

**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
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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 hydrophilic and hydrophobic interaction between water molecules and lipid and protein particles forming a lipid-protein complex typical of rapeseed (canola) and other oil seeds.

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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} - Isostatic 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, $i=1, 2, \dots, n$

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 Pfof 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 Pfoest (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 Isotheric Heat of Sorption

The isotheric 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 6×10^{-3} mol/g.

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

$$dE = TdS - PdV + \mu_1 dN_1 + \mu_a dN_a \quad (1)$$

$$dF = -SdT + VdP + \mu_1 dN_1 + \mu_a dN_a \quad (2)$$

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

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:

$$-\bar{S}_1 dT + \bar{V}_1 dP = -s_G dT + v_G dp \quad (4)$$

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

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

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

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

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

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

Eq.(6) can accordingly be reshaped as:

$$\left[\frac{d \ln p}{d(1/T)} \right]_T = - \frac{(h_G - \bar{H}_1)}{R} = - \frac{Q_{st}}{R} \quad (7)$$

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:

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

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:

$$\ln P = (L/L') \ln P' + C \quad (9)$$

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.