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The Study on the Application Equation for the Vaporization Heat of Water in Agricultural Products[1]

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Abstract : The heat of vaporization of water in agricultural products is an important factor to design the drying equipment. The thermal properties can be calculated by an equation that derived easily form ERH/EMC equation by the Clausius-Claperton thermodynamic theory. The modified-Oswin equation can serve as the good model to obtain the heat of vaporization of corn kernel, rough rice and soybeans. The empirical model derived from the Othmer method gives the larger deviation.

Key words : Heat of vaporization, ERH model, Modified-Oswin equation.

INTRODUCTION

Drying processing is required for many agricultural products to maintain the good quality. Therefore, the vaporization heat of water (also be called latent heat of vaporization, heat of desorption, desorption-vaporization, notes as Q values) in agricultural products is of practical interest in drying operation. The value of vaporization is neither constant nor equal to the heat of evaporization of pure water. It is a function of temperature and moisture content, that is, the value is varied throughout drying processing. A simple model including moisture content and temperature term is very useful to compute the vaporization heat. This mathematical model also provide a good qualititative standard on the simulation work.

The purpose of this study is : (a) to review the methods of computing heat of vaporization that already reported in literature : (b) to compare the effect of ERH/EMC model on the properties : (c) to compare the computed values by different method.

LITERATURE REVIEW

The methods to compute the heat of vaporization for agricultural products are reported as following:

A. The direct calorimetric measurement

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This technique measured the heat of vaporization directly and have the higher degree of accuracy when determined with careful. However, the technique needs to measure small quantities of heat evolvod precisely. By this reason, calorimetrical measured heat of sorption are much less common than those computed from sorption data. This measurement mostly only be adopted on isolated food components (Bettelheim, 1970).

B. The calculation by BET equation

According the BET theory that proposed by Brunnauer, Emmett, and Teller(1938), the BET model includes two important parameters in food drying and storage.

In this model

$$\frac{Aw}{(1-Aw)}=\frac{1}{CMo}+\frac{(C-1)Aw}{CMo} \quad \cdots\cdots(1)$$

Where

Aw : Water activity of food

M : Equilibrium moisture content

Mo : Monolayer value

C : BET costant

and

$$C : Exp(Ef-Ec)/RT_a \quad \cdots\cdots(2)$$

Ta : Temp. °k

R the is gas constant, Ef and Ec are the heat of sorption in the first layer and the heat of condensation of the adsorbate. The difference between Ef and Ec are assumed as the heat of vaporization. After cheacking thirty-five cases, Iglesias and Chirife (1976) found that the BET heats are much lower than the values obtained by the Clausius-Clayperton heats (introducing in follow section). The same results are found by Aguerce and Viollaz (1983) on the study of the desorption heat of rough rice. The BET model is only valid in the lower RH range, so the BET heats are not considered in this study.

C. The Othmer equation

The relationship between Ps (saturated water vapor pressure) and the Pv (vapor pressure of water in agricultural product) was given by Othmer (1940) as :

$$\text{In } Pv=Q*InPs/X+\text{constant} \quad \cdots\cdots(3)$$

Where X : the heat of evaporization for pure water

Q : the heat of evaporization of agricultural product

This model assumed the Q/X value was independent of temperature.

From the linear regression analysis technique, the slope, Q, can be found from ln (pv) and ln (Ps) data. The relationship of Q and temperature, moisture content then be found by another regression technique. This method has been adopted by many researchers. Wang (1978) proposed the form of Q (heat of vaporization) for rough rice.

$$Q=(a-b*T)*M^c \quad \cdots\cdots(4)$$

T : Temp. °C

Thompson and Shedd (1954) presented an equation for the Q value of shelled corn by this least square procedure fron EMC data.

Their model was :

$$Q=(1094-0.57*T)(1+4.35*\mathrm{Exp}(-0.2825*M)) \quad \cdots\cdots(7)$$

The Unit of Q is KJ/kg.

Brook and Foster (1979) developed an equation for the Q value of rough rice :

$$Q=2.32*[1094-1.026*(T_f+17.78)]*[1+2.4962*\mathrm{Exp}(-0.2173*M)]$$

T_f=Temp. °F $\cdots\cdots(8)$

The unit of Q is Btu/lb.

