.072	0.069
Desorption						
Mean, %db	10.516	8.217	6.961	5.777	5.189	4.407
Std. Dev.	0.012	0.022	0.107	0.056	0.025	0.012
95% Conf.	0.030	0.055	0.265	0.139	0.063	0.030

5th Drying and Rewetting Cycle

RH. %	69.6	58.4	47.5	39.4	27.4	17.1
Adsorption						
Mean, %db	10.682	8.476	6.750	5.926	5.151	4.695
Std. Dev.	0.046	0.045	0.044	0.050	0.036	0.018
95% Conf.	0.115	0.110	0.110	0.124	0.089	0.044
Desorption						
Mean, %db	10.384	8.161	6.492	5.669	4.886	4.542
Std. Dev.	0.039	0.051	0.056	0.025	0.026	0.037
95% Conf.	0.098	0.127	0.138	0.063	0.064	0.091

Table A2 Isotherm data for treatment B (drying of Westar canola at 50°C prior to moisture equilibration at 25.0°C)

1st Drying and Rewetting Cycle

RH, %	78.4	75.1	69.7	64.6	59.7	49.6	34.5
Adsorption							
Mean, %db	14.951	12.784	10.961	9.154	8.043	6.510	5.386
Std. Dev.	0.044	0.059	0.015	0.010	0.009	0.045	0.041
95% Conf.	0.108	0.146	0.037	0.025	0.021	0.111	0.100
Desorption							
Mean, %db	15.412	13.543	11.336	9.705	8.665	7.443	6.064
Std. Dev.	0.021	0.024	0.012	0.051	0.055	0.053	0.064
95% Conf.	0.053	0.060	0.030	0.127	0.136	0.131	0.158

2nd Drying and Rewetting Cycle

RH, %	69.6	64.1	63.3	54.2	48.1	41.3
Adsorption						
Mean, %db	10.665	9.065	9.032	7.114	6.542	5.971
Std. Dev.	0.020	0.024	0.037	0.018	0.015	0.011
95% Conf.	0.050	0.059	0.091	0.044	0.038	0.026
Desorption						
Mean, %db	10.843	9.534	9.441	7.918	7.190	6.726
Std. Dev.	0.008	0.081	0.053	0.016	0.025	0.012
95% Conf.	0.019	0.201	0.131	0.039	0.063	0.029

3rd Drying and Rewetting Cycle

RH, %	75.3	74.6	71.0	62.0	56.8	54.1	42.0	37.0
Adsorption								
Mean, %db	13.510	12.254	11.251	9.092	7.854	7.413	6.251	5.756
Std. Dev.	0.010	0.027	0.061	0.007	0.090	0.023	0.042	0.015
95% Conf.	0.024	0.066	0.151	0.017	0.223	0.056	0.104	0.037
Desorption								
Mean, %db	13.632	12.773	11.522	9.536	8.261	7.911	6.946	6.429
Std. Dev.	0.026	0.038	0.031	0.012	0.020	0.042	0.045	0.037
95% Conf.	0.063	0.093	0.077	0.030	0.048	0.103	0.111	0.093

5th Drying and Rewetting Cycle

RH, %	70.1	65.6	57.5	46.6	43.0	35.8
Adsorption						
Mean, %db	10.832	9.745	7.893	6.531	6.308	5.651
Std. Dev.	0.031	0.008	0.022	0.015	0.031	0.016
95% Conf.	0.078	0.019	0.054	0.036	0.076	0.039
Desorption						
Mean, %db	11.141	10.163	8.342	7.097	6.864	6.302
Std. Dev.	0.013	0.015	0.015	0.038	0.038	0.035
95% Conf.	0.032	0.037	0.037	0.094	0.094	0.087

Table A3 Isotherm data for treatment C (drying of Westar canola at 25°C prior to moisture equilibration at 40.0°C)

1st Drying and Rewetting Cycle

RH, %	72.3	64.4	55.1	46.9	44.9	34.0
			Adsorption			
Mean, %db	11.167	8.849	7.388	6.146	5.904	5.271
Std. Dev.	0.070	0.023	0.044	0.033	0.071	0.026
95% Conf.	0.173	0.056	0.109	0.081	0.175	0.065
			Desorption			
Mean, %db	11.651	8.972	7.486	6.318	5.977	5.231
Std. Dev.	0.040	0.060	0.015	0.021	0.074	0.060
95% Conf.	0.100	0.149	0.037	0.053	0.183	0.149

