Advancement in fruit drying through the analysis of moisture sorption isotherms: processing effects on Australian native fruits in comparison to apple

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Appendix 1: Additional Moisture Sorption Isotherms

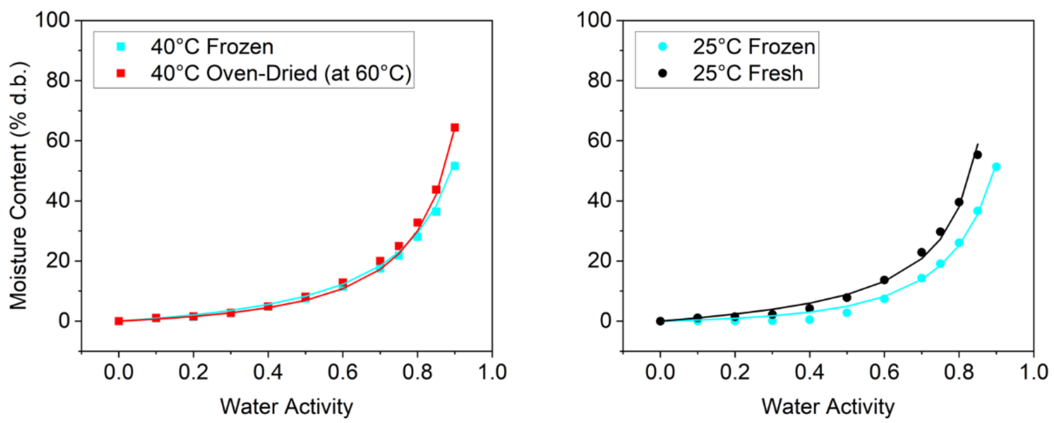

Figure S1: Select desorption isotherms of frozen and oven-dried (dried at 60°C) finger lime measured at 40°C (left); frozen and fresh muntrie measured at 25°C - data (▪) and GAB fit (–)

Appendix 2: Intermediate Moisture Sorption Isotherm Fitting Values

The scripts written to fit isotherm models to the moisture sorption isotherms as well as the net isosteric heat of sorption can be downloaded from the GitHub repository https://github.com/paulmichalski1/Moisture-Sorption-Fitting.git

Table S1: Several models' performance for one sample (the 60°C desorption isotherm of frozen muntries).

Model	Parameters			*SSE*
Oswin	*k*	*n*		
$M = k\left(\frac{a_w}{1-a_w}\right)^n$	0.1133	0.8175		6.7348×10^{-4}
BET	M_0	*c*		
$M = \frac{M_0 c a_w}{(1-a_w)+(c-1)(1-a_w)a_w}$	0.0765	2.6328		0.0015
GAB	M_0	*K*	*C*	
$M = \frac{M_0 K C a_w}{(1-Ka_w)(1+(C-1)Ka_w)}$	0.1608	0.8862	0.7612	7.8804×10^{-5}
Halsey	*k*	*n*		
$M = \left(-\frac{k}{\ln(a_w)}\right)^{\frac{1}{n}}$	0.0772	1.0043		0.0024
Chen	*k*	*c*	*b*	
$M = -\frac{1}{b}\ln\left(\frac{k - ln(a_w)}{c}\right)$	-0.1356	1.8546	9.1267	0.0039
Chung-Pfost	*k*	*c*		
$M = -\frac{1}{c}\ln\left(-\frac{RT}{k}ln(a_w)\right)$	4226.4	6.0432		0.0152
Henderson	*k*	*n*		
$M = \left(-\frac{\ln(1-a_w)}{kT}\right)^{\frac{1}{n}}$	0.0100	0.7082		2.7406×10^{-4}
Caurie	M_0	*C*		
$\frac{1}{M} = \frac{2}{M_0 C}\left(\frac{1-a_w}{a_w}\right)^{\frac{2C}{M_0}}$	0.7447	0.3044		6.7348×10^{-4}
Sips	K_s	*N*	*C*	
$M = \frac{K_s a_w^N}{1 + C a_w^N}$	0.1313	1.0659	-0.9020	9.7055×10^{-5}
Iglesias-Chirife	*k*	*c*		
$\ln\left(M + (M^2 + M_{0.5})^{\frac{1}{2}}\right) = ka_w + c$	1.3964	-1.3318		0.0889