Fon (1988) mention an Islam-Jindal model to calculate the Q value of rough rice.

$$L=a*(597.3-0.559*T) \quad \cdots\cdots(9)$$

$$a=1.315-0.0156*M+6.81E-5*M^2+3.836E-6*M^3 \quad \cdots\cdots(10)$$

The units of L is Kcal/kg.

D. The Clausius-Clapeyron equation

There are two methods to calculate the heat of evaporation by the Clausius-clapeyron thermodynamic model.

(a) Graphical method

From the Clausiusus-Claperton equation

$$\frac{\partial \mathrm{InPv}}{\partial(1/Ta)}=-\frac{Q}{R} \quad \cdots\cdots(11)$$

Where Pv : Partial pressure of water in agricultural product

Ta : Absolute temperature, K

R : Gas constant (0.4614 KJ/kg, K)

Q : Heat of vaporization, KJ/kg

By plotting lnPv (or ln Aw) vs. 1/Ta for a given constant grain average moisture content, Q could be computed from the slope of the curve.

(b) Integrated method

Integrating equation (11) for two isotherm temperatures, a new form of Q value is :

$$Q=R\left(\frac{Ta1*Ta2}{Ta1-Ta2}\right)*\mathrm{In}\left(\frac{Aw2}{Aw1}\right) \quad \cdots\cdots(12)$$

This method had to know two sets of isotherm data. Two temperature must closed enough so that the Q value could be applied for both isotherms.

Both method calculated the Q value at a specific moisture content. As the EMC/ERH relationships were estiablished by ERH determination, that is, the Aw data was measured at the constant moisture content, the error existed only in the experimental error. However, if the data sets of isotherm were obtained by tradictional EMC method, researchers need to plot the fitting curve from the scattering data and interporated the data from the plotting curve at the fixed moisture content. The errors of this method included the experimental error in the isotherm data and the graphical manipulation. The estimated error inherent in the process of plotting, curve drawing and interpolation was about 3.5% (Iglesias and Chirife, 1976). This technique is also a time-consuming operation.

E. Deriving from ERH model

The famous Clausius-Claperon thermodynamic model was :

$$\frac{\partial Pv}{\partial Ta}=\frac{Q}{Ta\triangle V}=\frac{Q}{Ta(Vg-Ve)} \quad \cdots\cdots(13)$$

Vg is the volume of gas, Ve is the volume of liquid. Vg is so large that Ve value can be neglected for (Vg−Ve) value.

$$\frac{\partial Pv}{\partial Ta}=\frac{Q}{Ta*Vg} \quad \cdots\cdots(14)$$

From the law of ideal gas, $Vg=R*Ta/Pv$, equation (14) can be writter as :

$$\frac{\partial Pv}{\partial Ta}=\frac{QPv}{R*Ta^2} \quad \cdots\cdots(15)$$

$$\frac{\partial Pv}{Pv\partial Ta}=\frac{\partial In(Pv)}{\partial Ta}=\frac{Q}{R*Ta^2} \quad \cdots\cdots(16)$$

By the definition of Aw,

$Pv=Aw*Ps$, substituting Pv value into equation(16)

$$Q=R*Ta^2*(\frac{\partial In(Aw)}{\partial Ta}+\frac{\partial In(Ps)}{\partial Ta}) \quad \cdots\cdots(17)$$

The second right-hand side term of equation is the heat of vaporization of pure water (X),

$$\text{so } X=R*Ta^2*\frac{\partial In(Ps)}{\partial Ta} \quad \cdots\cdots(18)$$

$$Q=R*Ta^2*\frac{\partial In(Aw)}{\partial Ta}+X \quad \cdots\cdots(19)$$

The similar results can be found for Zuritz and Singh (1985), Balaban et al. (1987), and Murata et al. (1988).

An Aw model can be substituted into equation (19) to obtain the Q value at different moisture content and temperature. Zuritz and Singh (1985) used this technique to find the Q value of rough rice. Three ERH models are adopted. The Day and Nelson equation, Chen-Clayton equation, and their new modified Henderson equation.

Balaban et al. (1987) estimated the heat of evaporation of some foods by same method. Four ERH/EMC models are selected to represent the relationhship among EMC, ERH and temperature. Murata et al. (1988) used the same method to calculate the thermal properties of five grains. They selected the Chen-Clayton equation as the best ERH/EMC model. However, the effect of inadequate model on the properties did not be metioned by researchers.

