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# A global sorption equation for raw and processed cassava based on a review and compilation of sorption properties

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## ARTICLE HISTORY

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## ABSTRACT

The objective of this study was to define, from literature data, the most relevant water sorption isotherm to use in simulation models for cassava root processing. The isotherm should be as global and generic as possible. Compiling isotherms from the literature showed that the variety of cassava and the level of processing generally have a negligible or unclear influence on the sorption behavior. Moreover, no significant hysteresis between adsorption and desorption is observed. For the purpose of simulation, measuring the sorption properties specific to each batch of product appears to be irrelevant. Actually, for this purpose, global properties, representing the average product behavior are preferred to propose equipment pre-design available for a large range of products. Following the wisdom of crowds theory, it is assumed that the mean value of sorption measurements with uncertainties on products from various origins from a dataset that is sufficiently large will represent the behavior of an average product with an accuracy sufficient for the purpose of simulation. A global, generic model (eq. 1) was obtained by fitting all the ad- and desorption data reviewed to a temperature-dependent model. A model of the heat of sorption was deduced from this global model (eq. 2). Both models are valid in a 25 – 90°C temperature range and a 0.05 – 0.93 water activity range.

$$X = \left( \frac{\exp(-0.0145172 \cdot T_K)}{-\log(a_w)} \right)^{1/1.86838} \quad (1)$$

$$L_p = 6.2111 \cdot 10^3 \cdot X^{-1.867} + L_v \quad (2)$$

where  $X$  is the moisture content (*d.b.*),  $T_K$  the temperature ( $K$ ),  $a_w$  the water activity,  $L_p$  the heat of sorption ( $J \cdot kg^{-1}$ ),  $L_v$  the latent heat of vaporization of free water ( $J \cdot kg^{-1}$ ).

## KEYWORDS

water activity; sorption; cassava; modelling

## Nomenclature

$A, B, C, D, F$  constant parameters of sorption isotherm models

$a, b, c, d, e, f, g$  constant parameters of heat of sorption models

$a_w$  water activity

Ad> adsorption

<De desorption

$E$  mean relative deviation on  $X$  between model and experimental data (%)

$EStd$  standard error on  $a_w$  between model and experimental data (%)

GAB	Guggenheim, Anderson, and De Boer
$L_v$	latent heat of vaporization of free water ( $J \cdot kg^{-1}$ )
$L_p$	heat of sorption of water in the product ( $J \cdot kg^{-1}$ )
$M$	molecular weight ( $kg \cdot mol^{-1}$ )
$p$	slope of $\log(a_w) = f(1/T_K)$ ( $K$ )
$P$	pressure ( $Pa$ )
$q_{st}$	net heat of sorption ( $= L_p - L_v$ ) ( $J \cdot kg^{-1}$ )
$R$	ideal gases constant ( $J \cdot mol^{-1} \cdot K^{-1}$ )
$T$	temperature ( $^{\circ}C$ )
$T_K$	temperature ( $K$ )
$X$	moisture content ( <i>d.b.</i> )
$X_m$	monolayer moisture content ( <i>d.b.</i> )

### ***Indices and subscript***

$v$	vapor
$sat$	at saturation
$w$	free water
$p$	product
$C$	modified Chung-Post model
$F$	Ferro-Fontan model
$G$	GAB model
$H$	Henderson model
$MH$	modified Halsey model
$MHe$	modified Henderson model
$O$	Oswin model
$Pe$	Peleg model
$S$	Smith model
$SG$	simplified GAB model
$SMH$	simplified modified Halsey model

## **1. Introduction**

Cassava is a major crop in humid tropical regions. Its starch-rich roots are processed for human food, animal feed and industry. Its nutritional value, agronomic yield, ability to grow in poor, scarcely irrigated soils for long periods of time make it a strategic crop and a staple food for nearly 500 million people in the tropics (1). Indeed, with  $250 \cdot 10^3$  kcal/ha/day<sup>1</sup>, it is considered as one of the most productive sources of carbohydrates among crops. In comparison, corn produces  $200 \cdot 10^3$ , rice  $176 \cdot 10^3$  and wheat  $110 \cdot 10^3$  kcal/ha/day (2). However, cassava roots have one weakness: their short shelf life of about 48 hours that is responsible for considerable losses and limits their sale.

Water activity ( $a_w$ , eq. 3) is a good indicator of food stability. It indicates the availability to water react chemically to enable a change in state or the growth of microorganisms. Reducing the water activity of a product, for example, by drying, is a common way to improve its conservation. Drying is widely used for cassava roots. Currently, in Africa, where 62% of the world's cassava-growing area is located (3), 49% of these roots are processed, mainly into dried flours or fermented pastes (4, 5). Flours can be fermented, unfermented, gelatinized and stir-fried (*e.g. gari*), sun or oven dried. Processing units are generally small with little mechanization and/or optimization. To increase their processing capacity, they often have to switch from sun drying to artificial drying. As artificial drying is expensive and energy-intensive, modeling is a good way to optimize this operation, improving profitability and the ecological impact of the whole

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<sup>1</sup>In comparison, a well-nourished adult consumes on average  $2.50 \cdot 10^3$  kcal/day

process.

$$a_w = \frac{P_v(T)}{P_{v,sat}(T)} \quad (3)$$

where  $P_v$  is partial vapor pressure in equilibrium with the humid product and  $P_{v,sat}$  the saturation vapor pressure of pure water at the same temperature  $T$ .

Water sorption isotherms are required to study cassava root product stability and drying (6, 7). Depending on the way of sorption these equilibrium data are measured, it can be either an adsorption or a desorption isotherm. These phenomena are not fully reversible. Several authors proposed mostly empirical equations to fit these data, thereby enabling their use to predict the sorption behavior of a product. In a computer program, a robust and invertible<sup>2</sup> model that confirms that  $a_w = 0$  when  $X = 0$  and  $X \rightarrow \infty$  when  $a_w \rightarrow 1$ , being temperature-dependent, would be preferred. The heat of sorption deduced from these isotherms should also be consistent with the latent heat of vaporization of pure water.

In many cases, for the purpose of simulation, the sorption isotherm of a mixture can be acceptably predicted with its compound isotherms (8, 9). As cassava is mostly composed of starch (75% d.b. according to CIQUAL online database (10)), and starch is composed of 28% of amylose and 72% of amylopectin (average from (11, 12)), it is assumed that sorption isotherms of starch, especially starches with a high amylopectin content, can be used as a reference for cassava.

The objective of this study was to define the most accurate, consistent, robust and reliable water sorption equation to simulate cassava processing. Its use to model several varieties or cassava-derived products will be discussed. Many sorption isotherms have already been measured in several cassava varieties and products. Since the model should be as generic and robust as possible, measurements made on a specific batch are not relevant here. A literature review is proposed below. Sorption measurements, either as raw data or as sorption models fitted to measurements, were collected from the literature and compared. Their validity and the influence of various parameters were used to choose the best model to simulate cassava processing.

## 2. Review of the literature

### 2.1. Sorption isotherm measurement methods and models

Most of the measurements compiled here were taken using discontinuous measurement methods. Most were taken on both cassava root-derived products (13–28) and other starches (29–32), obtained using the static gravimetric method. This well-known method is based on multiple salt or sulfuric acid solutions controlling air relative humidity. Samples are weighed regularly to determine the equilibrium moisture content. Chisté *et al.* (33) developed another method using water and silica gel to vary air relative humidity. These authors then modified the method, beginning by dehydrating the sample with a salt solution (34). Although static gravimetric methods (33–35) require little equipment, there are many sources of uncertainty. Indeed, a large number of salt solutions have to be prepared and the multiple manipulations could render the temperature and hygrometry conditions less stable. Gibert *et al.* (27) proposed low-tech measurement equipment that, automating the weighing, enabled a reduction in the number of manipulations, and hence the uncertainties.

In a previous study on various starches, Van den Berg (36) and Cova (37) used continuous gravimetric methods with continuous control of air relative humidity, with a *McBain* balance and a controlled atmosphere micro-balance, respectively. As the samples are not removed from their environment and no salt solutions are used, uncertainties are minimized.