3rd Drying and Rewetting Cycle

RH, %	71.5	63.5	55.0	47.9	45.6
			Adsorption		
Mean, %db	11.256	8.707	7.107	6.132	6.010
Std. Dev.	0.017	0.058	0.023	0.059	0.028
95% Conf.	0.042	0.143	0.058	0.147	0.069
			Desorption		
Mean, %db	11.608	9.041	7.178	6.438	6.077
Std. Dev.	0.041	0.069	0.029	0.017	0.036
95% Conf.	0.102	0.171	0.072	0.043	0.090

5th Drying and Rewetting Cycle

RH, %	73.1	65.9	55.1	50.4	43.5	31.5
			Adsorption			
Mean, %db	10.845	9.062	7.029	6.482	5.863	4.766
Std. Dev.	0.049	0.078	0.098	0.018	0.073	0.010
95% Conf.	0.121	0.195	0.243	0.044	0.182	0.024
			Desorption			
Mean, %db	10.999	9.134	7.039	6.577	5.964	4.754
Std. Dev.	0.091	0.056	0.108	0.040	0.060	0.040
95% Conf.	0.225	0.138	0.267	0.100	0.150	0.098

Table A4 Isotherm data for treatment D (drying of Westar canola at 25°C prior to moisture equilibration at 3.5°C)

1st Drying and Rewetting Cycle

RH, %	87.4	76.2	70.0	55.4	33.9	23.6	18.8
Adsorption							
Mean, %db	19.457	12.969	10.779	8.189	6.101	5.449	4.732
Std. Dev.	0.089	0.045	0.105	0.009	0.069	0.038	0.049
95% Conf.	0.218	0.111	0.254	0.022	0.169	0.093	0.121
Desorption							
Mean, %db	19.805	13.846	11.499	8.756	6.824	6.112	5.076
Std. Dev.	0.006	0.026	0.019	0.001	0.045	0.078	0.025
95% Conf.	0.015	0.064	0.047	0.002	0.110	0.191	0.061

3rd Drying and Rewetting Cycle

RH, %	89.2	82.4	71.6	60.0	42.1	26.4
Adsorption						
Mean, %db	19.569	15.501	10.782	8.337	6.422	5.569
Std. Dev.	0.101	0.004	0.006	0.024	0.069	0.007
95% Conf.	0.247	0.010	0.016	0.058	0.168	0.017
Desorption						
Mean, %db	19.745	16.299	11.581	9.068	6.870	5.887
Std. Dev.	0.124	0.019	0.001	0.006	0.018	0.003
95% Conf.	0.303	0.047	0.002	0.015	0.044	0.007

5th Drying and Rewetting Cycle

RH, %	85.1	74.6	65.1	45.7	31.3	25.6
			Adsorption			
Mean, %db	17.576	11.691	9.241	6.613	5.446	4.955
Std. Dev.	0.011	0.009	0.023	0.002	0.061	0.004
95% Conf.	0.027	0.022	0.056	0.005	0.149	0.010
			Desorption			
Mean, %db	17.971	12.469	9.784	7.198	5.988	5.299
Std. Dev.	0.114	0.101	0.005	0.031	0.001	0.008
95% Conf.	0.278	0.248	0.012	0.076	0.002	0.020

Table A5 Isotherm data for Westar canola equilibrated at 6.0°C

1st Drying and Rewetting Cycle

RH, %	92.0	76.6	53.6	30.8
		Adsorption		
Mean, %db	17.607	9.093	6.970	4.926
Std. Dev.	0.037	0.038	0.036	0.007
95% Conf.	0.093	0.094	0.089	0.017
		Desorption		
Mean, %db	17.927	9.987	7.386	6.094
Std. Dev.	0.038	0.066	0.011	0.065
95% Conf.	0.093	0.165	0.028	0.162

Table A6 Isotherm data for Westar canola equilibrated at 15.0°C

1st Drying and Rewetting Cycle

RH, %	72.6	46.9	41.1	39.8	39.4	34.9
Adsorption						
Mean, %db	10.244	6.546	6.073	5.924	5.775	5.707
Std. Dev.	0.025	0.038	0.033	0.036	0.015	0.051
95% Conf.	0.062	0.095	0.083	0.088	0.036	0.128
Desorption						
Mean, %db	10.474	7.118	6.342	6.104	5.962	5.901
Std. Dev.	0.036	0.050	0.008	0.013	0.072	0.016
95% Conf.	0.089	0.124	0.020	0.032	0.179	0.039