Hunter (1989) derived a similar equation with differental approuch to calculate the heat of sorption of Australian paddy rice.

From the ASHRAE handbook, Ps is the function of temperature,

$$Ps=Exp(54.63-6877/T-5.31*lnT) \quad \cdots\cdots(20)$$

T=Temp. °C

The Q values of pure water (X) is :

$$X=R*(6887-5.31*T) \quad \cdots\cdots(21)$$

Four ERH/EMC models incoperating temperature terms have been evaluated for sorption data of many agricultural products (Chen, 1988). These equations are adopted in this study to compute the Q value.

A. The Modified-Henderson equation

$$Aw=1-Exp(-A(T+C)*M^{b}) \quad \cdots\cdots (22)$$

Where Aw : water activity or ERH value (decimal)

M : m.c. in dry basis (%)

T : Temperature (°C)

A, b and C are constant.

Introducing equation (22) into equation (19),

$$Q=R*Ta^{2}*\frac{A*M^{b}*Exp[-A(T+C)*M^{b}]}{1-Exp[-A(T+C)M^{b}]}+X \quad \cdots\cdots (23)$$

B. The Chung-Pfost equation

$$Aw=Exp\left[-\frac{A}{T+C}Exp(-BM)\right] \quad \cdots\cdots (24)$$

$$Q=R\cdot Ta^{2}\left[\frac{A}{(T+C)^{2}}Exp(-BM)\right]+X \quad \cdots\cdots (25)$$

C. The Modified-Halsey equation

$$Aw=Exp(-Exp[A+B*T]*M^{-c}) \quad \cdots\cdots (26)$$

$$Q=Aw*Exp[A+B*T]*M^{-c}*B+X \quad \cdots\cdots (27)$$

D. The Modified-Oswin equation

$$Aw=\frac{1}{(\frac{A+B\cdot T}{M})^{c}+1} \quad \cdots\cdots (28)$$

$$Q=\frac{\frac{-RT^{2}B*C\left[\frac{A+B*T}{M}\right]^{c-1}}{M}}{(\frac{A+B*T}{M})^{c}+1}+X \quad \cdots\cdots (29)$$

The heat of vaporization calculted from equation (23), (25), (27), and (29) are compared with these computed from equation (12) to check the effect of fitting-agreement of ERH models on Q values.

MATERIALS AND METHODS

Isotherm data used in this study were introduced as following :

1. Rough rice (Tainun No. 67): Determined by Chen, Chou, and Tsao (1990) with hygrometric method.
2. Rough rice (U.S.A): Determined by Zuritz and Singh (1979) with gravimetric method.
3. Corn kernel : Determined by Chen (1988) with hygrometric method.
4. Corn cob : Determined by White et al. (1985) with hygrometric method.
5. Soybeans : Determined by Alam (1972) with gravimetric method.
6. Black tea : Determined by Yoshitomi (1985) with gravimetric method.
7. Oolong tea : Determined by Chen, Chou, and Tsao (1990) by hygrometric method.

8. Fench tea : Ddtermined by Wolf et al. (1973) with gravimetric method.

RESULTS AND DISCUSSIONS

To compare the effect of ERH model on heat of vaporization of corn kernel, the computed values from four ERH models and Thompson-Shedd equation are listed in Table 1 and showed in Figure 1. The Q values that calculated by equation (12) are scattered in Fig. 1. to check the fitting-agreement of the calculated values.

In Fig. 1, the Q values that computed from the Modified-Henderson equation and Modified-Oswin equation give the good fitting performance with scattering data. These values obtained from the Chung-Pfost equation were too low in the m.c. range of