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<sup>2</sup> $X = f(a_w, T)$  and  $a_w = f(X, T)$  are both needed

Apart for a few sorption measurements that were published as raw data (19–21, 38), all these authors fitted their measurements with one or more sorption equations. Some equations provided by the authors did not enable accurate regeneration of the isotherms. In these cases, we extracted raw data from the figures included in their articles (25, 39). A compilation of sorption equations used in the articles we reviewed is presented in table 1. In the literature, the GAB (Guggenheim, Anderson, and De Boer) model is the most widely used. This may be due to the fact that its parameters have a physical meaning, such as  $X_m$ , the monolayer moisture content, known to represent a moisture content at which the product is very stable. Unlike the other models, it is not invertible, meaning it is impossible to express analytically  $a_w$  as a function of  $X$ . The Peleg equation has the advantage of fitting a lot of food product sorption isotherms well (40) but does not include the expected boundaries and is not temperature dependent. In the end, only Halsey, Oswin and Henderson equations are invertible and respect the expected boundaries:  $X = 0$  when  $a_w = 0$  and  $X \rightarrow \infty$  when  $a_w \rightarrow 1$ . Among them, only the modified Halsey -empirical- equation is temperature dependent, and is therefore probably the most suitable to simulate drying. In our review at least, it was the only equation that satisfies all our criteria for inclusion in a simulation model of drying cassava.

**Table 1.** Sorption isotherm equations for cassava.

Model name	Equation	$X$ when $a_w \rightarrow 0$	$X$ when $a_w \rightarrow 1$
Modified Halsey (41)	$X = \left( \frac{\exp(A_{MH} - B_{MH} \cdot T_K)}{-\log(a_w)} \right)^{1/C_{MH}}$	0	$\infty$
Chung-Pfost (42)	$X = -\frac{1}{C_C} \cdot \log\left(\frac{T+B_C}{-A_C} \cdot \log(a_w)\right)$	$-\infty$	finite number
GAB (43–45)	$X = \frac{X_m \cdot A_G \cdot a_w}{(1 - B_G \cdot a_w) \cdot (1 - k \cdot a_w + A_G \cdot B_G \cdot a_w)}$	0	finite number
Simplified GAB (46)	$\frac{a_w}{X} = A_{SG} \cdot a_w^2 + B_{SG} \cdot a_w + C_{SG}$	0	finite number
Oswin (47)	$X = A_O \cdot \left( \frac{a_w}{1 - a_w} \right)^{B_O}$	0	$\infty$
Ferro-Fontan (48)	$X = \left( \frac{A_F}{\log(B_F/a_w)} \right)^{1/C_F}$	0	finite number
Peleg (49)	$X = A_{Pe} \cdot a_w^{C_{Pe}} + B_{Pe} \cdot a_w^{D_{Pe}}$	0	finite number
Smith (50)	$X = A_S + (B_S \cdot \log_{10}(1 - a_w))$	finite number	$\infty$
Henderson (51)	$X = \left( \frac{-\log(1 - a_w)}{A_H} \right)^{1/B_H}$	0	$\infty$
Modified Henderson (28)	$a_w = 1 - \exp(-A_{MHe} \cdot T_K^{B_{MHe}} \cdot X^{C_{MHe} + D_{MHe} \cdot T_K + F_{MHe} \cdot T_K^2})$	0	finite number

## 2.2. Heat of sorption calculation methods and models

In theory, the heat of sorption can be deduced from sorption isotherms using the Clausius-Clapeyron equation or directly by calorimetric measurement. However, we found no calorimetric measurement for cassava in the literature. Two methods based on Clausius-Clapeyron equation were used in the articles considered in our review, and both strictly require sorption isotherm equations at several temperatures. The calculated heat of sorption is usually presented either as a fraction ( $\frac{L_p(X)}{L_v}$ ) or as the difference ( $L_p(X) - L_v$ ) from the latent heat of vaporization of free water. Both methods can be used indifferently.

### 2.2.1. Method 1: Heat of sorption over latent heat of vaporization

The Clausius-Clapeyron equation is used to express the latent heat of vaporization of free water and the heat of sorption using eq. 4, leading to eq. 5 when integrated (13).

$$\frac{1}{L_p} \cdot \frac{dP_v}{P_v} = \frac{dT_K}{R \cdot T_K^2} = \frac{1}{L_v} \cdot \frac{dP_{v,sat}}{P_{v,sat}} \quad (4)$$

$$\log(P_v) = \frac{L_p}{L_v} \cdot \log(P_{v,sat}) + constant \quad (5)$$

where  $T_K$  is the temperature (K),  $L_p$  the cassava heat of sorption ( $J \cdot kg^{-1}$ ),  $L_v$  the latent heat of vaporization of free water ( $J \cdot kg^{-1}$ ),  $P_v$  the vapour pressure in the product (Pa),  $P_{v,sat}$  the saturation vapor pressure (Pa),  $R$  the perfect gas constant ( $J \cdot mol^{-1} \cdot K^{-1}$ ).

Sorption isotherms measured at several temperatures are used to create a non-parametric representation of  $\log(P_v)$  against  $\log(P_{v,sat})$  at several moisture contents. Each curve has its own slope, which is the ratio of the heat of sorption ( $L_p$ ) to the latent heat of vaporization ( $L_v$ ) of free water. Compiling these slopes makes it possible to express them as a function of the moisture content using empirical eq. 6.

$$\frac{L_p(X)}{L_v} = 1 + a \cdot \exp(-b \cdot X) \quad (6)$$

where  $a$  and  $b$  are constant –empirical– parameters.

### 2.2.2. Method 2: Net heat of sorption

The Clausion-Clapeyron equation also makes it possible to express the latent heat of vaporization of free water (eq. 7) and the heat of sorption (eq. 8). Subtracted, they lead to eq. 9.

$$L_v = -\frac{R}{M_w} \cdot \frac{d(\log(P_{v,sat}))}{d(1/T_K)} \quad (7)$$

$$L_p = -\frac{R}{M_w} \cdot \frac{d(\log(P_v))}{d(1/T_K)} \quad (8)$$

$$q_{st} = L_p - L_v = -\frac{R}{M_w} \cdot \left[ \frac{d(\log(\frac{P_v}{P_{v,sat}}))}{d(1/T_K)} \right]_{X=cst} = -\frac{R}{M_w} \cdot \left[ \frac{d(\log(a_w))}{d(1/T_K)} \right]_{X=cst} \quad (9)$$

where  $q_{st}$  is the net heat of sorption and  $M_w$  the molar weight of pure water ( $kg \cdot mol^{-1}$ ).

With sorption isotherms, curves of  $\log(a_w)$  versus  $1/T_K$  are plotted for several values of  $X$ , showing lines whose slopes  $p$  can be expressed as a function of  $X$ . Net heat of sorption is deduced from  $p(X)$ , like in eq. 10 and then fitted using eq. 11 or eq. 12.

$$q_{st} = \frac{R}{M_w} \cdot p(X) \quad (10)$$

$$q_{st}(X) = L_p(X) - L_v = c \cdot X^{-d} \quad (11)$$

**Table 2.** Data used for the cassava heat of sorption model ( $J.kg^{-1}$ ).  
 With  $\langle De$  the desorption,  $Ad \rangle$  the adsorption,  $a$  &  $b$  coefficients of eq. 6;  $c$  &  $d$  coefficients of eq. 11 and  $e$  &  $f$  &  $g$  coefficients of eq. 12.

Product	Sorption	a	b	c	d	e	f	g	X range	T range	Source
Root	$\langle De$	3.3446	10.9569	–	–	–	–	–	0.04 – 0.2	30 – 60°C	(14)
Root	$\langle De$	–	–	155964	0.836	–	–	–	0.04 – 0.3092	30 – 60°C	(16)
Root	$Ad \rangle$	–	–	138743	0.841	–	–	–	0.04 – 0.3092	30 – 60°C	(16)
<i>Gari</i>	$\langle De$	4.17	30.80	–	–	–	–	–	0.04 – 0.2	40 – 70°C	(13)
Mash	$\langle De$	–	–	636667	1.4	–	–	–	0.04 – 0.24	40 – 90°C	(22, 39)
Chips	$\langle De$	–	–	–	–	19.821	3.181	35.335	0.05 – 0.4	25 – 60°C	(25)

$$\log(q_{st}(X)) = e + f \cdot \log(X) - g \cdot X \quad (12)$$

where  $c$ ,  $d$ ,  $e$ ,  $f$ ,  $g$  are constant –empirical– parameters.