Table A7 Isotherm data for Westar canola equilibrated at 35.0°C

1st Drying and Rewetting Cycle

RH, %	76.2	65.4	55.3	51.8	48.9	20.9
			Adsorption			
Mean, %db	11.239	8.716	7.253	6.642	6.487	4.623
Std. Dev.	0.018	0.046	0.016	0.076	0.031	0.027
95% Conf.	0.044	0.115	0.040	0.189	0.077	0.067
			Desorption			
Mean, %db	11.212	9.047	7.495	6.887	6.717	4.897
Std. Dev.	0.012	0.079	0.040	0.121	0.016	0.070
95% Conf.	0.030	0.196	0.099	0.299	0.039	0.173

Table A8 Isotherm data for Westar canola equilibrated at 45.0°C

1st Drying and Rewetting Cycle

RH, %	69.9	66.7	58.5	46.3	44.8	44.2	35.4
Adsorption							
Mean, %db	10.146	8.897	7.521	5.798	5.692	5.577	4.893
Std. Dev.	0.016	0.031	0.029	0.063	0.016	0.051	0.023
95% Conf.	0.040	0.077	0.072	0.155	0.039	0.127	0.056
Desorption							
Mean, %db	10.302	9.197	7.770	5.810	5.736	5.618	4.902
Std. Dev.	0.046	0.050	0.013	0.037	0.025	0.016	0.014
95% Conf.	0.113	0.123	0.032	0.093	0.062	0.039	0.035

APPENDIX B

Appendix B Moisture sorption isotherm models tested in this study

1. Guggenheim-Anderson-de Boer (GAB) (Anderson 1946)

$$\frac{m}{m_0} = \frac{ABa_w}{(1-Aa_w)\,(1-Aa_w+ABa_w)}$$

where: m - equilibrium moisture content (percent dry basis),
m_0- monolayer moisture content (percent dry basis),
a_w- water activity (interchangeable with relative humidity, decimal),
A, B - constants

2. Brunauer-Emmett-Teller (BET) (Brunauer et al. 1938)

$$\frac{a_w}{(1-a_w)m} = \frac{1}{Am_0} + \frac{(A-1)}{Am_0}a_w$$

3. Oswin (1946)

$$m = A\left(\frac{a_w}{1-a_w}\right)^B$$

4. Halsey (1948)

$$a_w = \exp\left(-\frac{C}{m^B}\right)$$

where C is a constant.

5. Bradley (1936)

$$a_w = \exp(-AB^m)$$

6. Hailwood and Harrobin (1946)

$$\frac{a_w}{m} = A + Ba_w + Ca_w^2$$

7. Smith (1947)

$$m = A - B\ln(1-a_w)$$

8. Henderson (1952)

$$\ln(1-a_w) = -Am^B$$

9. Chung-Pfost (1967b)

$$a_w = \exp(-A exp(-Bm))$$

10. Caurie (1970)

$$\ln\frac{100}{m} = (\frac{1}{0.045m_0}) - Aa_w$$

11. Harkins-Jura (1944)

$$a_w = \exp(A - \frac{B}{m^2})$$

12. Mizrahi (Mizrahi et al. 1970)

$$a_w = \frac{A+m}{B+m}$$

13. Kuhn (1967)

$$a_w = \exp(\frac{A}{m-B})$$

14. Chen (1971)

$$a_w = \exp(A + B exp(Cm))$$

APPENDIX C

Appendix C: Section I-A

Estimated parameters and goodness-of-fit criteria for the isotherms of Westar canola measured in this investigation as fitted to the emipirical isotherm equation proposed in this study

