ARTICLE IN PRESS

Engineering in Agriculture, Environment and Food xxx (2016) 1–7

Contents lists available at ScienceDirect

Engineering in Agriculture, Environment and Food

journal homepage: http://www.sciencedirect.com/eaef

Research paper

Thermodynamic properties of moisture adsorption in tef (*eragrostis tef*) seed

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ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form
24 February 2016
Accepted 6 May 2016
Available online xxx

Keywords:
Eragrostis tef
Sorption isotherms
Equilibrium moisture content

ABSTRACT

The moisture adsorption isotherms of *tef* (*Eragrostis tef*) seeds were studied under temperature and relative humidity ranges of 10–40 °C and 15–90%, respectively. The equilibrium moisture content (EMC) decreased with increase in temperature and increased with increase in relative humidity significantly ($p < 0.05$). The adsorption isotherms exhibited sigmoid shape (type II) which is common for most biological and food materials. The GAB and Peleg models best described the moisture adsorption characteristics of *tef* seeds resulting in high R^2 (0.99), low mean relative percentage deviation, E (<5%) and Root Mean Square Error (*RMSE*) values with random distribution of residuals. The thermodynamic properties determined in this study were net isosteric heat, differential entropy, spreading pressure, net integral enthalpy and net integral entropy. The net isosteric heats and the differential entropy decreased exponentially with increase in moisture content. The spreading pressure increased with increase in water activity. The net integral enthalpy decreased with increase in moisture content whereas the net integral entropy increased with increase in moisture content and remained negative in value.

1. Introduction

Tef (*Eragrostis tef*) is an important cereal crop indigenous to Ethiopia comprising about 20% of the cereal production in the country. The crop provides the major daily calorie for the vast majority of the population (Bultosa and Taylor, 2004). *Tef* seed is a millet-like, tiny and prolate spheroid with average length and width of 1.01 and 0.59 mm, respectively (Zewdu and Solomon, 2007). The proximate composition (db) of *tef* seed is reported to be 9.4–13.3% protein, 73% carbohydrate, 1.98–3.5% crude fiber, 2.0–3.1% fat and 2.5–3.0% ash (Bultosa and Taylor, 2004; Kebede, 2006).

Sorption isotherms present an equilibrium state of all processes wherein water molecules combine reversibly with food solids (Lewicki, 2000) and have number of important applications in foods. They are used in specifying safe equilibrium moisture content (EMC) during drying, safe storage and handling of food products (Basunia and Abe, 2005), specifying the packaging conditions and prediction of shelf life (Chowdhury et al., 2006; Erbas et al., 2005; Zhang et al., 1996). Sorption isotherms also help in understanding the physico-chemical changes involved in product making and handling processes (Chowdhury et al., 2006; Zhang et al., 1996). The moisture sorption characteristics of various food products including cereals, beans and peas (Sun, 1999; Sun and Woods, 1994), fruits and vegetables (Arslan and Toğrul, 2005b), snacks, breakfast cereals and other dry products (Palou et al., 1997) and flours and powders have been studied under different ranges of temperature and relative humidity. However, no information is available on the moisture sorption characteristics of *tef* seeds.

The influence of temperature and relative humidity on EMC have been studied and modeled extensively using theoretical, semi-empirical and empirical sorption models to describe moisture sorption characteristics of wide ranges of food products (Iglesias and Chirife, 1976, 1995; Lewicki, 1998, 2000; Peleg, 1993). However, each model has relative success in representing experimental sorption behavior of different food products depending on the relative humidity range used, the type and composition of the food and the interaction of the constituents of the food with water in

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http://dx.doi.org/10.1016/j.eaef.2016.05.001
1881-8366/