### 2.2.3. Parameters of cassava heat of sorption models

As emphasized above, to be able to deduce the heat of sorption with the two methods, sorption isotherms must be available at several temperatures. With this limitation, in the sorption isotherms compiled in section 2, the heat of desorption was only estimated from cassava root (16), cassava chips (23), cassava mash (22, 39) and *gari* (13) isotherms, and the heat of adsorption from cassava root (14, 16) and fermented flour (26) isotherms. Parameters for the calculation of the heat of sorption with equations 6 and 11 are presented in table 2. Ajala *et al.* (23) and Sanni *et al.* (26) did not fit their heat of sorption to an equation. Data to be plotted were thus extracted from their plot and are discussed in section 3.4.

## 3. Discussion

### 3.1. Validity of the isotherms

#### 3.1.1. Measurement uncertainties

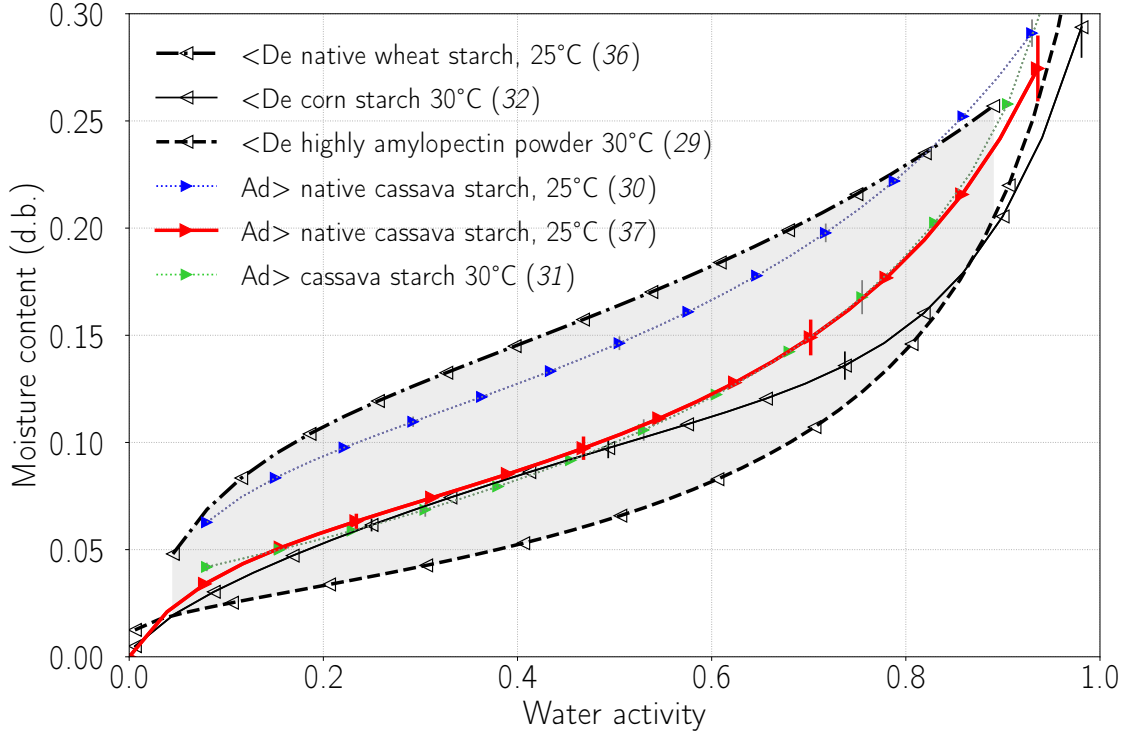
Measurements of adsorption and desorption isotherms using the gravimetric salt and acid method are subject to uncertainties such that deviations of 0.1–0.2 on the  $a_w$  are common. Furthermore, uncertainties on both  $X$  and  $T$  may add up. Possible origins of these deviations are:

- the different operators
- the different times left to allow the system to reach equilibrium (generally not mentioned)
- a specific measurement bias at relatively high temperatures: some of the water contained in the product may evaporate when it is removed from the desiccator for weighing. Thus, measurements taken between 10 °C and 40 °C are generally more reliable than those taken at higher temperatures.

Although some articles provide information on model uncertainties none provide data on the measurement uncertainties. Consequently, the figures presented hereafter may include error bars, as taken from respective articles and listed in tables 5 and 6.

#### 3.1.2. Comparison of cassava and starch isotherms

The starch curves in figure 1 are surprisingly very dispersed for an almost pure constituent. The span of moisture content values is quite constant from  $a_w = 0.2$  to  $a_w = 0.6$ . Below and above these values, the range of values is narrower, as expected near  $a_w = 0$  and  $a_w = 1$ . Discrepancies



**Figure 1.** Starch adsorption (Ad>: full triangles) and desorption (<De: empty triangles) isotherms at 25 – 30°C.

between sources can be partly explained by measurement uncertainties (see section 3.1.1) and differences in the starch composition or structure due to the use of different extraction processes and botanical origin (52). What is more, no significant hysteresis is visible between adsorption and desorption starch isotherms. Its influence may be weaker than measurement uncertainties, botanical origin or extraction processes.

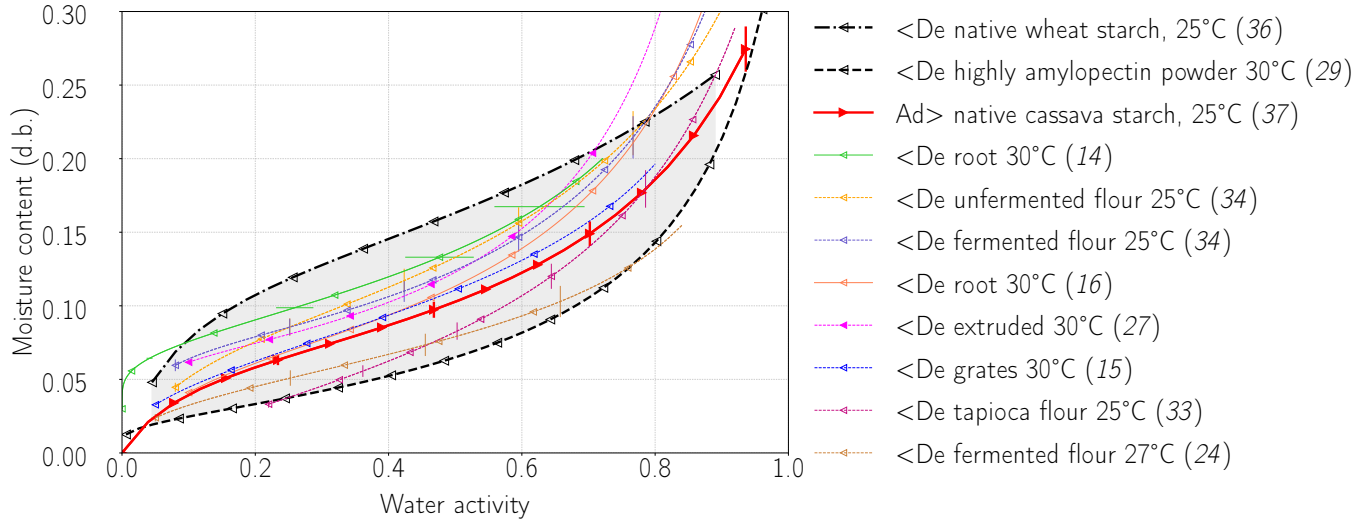
The Cova *et al.* (37) isotherm on cassava starch can be considered as a reference since, unlike the other authors, the measurement made by Cova *et al.* (37) is continuous and automated. Hence there cannot be a single inaccurate point: either the measured isotherm is entirely valid or entirely false. As this isotherm is in the same range of values as the ones measured by other authors, we consider it as a valid and accurate reference at 25°C both for ad- and de-sorption, as hysteresis is negligible (see previous and next section).