	A	B	C	P[1]	S.E.(%)[2]	Sum[3]	Residual[4]
Isotherms at 25.0°C (Treatment A)							
1st A/D Cycle							
Adsorption	1.6327	5.4961	999.88	2.36	0.45	0.025	R.D.*
Desoprtion	1.5684	5.3260	1023.8	5.43	0.82	0.045	S.P.**
2nd A/D Cycle							
Adsorption	1.2675	3.4497	103.78	3.20	0.42	0.023	R.D.
Desorption	1.2274	3.3777	124.90	0.79	0.20	0.011	R.D.
3rd A/D Cycle							
Adsorption	1.3877	4.2017	243.34	4.75	0.69	0.038	R.D.
Desorption	1.3337	4.0308	250.76	2.67	0.44	0.024	R.D.
4th A/D Cycle							
Adsorption	1.2648	3.6154	150.08	2.31	0.42	0.023	R.D.
Desorption	1.2345	3.4858	146.56	2.13	0.37	0.020	R.D.
5th A/D Cycle							
Adsorption	1.3148	3.6996	126.81	5.28	0.79	0.043	S.P.
Desorption	1.2938	3.6836	148.32	3.88	0.64	0.035	R.D.

1 Mean relative percentage deviation
2 Standard error of the estimated value
3 Sum of residual
4 Behavior of residual plot
* Randomly distributed
** Systematically patterned

	A	B	C	P	S.E.(%)	Sum	Residual
Isotherms at 25.0°C (Treatment B)							
1st A/D Cycle							
Adsorption	1.2228	2.4253	31.716	2.72	0.73	0.047	S.P.
Desorption	1.1554	2.9932	97.146	0.66	0.21	0.014	R.D.
2nd A/D Cycle							
Adsorption	1.2655	3.3846	90.628	0.98	0.29	0.016	R.D.
Desorption	1.2734	3.8842	280.71	0.88	0.24	0.013	R.D.
3rd A/D Cycle							
Adsorption	1.1259	2.5754	45.683	1.08	0.29	0.022	R.D.
Desorption	1.2205	3.5902	221.24	1.45	0.37	0.028	R.D.
5th A/D Cycle							
Adsorption	1.1906	2.9957	68.675	0.86	0.23	0.013	R.D.
Desorption	1.3304	4.2369	412.83	0.88	0.25	0.014	R.D.
Isotherms at 40.0°C (Treatment C)							
1st A/D Cycle							
Adsorption	1.1642	2.7211	42.847	2.27	0.52	0.008	R.D.
Desorption	1.1357	2.4905	33.461	1.34	0.36	0.012	R.D.
3rd A/D Cycle							
Adsorption	1.1146	2.2347	22.147	3.88	0.64	0.011	S.P.
Desorption	1.1139	2.2367	23.205	0.85	0.26	0.018	R.D.
5th A/D Cycle							
Adsorption	1.0570	1.9919	19.975	0.81	0.21	0.028	R.D.
Desorption	1.0361	1.8312	17.121	1.12	0.32	0.020	R.D.

Appendix C: Section I-A (Cont.)

	A	B	C	P	S.E.(%)	Sum	Residual
Isotherms at 3.5°C (Treatment D)							
1st A/D Cycle							
Adsorption	1.0709	2.3151	36.017	1.67	0.44	0.024	R.D.
Desorption	1.0944	2.6708	77.691	3.54	0.97	0.053	S.P.
3rd A/D Cycle							
Adsorption	1.0036	1.6518	14.629	4.67	0.57	0.043	S.P.
Desorption	0.9627	1.2801	10.990	2.71	0.40	0.030	R.D.
5th A/D Cycle							
Adsorption	1.0540	2.0746	22.756	2.08	0.41	0.022	R.D.
Desorption	1.0718	2.4187	47.545	2.29	0.52	0.028	R.D.
Isotherms at 6.0°C							
1st A/D Cycle							
Adsorption	0.9938	2.0088	28.038	1.33	0.52	0.018	S.P.
Desorption	1.1640	3.9531	533.45	2.59	0.92	0.032	S.P.
Isotherms at 15.0°C							
1st A/D Cycle							
Adsorption	1.0633	2.4296	48.587	1.89	0.47	0.026	S.P.
Desorption	0.7269	-0.5834	2.3017	2.47	0.56	0.031	S.P.
Isotherms at 35.0°C							
1st A/D Cycle							
Adsorption	1.1838	3.1860	93.213	1.51	0.39	0.021	R.D.
Desorption	1.1990	3.4266	146.64	1.99	0.50	0.027	R.D.
Isotherms at 45.0°C							
1st A/D Cycle							
Adsorption	1.1175	2.2611	21.686	0.80	0.20	0.013	R.D.
Adsorption	1.0695	1.8984	15.022	1.22	0.26	0.017	R.D.