Table S2: GAB fitting parameters

	Apple		Muntrie		Finger Lime	
	Frozen	Dried	Frozen	Dried	Frozen	Dried
M_0 (% d.b.)	9.67 [a] 10.04 [c]	11.81 [a] 15.58 [c]	7.09 [a] 10.62 [b] 9.66 [c]	13.89 [a] 24.60 [b] 21.62 [c]	13.81 [a] 12.37 [b] 11.53 [c]	7.37 [a] 10.59 [b] 10.46 [c]
K_0 (-)	0.9050	0.5483	0.8102	0.8839	0.9325	0.8180
C_0 (-)	1.887	0.6994	0.7379	0.2790	0.3401	0.5877
H_n -H_m (J/mol)	0.0345	0.1247	0.0034	0.0429	0.0552	0.3174
H_l -H_n (J/mol)	181.3	134.3	498.1	107.0	26.9	427.6
SSE	0.0167	0.0050	0.0098	0.0141	0.0075	0.0068
χ_v^2	0.0629	0.1162	0.0897	0.4211	0.0533	0.1573

[a] 25°C; [b] 40°C; [c] 60°C

Appendix 3: Detailed Derivation of Equation (6)

From the definition of the GAB model as outlined in equations (1),

$$M = \frac{M_0 K C a_w}{(1 - K a_w)(1 + (C - 1) K a_w)} \tag{1}$$

Where C and K follow the Arrhenius-type temperature relationship given by equations (2) and (3), grouping the differences in enthalpies for convenience

$$K = K_0 e^{\frac{H_l - H_n}{RT}} = K_0 e^{\frac{\Delta H_K}{RT}} \tag{2}$$

$$C = C_0 e^{\frac{H_n - H_m}{RT}} = C_0 e^{\frac{\Delta H_C}{RT}} \tag{3}$$

The derivatives of these constants with respect to reciprocal temperature are therefore

$$\frac{dK}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_K}{R} K$$

$$\frac{dC}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_C}{R} C$$

Multiplying equation (1) by the denominator of the right-hand-side and expanding yields equation

$$M(1 + K(C - 2)a_w + K^2(1 - C)a_w^2) = M_0 K C a_w \tag{1}$$

Solving equation (10) for a_w produces equation (11)

$$a_w = \frac{-(M(C-2) - M_0C) \pm \sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}}{2MK(1-C)} \tag{2}$$

Since the negative root is the one that recreates the isotherm shape, the positive one is discarded, leaving

$$a_w = \frac{M(C-2) - M_0C + \sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}}{2MK(C-1)}$$

From the Clausius-Clapeyron equation (4) and assuming:

- Negligible effects of temperature on the latent heat of vapourisation and on any excess energy required when water is bound to liberate it;
- Water vapour follows the ideal gas equation of state; and
- The specific volume of the bulk water is far greater than that of any adsorbed water;

Then the net isosteric heat of sorption q_{st} is

$$q_{st}(M) = R\left(\frac{\partial \ln a_w}{\partial\left(\frac{1}{T}\right)}\right)_M$$

Defining proxy variables *u* and *v* to simplify the calculation:

$$u \equiv M(C-2) - M_0C + \sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}$$

$$v \equiv 2MK(C-1)$$

So that

$$a_w = \frac{u}{v}$$

The derivative in (4) then becomes

$$\frac{\partial \ln a_w}{\partial\left(\frac{1}{T}\right)} = \frac{v}{u}\left(\frac{\frac{\partial u}{\partial\left(\frac{1}{T}\right)}v - \frac{\partial v}{\partial\left(\frac{1}{T}\right)}u}{v^2}\right)$$

$$= \frac{\frac{\partial u}{\partial\left(\frac{1}{T}\right)}v - \frac{\partial v}{\partial\left(\frac{1}{T}\right)}u}{uv}$$