To check the validity of cassava isotherms while ensuring readability, figure 2 presents cassava desorption isotherms at 25 – 30°C (14–16, 24, 27, 33, 34) and three starch sorption isotherms: the extremum (29, 36) and the one of native cassava starch (37), as explained above. Cassava desorption isotherms are intermediate between powder with high amylopectin content (29) and wheat starch (36) isotherms. Except tapioca flour (33) and fermented flour (24) isotherms, cassava isotherms remain within a consistent range of values if the measurement uncertainties presented in section 2.1 are taken into consideration. The same observation applies to cassava adsorption isotherms (16–18, 20, 21, 24, 33, 34, 38).

At higher temperatures, starch isotherms are available only for highly amylopectin powder (29) and corn starch (32). Powder with high amylopectin content (29) was found to have the lowest moisture content at all water activity values. On the contrary, at 30°C, the corn starch isotherm (32), is the average of the other starch isotherms and similar to the native cassava starch isotherm (37) for  $a_w \leq 0.6$ . For this reason, the corn starch isotherm (32) seems to be a good reference for a wide range of temperatures. As a matter of fact, at higher temperatures, cassava isotherms closely resemble corn starch isotherms (32) and are higher than those of highly amylopectin powder (29) (data not shown).

All the above observations are consistent with the characteristics of type-II isotherms, reflecting similar material structure that is either non-porous or macro-porous. Thus, since the





**Figure 2.** Cassava desorption (<De) isotherms at 25 – 30°C and reference sorption isotherms for starch.

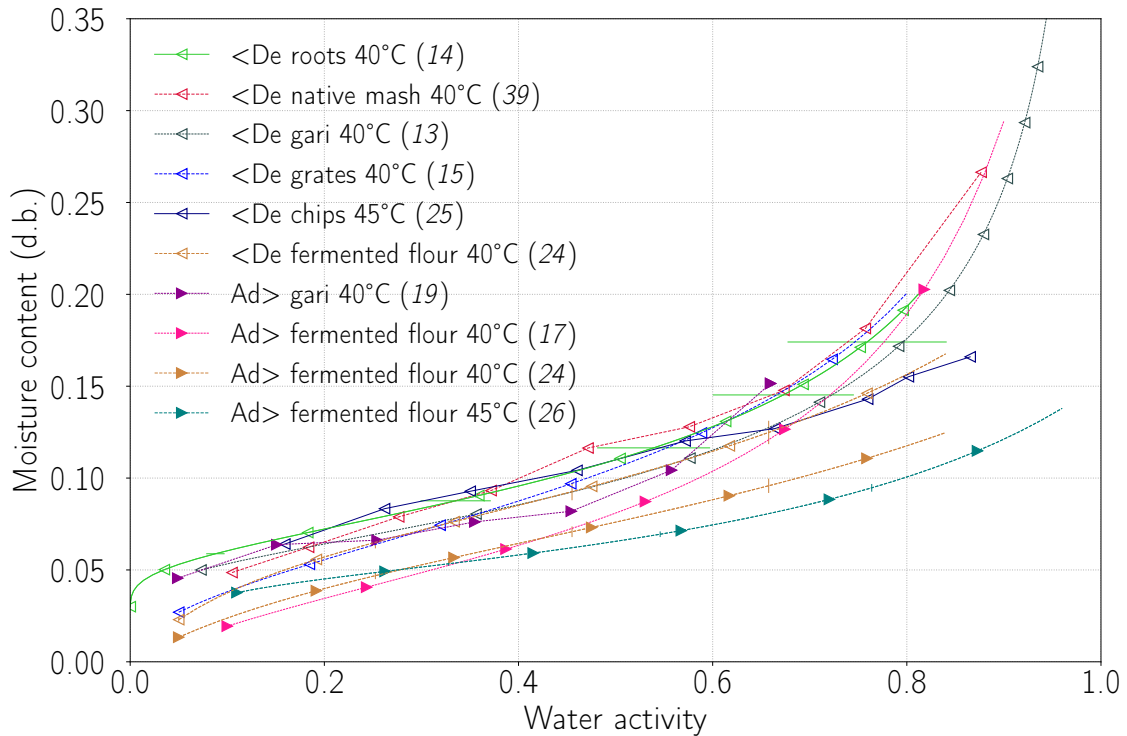
cassava sorption isotherms we reviewed are consistent with starch isotherms, they are considered valid, whereas the validity of tapioca flour (33) and fermented flour (24) isotherms is questionable, as they are not fully consistent with the measurements reported by the other authors.

### 3.2. *Hysteresis between adsorption and desorption*

Hysteresis is often observed between the adsorption and desorption of water in a product. This phenomena is generally explained by the nature of bonds between water and the product. It can be partially explained because capillary filling of micropores is often easier than emptying. Moreover, during adsorption, the structure of the starch can change, in which case desorption would not follow the same path (53). In fact, adsorption and desorption phenomena depend on the initial degree of crystallinity of the product (54).

Figure 3 groups adsorption and desorption isotherms of cassava roots and derived products at 40°C. The curves are remarkably similar, except for two fermented flour isotherms (24, 26), that are located slightly below the others and are less curved. Fermented flour isotherms in Hawa *et al.* (24) were considered as not consistent with the isotherms of the other cassava products at 30°C presented in section 3.1. The same kind of discrepancy was observed between the isotherms presented in Sanni *et al.* (26) and reported by the other authors mentioned in section 3.5. The reason for these discrepancies is not clear but seems to be less due to hysteresis than to the origin of the product or to the validity of the measurement, as the seven other ad- and de-sorption isotherms plotted here are similar. While the maximum deviation for starchy food occurs around  $a_w = 0.7$  (54), above  $a_w = 0.65$ , the seven similar isotherms are in the range of prediction error of the model fitted by Aviara *et al.* (14). For lower  $a_w$ ; only the one measured by Cahyanti *et al.* (17) is located at a short distance from the others, all of which are located close together. Thus, no significant difference between adsorption and desorption can be highlighted. The same observation applies when cassava product isotherms at 30°C and 60°C are compiled.

The existence of hysteresis between adsorption and desorption is not questionable and most authors have observed this phenomenon (16, 33, 34). Nevertheless, when we compare isotherms from different works, *i.e.* obtained using different techniques and different materials, beyond measurement or model uncertainties, the poor reproducibility and the different origins of the products mask the less noticeable hysteresis. In other words, hysteresis is not numerically significant compared to the discrepancies between authors. Likewise, Roman *et al.* (9) considered hysteresis to be negligible in their model predicting food sorption isotherms.