Appendix C: Section I-B

Estimated parameters and goodness-of-fit criteria for the isotherms of various canola (rapeseed) varieties available in literature as fitted to the emipirical isotherm equation proposed in this study

		A	B	C	P	S.E.(%)	Sum	Residual
Variety Candle, Henderson and Pixton (1981)								
5°C -	Adsorption	1.0224	2.0276	28.483	0.09	0.04	0.003	R.D.
	Desorption	1.0328	2.2693	47.488	0.20	0.07	0.004	R.D.
15°C -	Adsorption	1.0114	1.8872	22.150	0.18	0.08	0.005	R.D.
	Desorption	0.9722	1.5403	16.028	1.62	0.36	0.027	S.P.
25°C -	Adsorption	1.0107	1.8609	20.108	0.18	0.08	0.005	R.D.
	Desorption	0.9850	1.6323	16.152	1.14	0.26	0.020	S.P.
35°C -	Adsorption	1.0173	1.9119	20.010	0.24	0.09	0.006	R.D.
	Desorption	0.9943	1.6685	14.852	0.55	0.14	0.010	S.P.
Variety Tobin, Sokhansanj et al. (1986)*								
5°C		0.9907	1.8311	33.257	2.30	0.51	0.028	S.P.
10°C		0.9364	1.1154	9.6936	2.17	0.74	0.041	R.D.
15°C		0.9735	1.4724	16.080	3.72	0.87	0.048	S.P.
20°C		0.9398	1.1219	9.5932	1.68	0.60	0.033	R.D.
25°C		1.0473	2.4758	61.797	0.23	0.12	0.005	R.D.
Variety Global, Otten et al. (1990)*								
25°C		0.8792	0.9740	13.667	2.21	0.40	0.014	R.D.
50°C		0.9689	1.3525	10.342	3.32	0.52	0.018	R.D.
75°C		1.1119	1.8034	6.5356	10.2	1.49	0.052	R.D.
Variety Westar, X-Sample, Bielewicz (1991)								
25.0°C -	Adsorption	1.0900	1.9482	13.749	4.41	0.51	0.06	R.D.
	Desorption	1.1976	3.0042	65.902	4.27	0.60	0.07	S.P.

* Isotherms consisted of the mixture of adsorption and desorption EMC data

Appendix C: Section II-A

Estimated parameters and goodness-of-fit criteria for the isotherms of Westar canola measured in this study as fitted to the Halsey isotherm equation

	B	C	P	S.E.(%)	Sum	Residual
Isotherms at 25.0°C (Treatment A)						
1st A/D Cycle						
Adsorption	2.2097	56.213	8.86	1.20	0.066	S.P.
Desorption	2.2123	60.602	9.39	1.31	0.072	S.P.
2nd A/D Cycle						
Adsorption	2.0205	36.362	3.98	0.74	0.041	S.P.
Desorption	2.0185	38.325	3.68	0.67	0.037	S.P.
3rd A/D Cycle						
Adsorption	1.9875	35.567	9.71	1.22	0.067	S.P.
Desorption	2.0194	40.716	7.46	1.02	0.056	S.P.
4th A/D Cycle						
Adsorption	1.8926	27.823	7.17	0.90	0.050	S.P.
Desorption	1.9707	35.515	4.85	0.71	0.039	S.P.
5th A/D Cycle						
Adsorption	1.8333	24.440	8.06	1.19	0.065	R.D.
Desorption	1.8643	27.868	6.92	1.06	0.058	R.D.
Isotherms at 25.0°C (Treatment B)						
1st A/D Cycle						
Adsorption	1.4169	10.372	3.81	0.93	0.060	S.P.
Desorption	1.6315	18.896	2.76	0.70	0.045	S.P.
2nd A/D Cycle						
Adsorption	1.5231	12.900	1.69	0.49	0.027	S.P.
Desorption	1.8436	28.571	1.43	0.38	0.021	S.P.

Appendix C: Section II-A (Cont.)