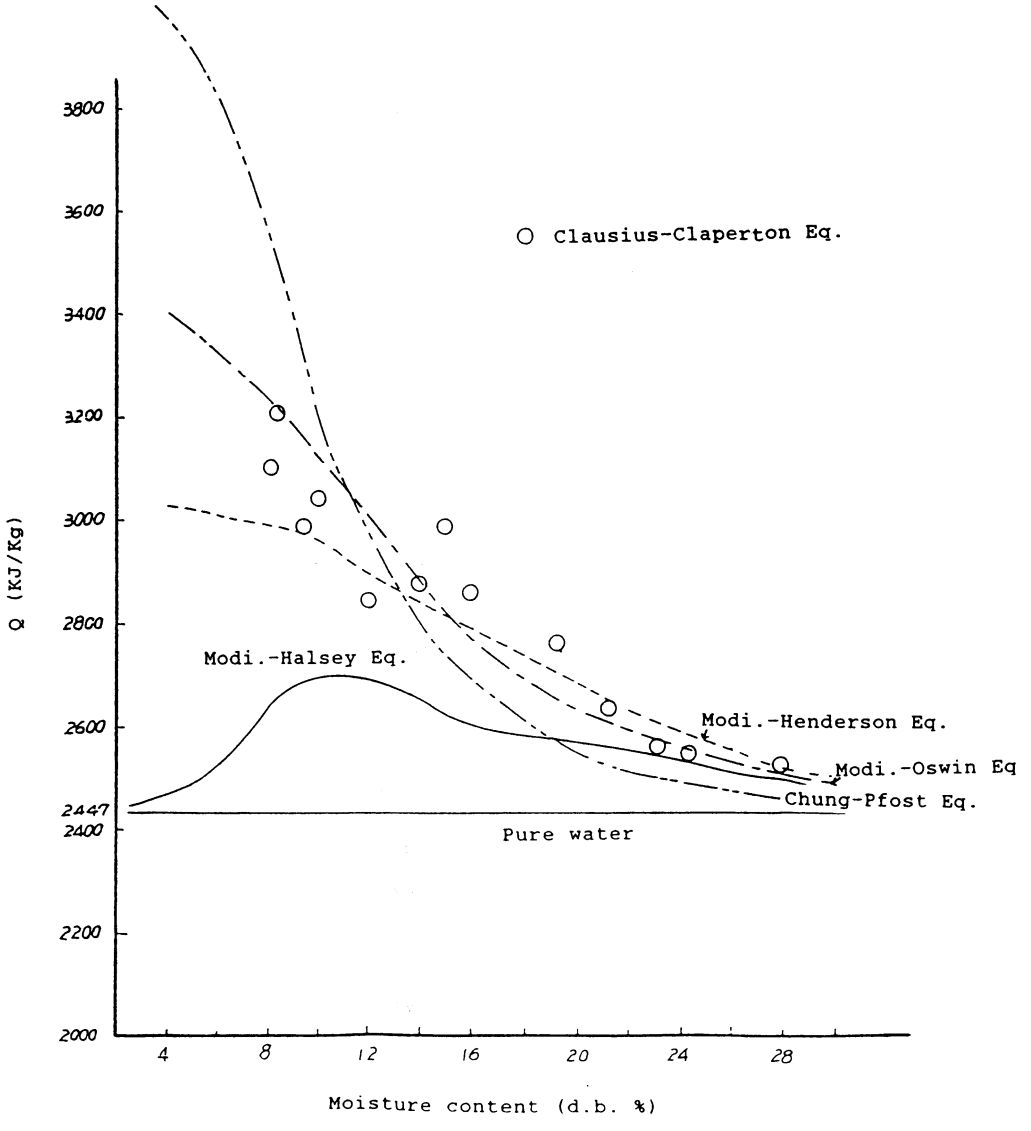


Figure 1. Heat of vaporization for corn kernel at 25°C

above 14% and too high below the m.c. range of 14%. The Q values obtained from the Modified-Halsey equation always lower than those calculated from equation (12). Chen (1988) had reported the Modified-Henderson and Modified-Oswin equation were the adequate models for the specific variety of corn kernel. This results suggested the important to use the adequate ERH model to calculated the Q values.

The Q values calculated from Thompson-Shedd equation were too high at low m.c. in Table 1.

Table 1. Q values computed with four ERH models for corn kernel

Temp (°C)	m.c. (%,d.b)	Modified -Henderson	Chung -Pfost	Modified -Oswin	Modified -Halsey	Thompson and Shedd
5 X=2,496	4	3,235	7,200	3,228	2,496	5,990
	6	3,214	5,735	3,197	2,524	4,565
	10	3,148	4,031	3,086	2,698	3,192
	16	3,009	2,998	2,825	2,684	2,658
	20	2,902	2,734	2,709	2,638	2,577
	26	2,747	2,573	2,610	2,588	2,545
	30	2,662	2,533	2,574	2,566	2,541
25 X=2,447	4	3,037	4,711	3,412	2,449	5,928
	6	3,012	4,006	3,350	2,533	4,517
	10	2,940	3,186	3,120	2,700	3,159
	16	2,793	2,688	2,779	2,627	2,630
	20	2,690	2,561	2,650	2,575	2,550
	26	2,564	2,484	2,550	2,527	2,519
	30	2,509	2,464	2,517	2,507	2,514
45 X=2,398	4	2,910	3,807	3,681	2,413	5,865
	6	2,883	3,368	3,547	2,575	4,469
	10	2,802	2,858	3,142	2,678	3,126
	16	2,650	2,548	2,706	2,561	2,062
	20	2,554	2,469	2,574	2,509	2,523
	26	2,455	2,421	2,483	2,465	2,492
	30	2,422	2,409	2,455	2,449	2,487