**Figure 3.** Comparison of adsorption (Ad>) and desorption (<De) isotherms of cassava products at 40°C.

### 3.3. Effect of temperature

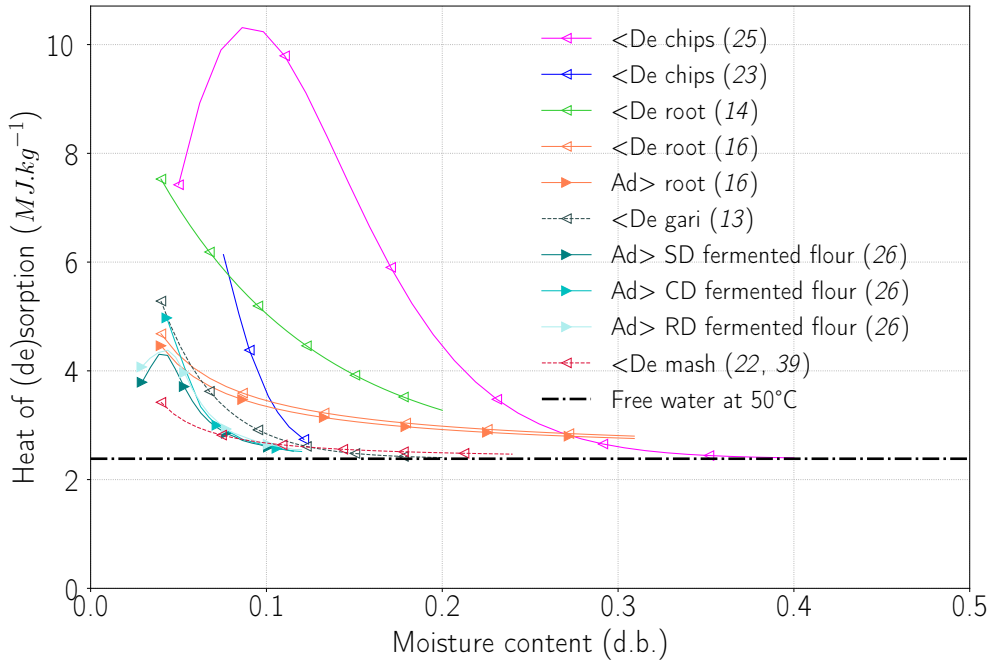
Temperature affects the phase equilibrium of water and, more generally, the capacity of a substance to trap moisture in the air (54), called hygroscopicity, which is well represented by sorption isotherms. At constant water activity, the moisture content of most cassava products (roots, flour, *gari*, mash, fermented or unfermented) decreases with an increase in temperature (13–18, 22–24, 26, 28, 39, 55, 56), in agreement with the behavior generally observed in food products (54). Conversely, different behavior representative of low-molecular-weight food constituents (54), was observed by two authors (19, 20) on *gari*. Zakhia *et al.* (20) observed that, for  $a_w$  greater than 0.5 – 0.7, an increase in temperature led to an increase in the equilibrium moisture content. At constant water activity, Adeteju *et al.* (19) measured an increase in *gari* moisture content between 40°C and 50°C but a decrease between 50°C and 55°C, which could be explained by *gari* different forms of processing, including grating, fermentation and partial gelatinization, that damage the cells. According to (20), thanks to the plasticizing effect of water, free spaces are created within *gari* matrix thereby increasing the water sorption capacity. Contradictory conclusions were drawn by (13, 22, 39), possibly due to differences in processing procedures not identified in the articles concerned. Comparing different sources and their own measurements, Gevaudan *et al.* (22, 39), reported that the effect of gelatinization on the sorption process of cassava is very weak. Depending on the preparation, the composition of *gari* and measurement uncertainties, different authors reported gelatinization to either increase or decrease product hygroscopicity.

Temperature-induced variations in hygroscopicity are weak in starch (29, 32), which we consider as a reference, as well as in native cassava mash (22, 39), cassava grates (15), cassava chips (23, 28), fermented cassava flour (17, 24, 26) and *gari* (13, 19, 20, 56). Conversely, few works report a strong influence of temperature on the hygroscopicity of cassava flour (18) and cassava roots (14, 16). These conclusions can be questioned. For instance, the results reported for cassava flour from (18) do not match those reported for similar products: cassava grates (15) or fermented cassava flour (17, 24, 26). Similarly, results for whole cassava roots (14, 16) surprisingly differ from those of native cassava mash (22, 39). Moreover, the temperature-

induced difference between the isotherms measured by Koua *et al.* (16) increased with  $a_w$ , which is doubtful since the isotherms of the same product generally converge when  $a_w \rightarrow 1$ . Secondly, the isotherm measured at 60°C is also doubtful, since it is far from the one measured at 45°C and shows no asymptote for  $a_w = 1$ . Further, the high temperature influence observed by Aviara and Ajibola (14) needs to be confirmed either by other measurements or by re-interpreting the calculated heat of desorption. Overall, the data from the reviewed literature is not robust enough to make a conclusion on the effect of temperature. From the measurements of Koua *et al.* (16) and Aviara and Ajibola (14), it seems that the sorption behavior of cassava roots would be strongly influenced by temperature while that of processed cassava would not. However, these sorption data are doubtful because they lead to unrealistic values of heat of desorption.

### 3.4. Physical consistency of estimated heat of sorption

Heats of sorption have been deduced from sorption isotherms by several authors using methods detailed in section 2.2. In figure 4, no significant difference between heat of adsorption and desorption can be identified. As discussed in relation to the significance of hysteresis, the difference between heats of adsorption and desorption is significant for a given author (16) but becomes insignificant when different authors are compared.



**Figure 4.** Heat of adsorption (Ad>) and desorption (<De) for cassava products. With SD, CD, RD respectively sun dried, cabinet dried, and rotary dried fermented flour.

On average, for the range of moisture content considered here, the net heat of sorption of food products  $q_{st} = L_p - L_v$  represents 10 – 20% of the total heat of desorption  $L_p$  (57), which is often neglected in drying simulators in which only the latent heat of vaporization of pure water is considered. Table 3 and Figure 4 show that the heat of desorption deduced by Aviara *et al.* (14), Ajala *et al.* (23) and Salgado *et al.* (25), which has never been reported elsewhere in drying, are way too high to be physically consistent. Similarly, the heat of sorption calculated by Koua *et al.* (16) is also significantly higher than the latent heat of vaporization of free water at  $X = 0.3$ , for instance. At this moisture content, at 30°C – 60°C, water activity is close to one, *i.e.* 0.8 – 0.9, and one would expect desorption heat to be closer to the latent heat of

vaporization of free water. For Koua *et al.* (16) and Aviara *et al.* (14), these differences may be related to the influence of high temperature on sorption isotherms, which was only observed by these two authors. It should be noted that calculating the heat of sorption involves numerical derivation of the measured temperature, thereby amplifying errors, and possibly leading to physical inconsistencies. In contrast to works by (14, 16), it also reinforces the hypothesis that temperature has a weak influence on sorption isotherms. In other words, all cassava products may have their sorption isotherms modeled by a weak temperature influenced model. Furthermore, the net heat of sorption reported by Salgado *et al.* (25) and Sanni *et al.* (26) surprisingly decreases below a certain moisture content. It is physically questionable, as it is usually considered that the lower the moisture content of a product, the stronger the bonds between the water and the solid and, hence, the greater the energy required to extract, *i.e.* desorb, the water. Therefore, the physical consistency of these isotherms (23, 25, 26) are questionable. What is more, Ajala *et al.* (23) measured sorption isotherms at high temperatures, where measurement uncertainties are greater (see section 3.1). Physically more consistent heats of sorption were found by Fasina *et al.* (13) and Gevaudan *et al.* (22, 39), 20% higher or less than the latent heat of vaporization of free water and very close to free water enthalpy at high equilibrium moisture content.

**Table 3.** Importance of net heat of sorption of cassava products.

Product	Sorption	Mean	$\frac{L_p - L_v}{L_p}$	$X_m$	$\frac{L_p - L_v}{L_p}$ at $X_m$	Source
Chips	< De	37%	0.0663 <sup>a</sup>	0.0663 <sup>a</sup>	74%	(25)
Chips	< De	36%	0.1 <sup>c</sup>	0.1 <sup>c</sup>	61%	(23)
Root	< De	36%	0.0663 <sup>a</sup>	0.0663 <sup>a</sup>	63%	(14)
Root	Ad >	24%	0.0506 <sup>b</sup>	0.0506 <sup>b</sup>	42%	(16)
Root	< De	23%	0.0551 <sup>b</sup>	0.0551 <sup>b</sup>	42%	(16)
Rotary dried fermented flour	Ad >	24%	0.067 <sup>c</sup>	0.067 <sup>c</sup>	26%	(26)
Sun dried fermented flour	Ad >	23%	0.067 <sup>c</sup>	0.067 <sup>c</sup>	22%	(26)
Cabinet dried fermented flour	Ad >	22%	0.067 <sup>c</sup>	0.067 <sup>c</sup>	24%	(26)
<i>Gari</i>	< De	17%	0.0633 <sup>a</sup>	0.0633 <sup>a</sup>	37%	(13)
Mash	< De	7%	0.0731 <sup>b</sup>	0.0731 <sup>b</sup>	16%	(22, 39)

<sup>a</sup> Average  $X_m$  of all the GAB models reviewed here (see table 6).

<sup>b</sup>The average  $X_m$  of all those proposed by these authors at different temperatures.

<sup>c</sup> Considering all the GAB models reviewed here, the  $X$  value closest to the average  $X_m$  at which the net heat of sorption was calculated by the authors.