The partial derivatives of *u* and *v* with respect to reciprocal temperature can then be found

$$\frac{\partial u}{\partial\left(\frac{1}{T}\right)} = M\frac{dC}{d\left(\frac{1}{T}\right)} - C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{dC}{d\left(\frac{1}{T}\right)} + \frac{2(M(C-2)-M_0C)\left(M\frac{dC}{d\left(\frac{1}{T}\right)} - C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{dC}{d\left(\frac{1}{T}\right)}\right) + 4M^2\frac{dC}{d\left(\frac{1}{T}\right)}}{2\sqrt{(M(C-2)-M_0C)^2 - 4M^2(1-C)}}$$

$$\frac{\partial u}{\partial\left(\frac{1}{T}\right)} = M\frac{\Delta H_C}{R}C - C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{\Delta H_C}{R}C + \frac{(M(C-2)-M_0C)\left(M\frac{\Delta H_C}{R}C - C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{\Delta H_C}{R}C\right) + 2M^2\frac{\Delta H_C}{R}C}{\sqrt{(M(C-2)-M_0C)^2 - 4M^2(1-C)}}$$

$$\frac{\partial v}{\partial\left(\frac{1}{T}\right)} = 2M\left(\frac{\partial K}{\partial\left(\frac{1}{T}\right)}(C-1) + \frac{\partial C}{\partial\left(\frac{1}{T}\right)}K\right)$$

$$\frac{\partial v}{\partial\left(\frac{1}{T}\right)} = 2M\left(\frac{\Delta H_K}{R}K(C-1) + \frac{\Delta H_C}{R}CK\right)$$

$$\frac{\partial v}{\partial\left(\frac{1}{T}\right)} = 2MK\left(\frac{\Delta H_K}{R}(C-1) + \frac{\Delta H_C}{R}C\right)$$

Substitution of u, v, and their partial derivatives with respect to reciprocal temperature into (4) yields

$$q_{st}(M) = \frac{R}{\left(M(C-2) - M_0C + \sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}\,\right)2MK(C-1)}\Bigg(\Bigg(\Bigg(M\frac{\Delta H_C}{R}C$$

$$- C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{\Delta H_C}{R}C$$

$$+ \frac{(M(C-2) - M_0C)\left(M\frac{\Delta H_C}{R}C - C\frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{\Delta H_C}{R}C\right) + 2M^2\frac{\Delta H_C}{R}C}{\sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}}\Bigg)2MK(C$$

$$-1)$$

$$- 2MK\left(\frac{\Delta H_K}{R}(C-1) + \frac{\Delta H_C}{R}C\right)\Big(M(C-2) - M_0C$$

$$+ \sqrt{(M(C-2) - M_0C)^2 - 4M^2(1-C)}\Big)\Bigg)$$

After cancellations, grouping, and substitutions of ζ and Ψ for simplicity using the definitions

$$\zeta \equiv M(C-2) - M_0C$$

$$\Psi \equiv M\frac{\Delta H_C}{R} - \frac{dM_0}{d\left(\frac{1}{T}\right)} - M_0\frac{\Delta H_C}{R}$$

The final expression for q_{st} is

$$q_{st}(M) = R\frac{\left(\Psi + \frac{\zeta\Psi + 2M^2\frac{\Delta H_C}{R}}{\sqrt{\zeta^2 - 4M^2(1-C)}}\right)C(C-1) - \left(\frac{\Delta H_K}{R}(C-1) + \frac{\Delta H_C}{R}C\right)\left(\zeta + \sqrt{\zeta^2 - 4M^2(1-C)}\right)}{\left(\zeta + \sqrt{\zeta^2 - 4M^2(1-C)}\,\right)(C-1)}$$

Appendix 4: Example Drying Heat Calculation Using New Equation for Net Isosteric Heat of Sorption Together with Moisture Sorption Isotherms

The following is an illustration of how the newly proposed equation for the net isosteric heat of sorption may be applied. Consider the case where 1 kg of frozen muntries and 1 kg of frozen apples are to be dried for use in a product and require a water activity of 0.4 when at 25°C.