The Q value of rough rice calculated fron four ERH models are showed in Fig. 2. The curve of Q values obtained from the Modified-Oswin equation had the best fitting performance with the scattering data calculated from Eq. (12). Chen et al. (1990) found this ERH model is the only adequate model to represent the relationships among ERH, EMC, and temperature of rough rice. This results also indicated the effect of ERH model on the Q values.

Four sets of Q values of rough rice from difference or method are listed in Table 2. Some differences exist between the Q values from two sources (Zuritz et al., 1979 and Chen et al., 1990). Q values are affected by various factors.

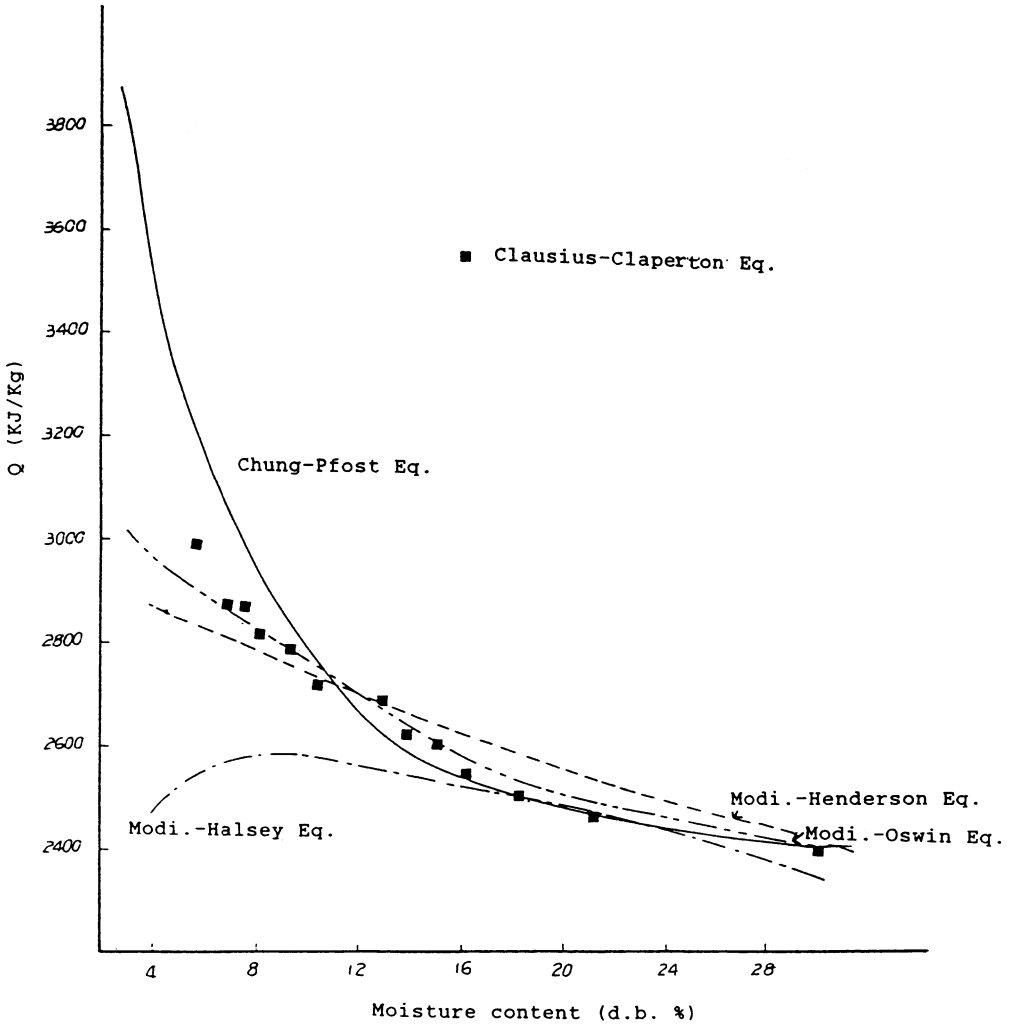


Figure 2. Heat of vaporization for rough rice at 25°C

Table 2. Comparing the computed Q value of rough rice at 25°C

	data source			
m.c. (%,d.b)	Zuritz	Chen	Brook and Foster equation	Islam and Jindal
4	3,212	2,969	4,986	2,622
6	3,185	2,907	4,087	2,618
10	3,090	2,739	3,128	2,610
14	2,951	2,611	2,726	2,603
16	2,871	2,570	2,624	2,600
20	2,711	2,520	2,515	2,595
24	2,583	2,492	2,470	2,590
26	2,536	2,483	2,458	2,588
30	2,478	2,471	2,445	2,586

The Q values obtained from the Brook-Foster equation were too high at low m.c. range. The Islam-Jindal equation gave very low values. This results showed that the Qs model derived fron the Othmer method were inadequately.

The Q values of Soybeans from four ERH models and equation (12) are showed in Figure 3. Chen (1988) reported the Modified-Halsey equation and the Modified-Oswin equation can be accepted as the good models for ERH/EMC properties. However, the Q values calculated from the Modified-Halsey equation is too low. The results can be explained from the structure of the model. From the mathematic form of equation (26), it is meaningless for the moisture content as ERH apporaching zero, that is, the Modified-Halsey equation cannot describe the ERH/EMC properties at very low m.c. value or ERH value. The Modified-Oswin equation was the only adequate model to calculate the Q values of all RH range.