In most drying simulations, the moisture content at the surface of the product decreases drastically to converge towards equilibrium moisture content. Table 3 compares the importance of the net heat of sorption versus the global heat of sorption of free water at  $X_m$ . The table shows that, except for Gevaudan *et al.* (22, 39), the net heat of sorption is not negligible at low moisture content. At even lower moisture content, the heat of desorption increases, and is consequently no longer negligible even for Gevaudan *et al.* (22, 39). Indeed, (i) the equation to which the heat of desorption is fitted must have an asymptote at  $X = 0$  and (ii) no measurement is currently available at or under  $X_m$  where uncertainties are high. Such high values for desorption heat at low moisture content have a poor physical basis and should be avoided in a drying model.

### 3.5. Product dependence

Intuitively, the fact that cassava is processed or not is expected to influence its sorption isotherms. For a simple comparison, two groups of sorption isotherms were selected: one representing products containing whole –intact– cells and another containing partially de-structured cells. As shown in figure 5, apart from the fermented flour isotherms measured by two authors (24, 26), the groups representing the two "processing levels" are completely mixed. The discrepancy between these two fermented flour isotherms and isotherms provided by other authors was already

highlighted in sections 3.1, 3.2 and 3.4. What is more, the discrepancy between these fermented flour isotherms and the other isotherms plotted in figure 5 does not seem to be linked to the level of processing. Indeed, a fermented flour isotherm measured by another author (33) is more similar to the five other isotherms plotted here. Moreover, the extruded cassava isotherm (27), which is the isotherm of the most highly processed product, is similar to cassava root isotherms (14, 16). As a first –counter intuitive– conclusion, the influence of the structure of cassava cells, *e.g.* the level of processing is negligible.

The isotherms measured by three authors (23, 24, 26) look slightly different from the others. This discrepancy was mentioned in each preceding section but could not be clearly explained. It is neither due to hysteresis, nor to the level of processing. As the heats of sorption calculated using the Sanni *et al.* (26) and Ajala *et al.* (23) isotherms were physically inconsistent, these isotherms are questionable. Likewise, the discrepancy between the fermented flour isotherm (24) and the other authors’ isotherms may be due to a property that could not be investigated in the present study: the composition, *i.e.* the variety or the maturity of the root.

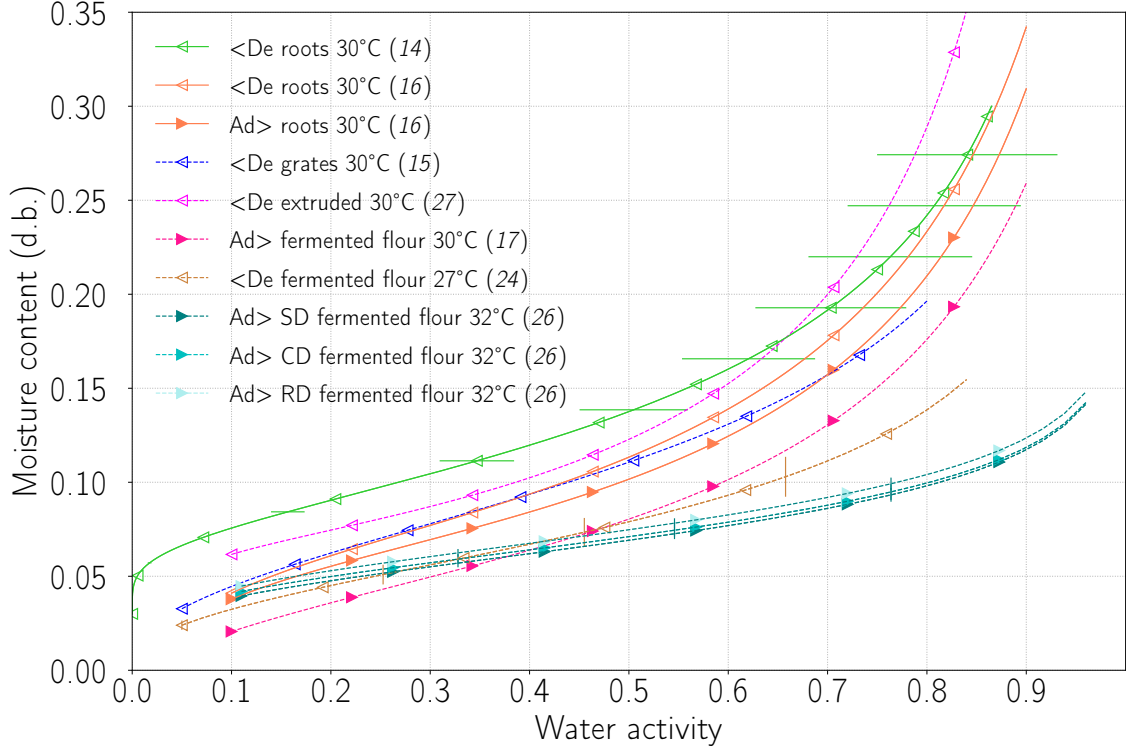
The figures in previous sections, with the exception of three authors (23, 24, 26), as discussed above, suggest that the influence of the level of processing on sorption phenomena is weaker than the influence of the methods of measurement, model uncertainties or other parameters on which we could not discriminate the measurements as they are not mentioned in the reviewed articles. These unexplored parameters could be the origin, variety, maturity of the roots or environmental factors affecting their growth and characteristics. Furthermore, the discrepancies observed between cassava sorption isotherms of different varieties, processed differently, measured by different authors, as plotted in figure 2, are smaller than the discrepancy between the starch sorption isotherms measured by several authors.

Possibly due to partial gelatinization or stir-frying in vegetable oil, above a certain water activity and/or temperature, the hygroscopic behavior of *Gari* may differ from that of other cassava products, as reported in only two works (19, 20) (see section 3.3). In any case, the difference is small and is not clearly explained by these authors. Consequently, until specific complementary work is undertaken, modeling *gari* sorption exactly like any other cassava products should be acceptable.

### 3.6. *A generic water sorption model for cassava products*

As discussed in previous sections, neither significant hysteresis between adsorption and desorption, nor a clear influence of the level of processing was found. The influence of the raw cassava origin, *i.e.* variety, maturity, growing techniques and environment, could not be really discussed as it is generally not specified in the articles. In fact, it is difficult to study the influence of roots origin, as it depends on a lot of uncontrolled environmental factors. Nonetheless, most of the measurements collected in this study, measured on products from various origins, present consistent and similar trends and values. Therefore, in the absence of additional data, neglecting the effect of the raw product origin is acceptable for the purpose of simulation. Thus, a robust sorption model for cassava products simulation could be deduced by fitting a selection of the data compiled here to the modified Halsey equation. All data were included, except the isotherms measured by three authors (23, 24, 26), for the reasons given in section 3.5. By freeing itself from the measurement uncertainties specific to each author and from unclear or unexplained variabilities which then offset each other, we believe this model best represents the average behavior of cassava products during adsorption and desorption. This approach is similar to those based on the wisdom of crowds used in other fields (58, 59). As an illustration, the diagnosis of a group of medical students often proves to be better than that of an experienced specialist, as their individual mistakes offset each other’s (58, 59). Likewise, assuming that the dataset is large enough, the mean value of measurements with uncertainties on products from various origins should be close to the physical reality being measured on a representative, average product, using a method free of uncertainties.