	B	C	P	S.E.(%)	Sum	Residual
3rd A/D Cycle						
Adsorption	1.5428	14.296	1.97	0.48	0.036	R.D.
Desorption	1.7361	23.971	2.67	0.64	0.048	R.D.
5th A/D Cycle						
Adsorption	1.6264	16.681	1.82	0.44	0.024	S.P.
Desorption	1.8420	29.215	2.20	0.55	0.030	S.P.
Isotherms at 40.0°C (Treatment C)						
1st A/D Cycle						
Adsorption	1.5679	13.610	2.88	0.67	0.037	R.D.
Desorption	1.5090	12.426	2.29	0.55	0.030	R.D.
3rd A/D Cycle						
Adsorption	1.3554	8.6901	1.15	0.33	0.014	R.D.
Desorption	1.3361	8.6712	1.18	0.38	0.017	R.D.
5th A/D Cycle						
Adsorption	1.5952	13.782	1.18	0.28	0.015	R.D.
Desorption	1.5757	13.460	1.15	0.34	0.019	R.D.
Isotherms at 3.5°C (Treatment D)						
1st A/D Cycle						
Adsorption	1.7442	19.926	3.08	0.73	0.040	R.D.
Desorption	1.8058	28.037	4.81	1.23	0.068	S.P.
3rd A/D Cycle						
Adsorption	1.6930	17.082	7.23	1.24	0.093	R.D.
Desorption	1.6424	17.371	7.87	1.18	0.088	R.D.
5th A/D Cycle						
Adsorption	1.6742	15.552	2.22	0.57	0.032	S.P.
Desorption	1.8373	25.680	2.04	0.70	0.039	S.P.

Appendix C: Section II-A (Cont.)

	B	C	P	S.E.(%)	Sum	Residual
Isotherms at 6.0°C						
1st A/D Cycle						
Adsorption	2.2152	41.487	3.88	1.45	0.050	R.D.
Desorption	2.8702	202.94	2.80	1.01	0.037	S.P.
Isotherms at 15.0°C						
1st A/D Cycle						
Adsorption	1.9551	30.072	1.99	0.48	0.026	R.D.
Desorption	1.9264	30.938	3.39	0.73	0.040	R.D.
Isotherms at 35.0°C						
1st A/D Cycle						
Adsorption	2.0046	31.516	3.72	0.76	0.042	S.P.
Desorption	2.1127	41.867	4.02	0.81	0.044	R.D.
Isotherms at 45.0°C						
1st A/D Cycle						
Adsorption	1.4759	10.492	1.30	0.30	0.019	R.D.
Desorption	1.4168	9.5721	1.37	0.29	0.019	R.D.

Appendix C: Section II-B

Estimated parameters and goodness-of-fit criteria for the isotherms of various canola (rapeseed) varieties available in literature as fitted to the Halsey isotherm equation

		B	C	P	S.E.(%)	Sum	Residual
Variety Candle, Pixton and Henderson (1981)							
5°C -	Adsorption	1.7920	20.997	0.40	0.14	0.009	S.P.
	Desorption	1.9286	30.618	0.59	0.20	0.013	S.P.
15°C -	Adsorption	1.7665	18.953	0.22	0.10	0.006	S.P.
	Desorption	1.7828	20.666	2.12	0.42	0.032	S.P.
35°C -	Adsorption	1.7302	15.830	0.33	0.13	0.008	R.D.
	Desorption	1.7168	15.606	0.58	0.15	0.011	R.D.
Variety Tobin, Sokhansanj et al. (1986)*							
5°C		1.1914	36.512	2.11	0.51	0.028	R.D.
10°C		1.8010	23.440	2.79	0.83	0.046	R.D.
15°C		1.7067	20.818	3.77	0.89	0.049	S.P.
20°C		1.6744	17.572	2.45	0.76	0.042	R.D.
25°C		2.0421	36.842	0.65	0.26	0.012	R.D.
Variety Global, Otten et al. (1990)*							
25°C		1.9657	35.649	6.09	1.27	0.045	S.P.
50°C		1.5571	12.095	5.02	0.63	0.022	S.P.
75°C		1.2227	4.7669	7.81	2.21	0.077	R.D.
Variety Westar, X-Sample, Bielewicz (1991)							
25.0°C -	Adsorption	1.4087	9.1210	4.59	0.61	0.070	S.P.
	Desorption	1.6963	19.545	6.86	0.79	0.091	S.P.

* Isotherms consisted of the mixture of adsorption and desorption EMC data