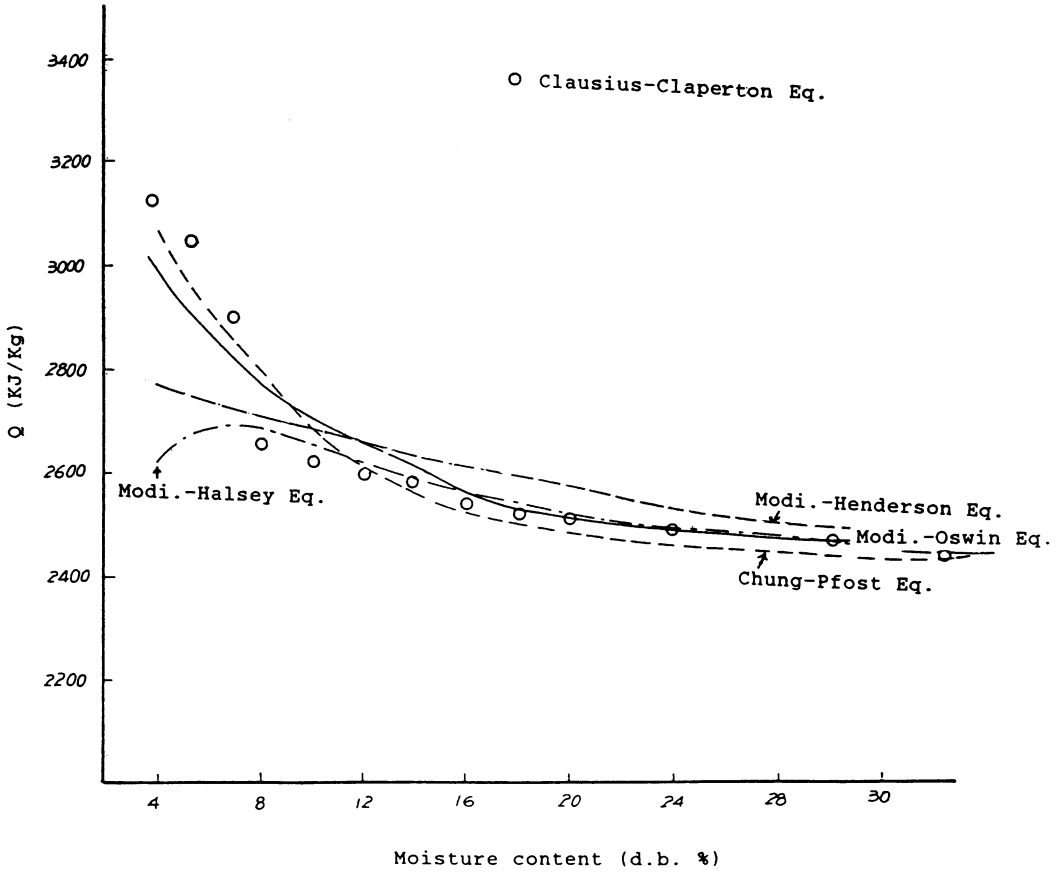


Figure 3. Heat of vaporization for soybeans at 25°C

The Q values for three tea products are showed in Figure 4. The Black tea had the highest heat of vaporization at the same moisture content. The results indicated the Q values were affected by different processing method or variety.

The comparison of Q values for five agricultural products are showed in Figure 5. The ranks of Q values are : Corn kernel > Rough rice > Corn cob > Soybeans > Tea. The heat of evaporization of starchy grains and fibrous is higher than those of high oil and protein products at the same moisture content.