A fit with all the 3 parameters ( $A_{MH}, B_{MH}, C_{MH}$ ) was first calculated, see table 4. The



**Figure 5.** Desorption and adsorption isotherms of cassava products with whole (solid lines) and partially destructured cells (dotted lines) at 30°C. With SD, CD, RD fermented flour respectively sun dried, cabinet dried and rotary dried.

large uncertainty (e.g. 36%) on parameter  $A_{MH}$  and its weak influence favored a second fit with  $A_{MH} = 0$  denoted "simplified modified Halsey" (eq. 13). The uncertainties on  $B_{MH}$  parameter also notably reduced from 8% down to 2%. Indeed, figure 6 shows that the model with two parameters is equally accurate.

$$X = \left( \frac{\exp(-B_{SMH} \cdot T_K)}{-\log(a_w)} \right)^{1/C_{SMH}} \quad (13)$$

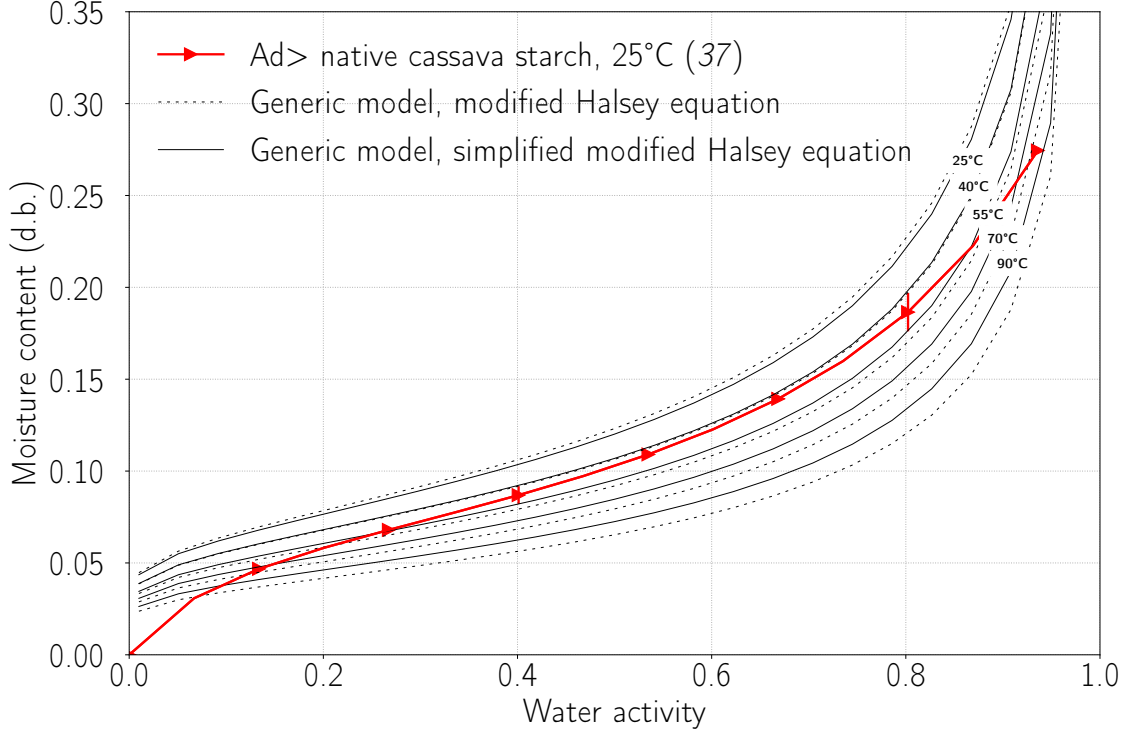
where  $X$  is the moisture content (d.b.),  $a_w$  the water activity,  $T_K$  the temperature (K),  $B_{SMH}$  and  $C_{SMH}$  are empirical coefficients.

This generic isotherm model is in the same range as the cassava starch sorption isotherm measured by Cova *et al.* (37) (see figure 6) we used as a reference for this study (see section 3.1). This tends to confirm both the validity of this model and the first assumption of this article: the sorption isotherm of a mixture can be acceptably predicted with its compound isotherms (8) for the purpose of simulation. Thus, raw and processed cassava sorption phenomena can be modeled by sorption isotherms of powder with high amylopectin content, itself well modeled by the model proposed here. After checking, this assumption could be extrapolated to other starchy roots, such as yam, sweet potato or taro.

**Table 4.** Parameters of a generic model of the cassava sorption isotherm.

Model	$A$	$B$	$C$	$a_w$	$T$ (°C)	Residues
<i>Modified Halsey</i>	$1.15075 \pm 0.4175$	$0.0182291 \pm 0.001391$	$1.8693 \pm 0.04182$	0.05 – 0.93	25 – 90	0.473329
<i>Simplified modified Halsey</i>	0	$0.0145172 \pm 0.0002362$	$1.86838 \pm 0.04204$	0.05 – 0.93	25 – 90	0.473913

Heat of sorption (eq. 14) was deduced from this simplified modified Halsey model following the method explained in section 2.2. As the isotherm model, it should be valid both for adsorption



**Figure 6.** Generic ad- and desorption isotherms of cassava products (obtained by fitting measurements made by 17 authors).

and desorption. It is on average 18% higher than the latent heat of vaporization of free water and really close to it at high water activity (see fig. 7). Thus, this heat and isotherm of sorption can be considered as physically consistent (see section 2.2).

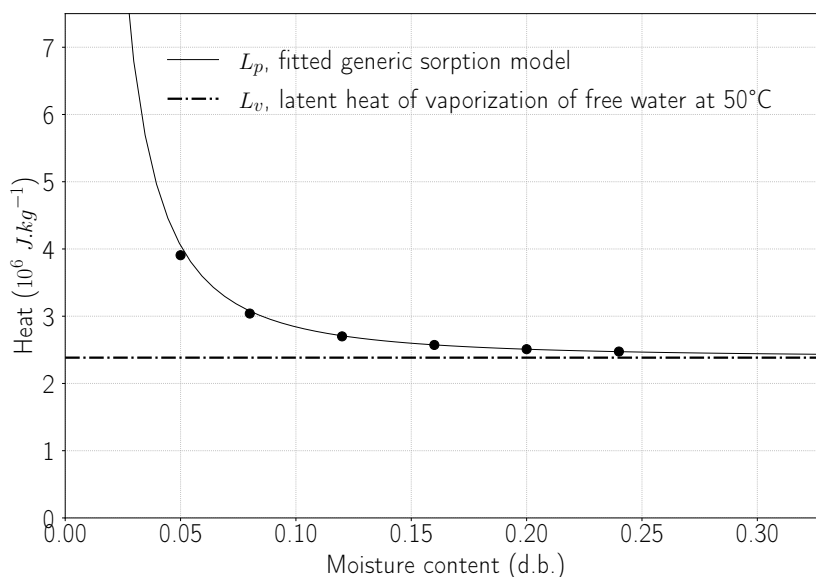
$$L_p = 6.2111 \cdot 10^3 \cdot X^{-1.867} + L_v \quad (14)$$

where  $X$  is the moisture content (d.b.),  $L_p$  the cassava heat of sorption ( $J \cdot kg^{-1}$ ),  $L_v$  the latent heat of vaporization of free water ( $J \cdot kg^{-1}$ ).

At  $X = 0.111$  (i.e. 10% w.b.), i.e. the cassava flour standard in Nigeria (60), this heat of sorption is 14% higher than the latent heat of vaporization of free water. On one hand, this observation confirms that it is better not to neglect the heat of sorption. On the other hand, available sorption measurements at moisture contents below 5% d.b. are rare and involve high measurement uncertainties thus making estimates of heat of sorption less reliable than the well-known latent heat of vaporization of pure water. It is thus advisable to consider  $L_p$  constant at moisture contents lower than the lowest moisture content at which sorption was measured.

#### 4. Conclusion

The objective of the study was to define the best sorption isotherm to be used for simulations of cassava processing, particularly drying. Many ad- and de- sorption isotherms measured by different authors on various cassava products (roots of different origin, level of processing, etc.) at several temperatures, are available in the literature. We first compiled and compared these sorption isotherms and found no clear or significant influence of the hysteresis between adsorption and desorption, nor of the level of processing nor of the origin of the product. For the purpose of simulation, we thus considered it was appropriate to use a generic, global model for all cassava



**Figure 7.** Generic heat of sorption of cassava products compared to the latent heat of vaporization of free water

products. What is more, according to the wisdom of crowds theory, a mean measurement based on a sufficiently large dataset can be considered an accurate approximation of the physical reality.

Therefore, second, we fitted all valid sorption data we compiled to a temperature dependent model and propose a global, generic, sorption isotherm model. A heat of sorption model was deduced from this isotherm model. Both models are valid in a 25 – 90°C temperature range and a 0.05 – 0.93 water activity range.

Furthermore, cassava being mainly composed of starch, the global model proposed here was compared to a starch sorption isotherm considered as reliable. The model could well represent starch sorption behavior. Firstly, this tends to confirm the assumption that the sorption behavior of a product can be predicted by the sorption behavior of its components. Secondly, it opens the way for using this model for other starchy products. Finally, the approach proposed here, *i.e.* fitting literature data to an equation to obtain a global, generic model, could also be applied to other product characteristics.