From moisture content analysis as reported in Table 3, the apples will have an initial moisture content of 84.14% d.b. and the muntries an initial moisture content of 79.70%. Based on the moisture sorption isotherms in Figure 1 (a-b), the final moisture content if dried to a water activity of 0.4 is 5.44% for apples and 2.09% for muntries.

Using Eq. (6) and the fitting parameters reported in Table 2, the net isosteric heat of sorption can be determined as a function of moisture content. Integrating this expression numerically in Eq. (9) allows the calculation of the heat required to perform this drying operation. Using this approach, it can be determined that the heat required to dry 1 kg of frozen apples and 1 kg of frozen muntries is 48.97 kJ and 81.90 kJ respectively. This is the minimum heat required to achieve this drying; the real heat required by a dryer must also accommodate for any heat losses associated with the particular dryer.

Code for this calculation can be found with the codes for isotherm fitting in the GitHub repository https://github.com/paulmichalski1/Moisture-Sorption-Fitting.git.

Appendix 5: Detailed XRD Data and Analysis

Table S3: Detailed XRD analysis using DIFFRAC.EVA

	Global Area	Reduced Area
Freeze-Dried Muntrie	486	399
Oven-Dried (at 60°C) Muntrie	474	338
Reduction (Oven-Dried Relative to Freeze-Dried)		15.3%
Freeze-Dried Finger Lime	459	367
Oven-Dried (at 60°C) Finger Lime	428	331
Reduction (Oven-Dried Relative to Freeze-Dried)		9.8%
Freeze-Dried Apple	555	440
Oven-Dried (at 60°C) Apple	518	401
Reduction (Oven-Dried Relative to Freeze-Dried)		8.9%

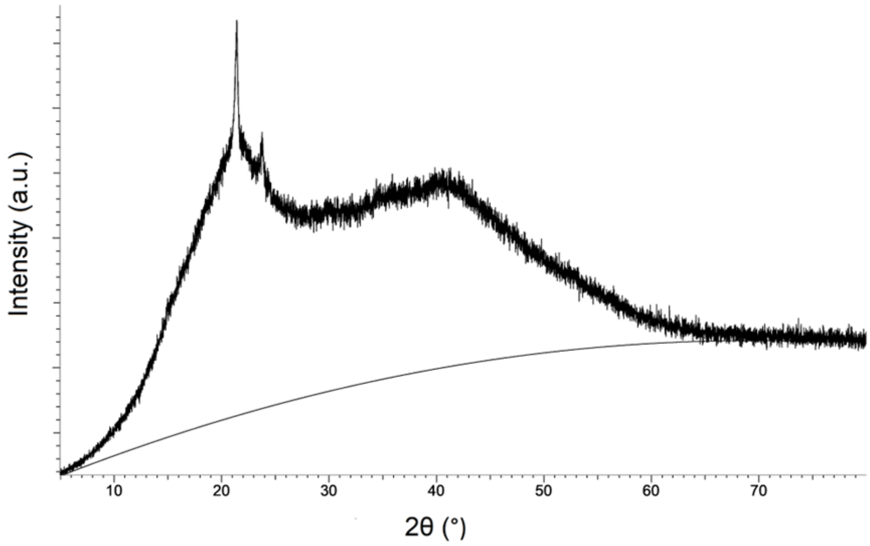

Figure S2: Example of XRD analysis for oven-dried (at 60°C) muntries performed in DIFFRAC.EVA. The background set appears as a solid line below the data. Background was set in DIFF RAC.EVA such that it had minimum curvature while approaching a constant value at high 2θ