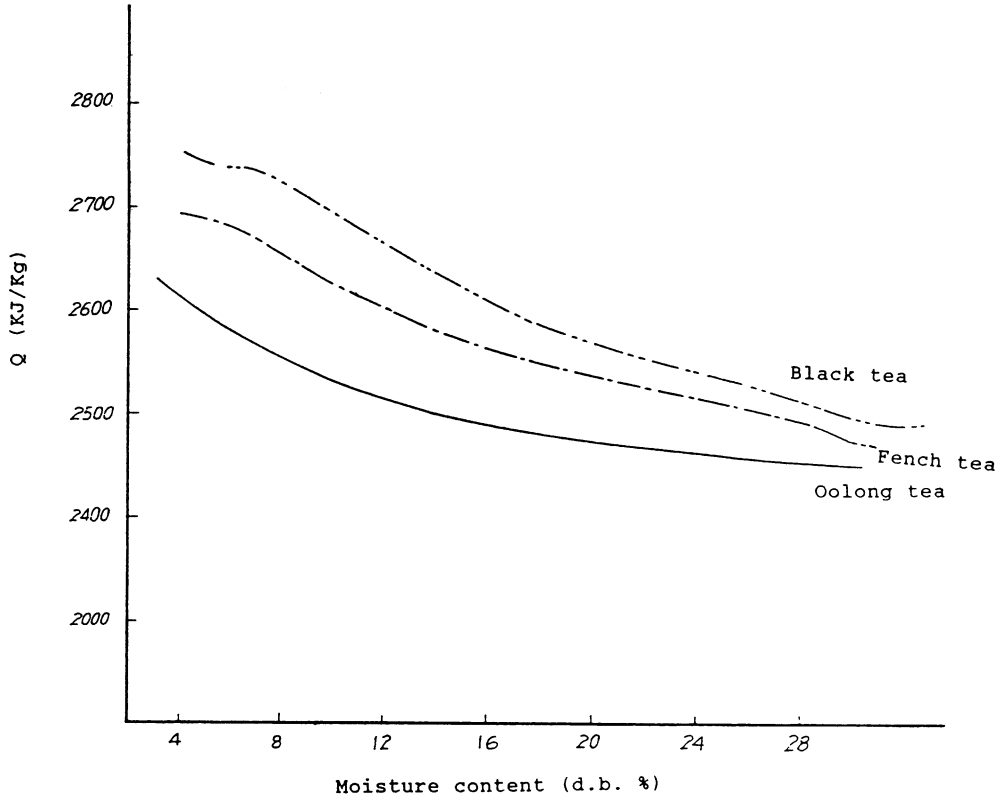


Figure 4. Heat of vaporization for tea at 25°C

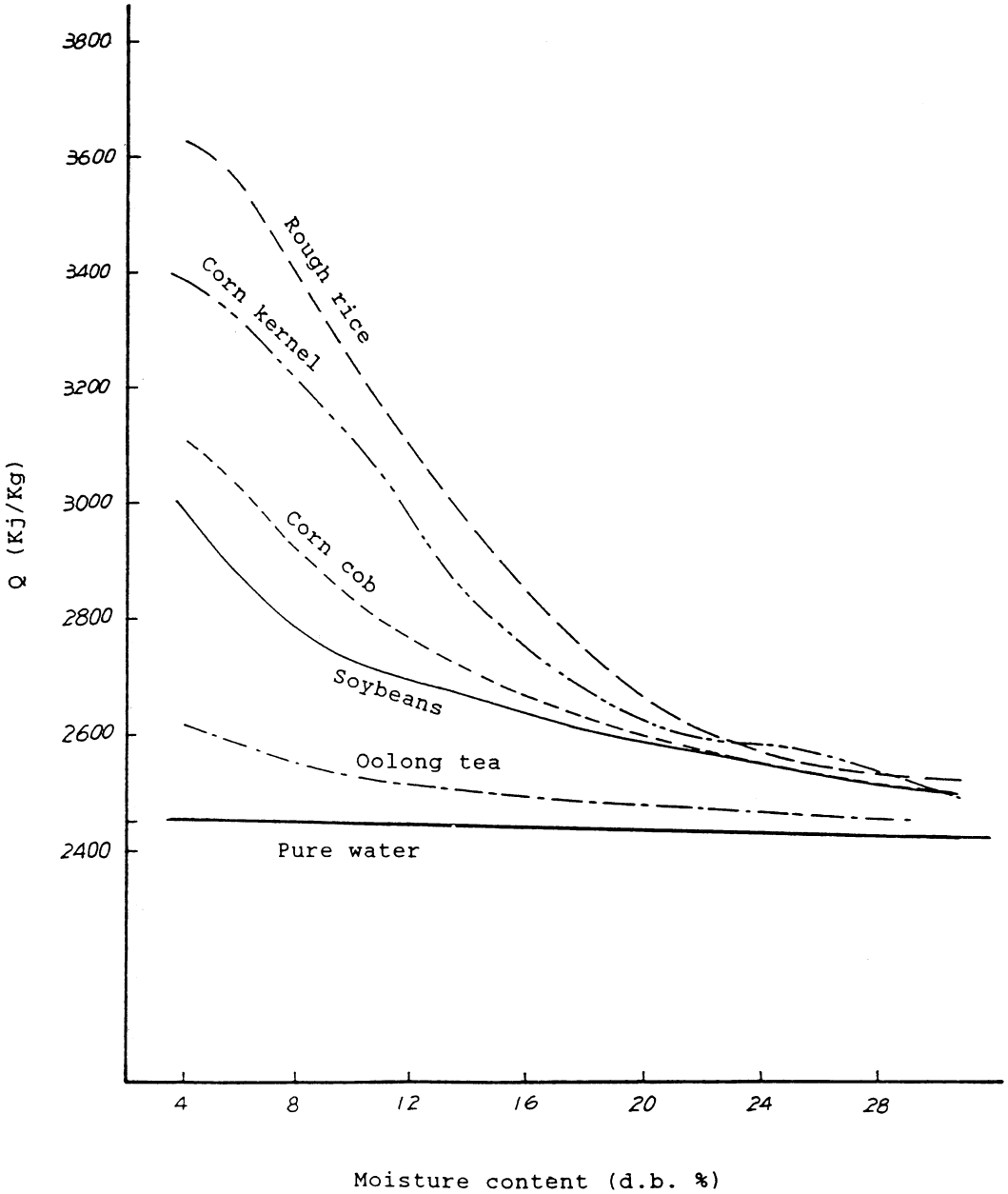


Figure 5. Heat of vaporization for five agricultural products at 25°C

CONCLUSIONS

1. An equation of heat of evaporation can be derived easily from the ERH/EMC model by the Clausius -Clapeyron theory.
2. The fitting performance of the ERH/EMC equation affects the values of heat of evaporization. The Modified-Oswin equation is the good model to evaluate the heat of evaporization of water in corn kernel, rough rice, and soybeans.
3. The empirial model obtained from the Othmer method did not give the satisfactory result.

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農產品水份蒸發熱之應用模式研究[1]

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摘　要

農產品內部水份蒸發熱物性在乾燥設備之設計上十分重要。在此研究中，由 Clausius-Clapert-ton 熱力動力學原理可自平衡相對濕度模式推衍一簡易應用模式以計算此熱學物性。由修正歐思文模式推導所得的計算公式可應用於玉米粒，稻穀和大豆此項物性之計算。由 Othmer 方法所得的經驗公式存有極大的誤差。

關鍵詞：水份蒸發熱，平衡相對濕度模式，修正歐思文公式。

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