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## Appendix: Parameters from cassava and starch sorption isotherm models

**Table 5.** Data for sorption isotherm models of starches (NCS = Native Cassava Starch; NWS = Native Wheat Starch; ACS = Amorphous Cassava Starch; HAP = Highly Amylopectin Powder; CS = Corn Starch).

Product	Sorption	T (°C)	Coefficients				$a_w$ range	E (%)	Source
<b>Smith model</b>			$A_S$	$B_S$	–	–			
ACS	Ad >	30	0.34	-0.219	–	–	0.08 – 0.98	4.73	(31)
<b>GAB model</b>			$X_m$	$A_G$	$B_G$	–			
NCS	Ad >	25	0.068	13.07	0.81	–	0.000 – 0.936	5.6	(37)
NCS	Ad >	25	0.101	23.5	0.71	–	0.08 – 0.93	2.2	(30, 61)
NWS	< De	25	0.1288	21.1	0.584	–	0.045 – 0.89	–	(36)
<b>Ferro Fontan model</b>			$A_F$	$B_F$	$C_F$	–			
HAP	< De	30	0.034	1.1	1.15	–	0.0059 – 0.9808	2.88	(29)
HAP	< De	45	0.045	1.15	1.04	–	0.0077 – 0.9812	3.41	(29)
HAP	< De	60	0.045	1.16	0.962	–	0.0103 – 0.9818	4.53	(29)
<b>Peleg model</b>			$A_{Pe}$	$B_{Pe}$	$C_{Pe}$	$D_{Pe}$			
CS	< De	30	0.1682	0.1563	9.7839	0.6722	0.0059 – 0.9808	4.8581	(32)
CS	< De	45	0.1697	0.1478	11.5091	0.7333	0.0077 – 0.9812	5.3209	(32)
CS	< De	60	0.1666	0.1419	11.7917	0.7504	0.0103 – 0.9818	6.6539	(32)

**Table 6.** Data for sorption isotherm models of cassava products. With RD, CD and SN respectively rotary, cabinet and sun dried fermented flour; \* standard error.

Product	Sorption	T (°C)	Coefficients				$a_w$ range	E (%)	Source	
<b>GAB model</b>			$X_m$	$A_G$	$B_G$					
tapioca flour	Ad >	25	0.0512	8.33	0.9	–	–	0.22 – 0.92	1.9	(33)
unfermented flour	Ad >	25	0.09	12.86	0.79	–	–	0.07 – 0.93	5.7	(34)
fermented flour	Ad >	25	0.0722	44.17	0.87	–	–	0.07 – 0.93	5.1	(34)
flour	Ad >	25	0.0731	34.96	0.8919	–	–	0.12 – 0.90	5.1541	(18)
flour	Ad >	35	0.0632	30.39	0.8677	–	–	0.12 – 0.90	3.1647	(18)
roots	Ad >	30	0.0616	12.9004	0.8939	–	–	0.1 – 0.9	0.035	(16)
roots	Ad >	45	0.0536	10.9047	0.8731	–	–	0.1 – 0.9	0.018	(16)
roots	Ad >	60	0.0366	5.6697	0.7498	–	–	0.1 – 0.9	0.008	(16)
fermented flour	Ad >	30	0.0556	5.2641	0.8835	–	–	0.1 – 0.9	–	(17)
fermented flour	Ad >	40	0.0553	4.6685	0.9117	–	–	0.1 – 0.9	–	(17)
fermented flour	Ad >	40	0.07352	0.601	0.070	–	–	0.05 – 0.84	4.088	(24)
fermented flour	Ad >	50	0.02544	0.087	0.749	–	–	0.05 – 0.84	10.510	(24)
extruded	Ad >	30	0.06092	21.954	0.973	–	–	0.1 – 0.9	–	(27)
tapioca flour	< De	25	0.0732	2.58	0.84	–	–	0.22 – 0.92	7.1	(33)
flour	< De	25	0.09	12.86	0.79	–	–	0.08 – 0.93	6.9	(34)
fermented flour	< De	25	0.0722	44.17	0.87	–	–	0.08 – 0.93	6.7	(34)
roots	< De	30	0.0696	11.9016	0.89	–	–	0.1 – 0.9	0.034	(16)
roots	< De	45	0.0536	10.9047	0.8731	–	–	0.1 – 0.9	0.028	(16)
roots	< De	60	0.0421	4.68	0.7379	–	–	0.1 – 0.9	0.009	(16)
fermented flour	< De	40	0.11644	0.683	0.076	–	–	0.05 – 0.84	5.085	(24)
fermented flour	< De	50	0.02360	0.105	0.793	–	–	0.05 – 0.84	10.593	(24)
extruded	< De	30	0.06410	60.882	0.974	–	–	0.1 – 0.9	–	(27)
<b>Oswin model</b>			$A_O$	$B_O$						
chips	Ad >	53	10.1	0.131	–	–	–	0.1 – 0.8	–	(23)
chips	Ad >	60	9.86	1.28	–	–	–	0.1 – 0.8	–	(23)
chips	Ad >	70	9.505	0.131	–	–	–	0.1 – 0.8	–	(23)
chips	Ad >	80	9.143	0.135	–	–	–	0.1 – 0.8	–	(23)
chips	Ad >	86	8.917	0.140	–	–	–	0.1 – 0.8	–	(23)
fermented flour	Ad >	27	0.075	0.390	–	–	–	0.05 – 0.84	6.011	(24)
grates	< De	30	0.110676	0.41373	–	–	–	0.05 – 0.80	–	(15)
grates	< De	40	0.105563	0.46305	–	–	–	0.05 – 0.80	–	(15)
grates	< De	50	0.0865496	0.58102	–	–	–	0.05 – 0.80	–	(15)
chips	< De	53	10.61	0.130	–	–	–	0.1 – 0.8	–	(23)
chips	< De	60	10.27	0.129	–	–	–	0.1 – 0.8	–	(23)
chips	< De	70	9.846	0.121	–	–	–	0.1 – 0.8	–	(23)
chips	< De	80	9.562	0.122	–	–	–	0.1 – 0.8	–	(23)
chips	< De	86	9.236	0.127	–	–	–	0.1 – 0.8	–	(23)
fermented flour	< De	27	0.079	0.405	–	–	–	0.05 – 0.84	10.311	(24)
<b>Modified Halsey model</b>			$A_{MH}$	$B_{MH}$	$C_{MH}$					
roots	< De	30 – 60	18.53	0.045	2.007	–	–	0.07 – 0.90	10.8*	(14)
gari	< De	40 – 70	10.07	0.01902	1.958	–	–	0.11 – 0.80	–	(13)
<b>Simplified GAB model</b>			$A_{SG}$	$B_{SG}$	$C_{SG}$					
mash	< De	40	-0.105	0.119E	0.0103	–	–	0.1 – 0.9	–	(22, 39)
mash	< De	60	-0.135	0.146	0.0114	–	–	0.1 – 0.9	–	(22, 39)
mash	< De	75	-0.110	0.121	0.0193	–	–	0.1 – 0.9	–	(22, 39)
mash	< De	90	-0.127	0.132	0.0244	–	–	0.1 – 0.9	–	(22, 39)
<b>Modified Henderson model</b>			$A_{MHe}$	$B_{MHe}$	$C_{MHe}$	$D_{MHe}$	$E_{MHe}$			
chips	< De	60 – 65	exp(-44.8)	8.66	-6.41	0.049	-6.7 · 10 <sup>-5</sup>	–	–	(28)
<b>Modified Chung-Pfost model</b>			$A_C$	$B_C$	$C_C$					
RD fermented flour	Ad >	25 – 45	482.15	-266.28	0.38643	–	–	0.11 – 0.96	3.3	(26)
CD fermented flour	Ad >	25 – 45	417.37	-269.25	0.39728	–	–	0.11 – 0.96	4.487	(26)
SD fermented flour	Ad >	25 – 45	412.50	-265.26	0.3914	–	–	0.11 – 0.96	3.905	(26)