Nomenclature

A, B, C	model constants
A_m	area of water molecule (1.06×10^{-19} m^2)
a_w	water activity
E	mean relative percentage deviation (%)
EMC	equilibrium moisture content
ERH	equilibrium relative humidity
H_1	heat of condensation of pure water (kJ/mol)
H_m	heat of sorption of monolayer moisture (kJ/mol)
H_n	heat of sorption of multilayer moisture (kJ/mol)
k, x	model parameters in GAB model
k_0, x_0	GAB coefficients
$k_{1,2}$, $n_{1,2}$	constants in Peleg's model
K_B	Boltzmann's constant (1.38×10^{-23} J/K)
M	equilibrium moisture content (% dry basis)
M_m	moisture content corresponding to an adsorbed monolayer (% dry basis)
M_{exp}	experimental equilibrium moisture content (% dry basis)
M_{est}	estimated equilibrium moisture content (% dry basis)
N	number of data points
Q_{st}	Isosteric heat of sorption (kJ/mol)
q_{st}	net isosteric heat of sorption (kJ/mol)
R	universal gas constant (8.314 kJ/kmol/K)
R^2	coefficient of determination
RMSE	root mean square error
S_d	differential entropy (J/mol/K)
T	temperature (°C)
T_k	absolute temperature (K)
ΔH_1, ΔH_2	coefficients (functions of heat of sorption of water) (kJ/mol)

thermodynamic equilibrium conditions (Lasekan and Lasekan, 2000; Lewicki, 1998; Mcminn et al., 2007; Peleg, 1993).

Therefore, foods with the same chemical composition but diverse structure may not have the same equilibrium moisture content. Thus, experimental data of sorption are necessary even for chemically similar products to assess the applicability of the different isotherm equations while determining the specific parameters for each product under a set of temperature and relative humidity conditions (Vullioud et al., 2004; Mcminn et al., 2007). Nevertheless, no study has been conducted to identify models that can best describe the moisture sorption characteristics and thermodynamic properties of *tef* seeds.

It is necessary to know the EMC isotherms of and thermodynamic properties of tef for several relative humidities and temperatures since they give vital information for the designing a drying process condition and equipment. Moreover, the information would be used for proper choice of the optimum residual moisture content and the domain of stability and predict the optimum storage conditions of tef after drying (Chowdhury et al., 2006; Erbas et al., 2005). Knowledge and modeling of the EMC and thermodynamic parameters is also useful for numerical modeling of heat and mass transfer during the drying process of tef.

The objective of this work was to study the moisture adsorption characteristics and identify a suitable model that can adequately describe adsorption isotherms and thermodynamic properties of *tef* seeds under a set of temperature and relative humidity conditions.

2. Materials and methods

2.1. Sample preparation

Tef seed was procured from the local market and cleaned to remove foreign materials and impurities. The moisture content of the seed as brought from the market was determined by drying samples in a convective air oven set at 105 °C (±1 °C) for 24 h (ASAE, 1994) and was found to be 11.40% dry basis (d.b). Since this moisture was high to carry out the adsorption study, the seeds were dried at 40 °C for 10 h in hot air oven to reduce the moisture content to 6.05% (d.b.) (Basunia and Abe, 2005).

2.2. Adsorption tests

The adsorption experiments were conducted using temperature and relative humidity combinations of 10, 20, 30 and 40 °C and 15, 30, 45, 60, 75 and 90%, respectively. About 3 g of *tef* seed in aluminum foil cups was placed in programmable environmental chamber (Termax, type KBP 6395 F, Bergen, Norway) which control temperature and relative humidity with an accuracy of ±0.1 °C and ±0.1% RH, respectively. Similar method has been used in earlier moisture sorption studies of food materials (Arslan and Toğrul, 2005a, 2005b; Basunia and Abe, 2005; Toğrul and Arslan, 2006, 2007). Samples were weighed at time interval of 3–4 days using electronic balance (CP 124S, Data Weighing Systems, Gottingen, Germany) with 0.1 mg accuracy. Equilibrium was assumed to be attained when the difference between three consecutive weight measurements was less than 0.001 g (Singh et al., 2001). Reaching equilibrium condition took between 13 and 18 days depending on the temperature and relative humidity used. At higher temperature equilibrium was attained in shorter time. The moisture content was determined by drying samples in a convective air oven at 105 °C (±1 °C) for 24 h. Each test was repeated four times to determine mean values.

2.3. Fitting sorption isotherm models

The following frequently used EMC models were fitted to the data to describe the moisture sorption characteristics of *tef* seeds.

Modified Henderson (Thomson et al., 1968)

$$M = \left[\frac{\ln(1-a_w)}{-A(T+B)}\right]^{\frac{1}{C}} \tag{1}$$

Modified Chung-Pfost (Pfost et al., 1976)

$$M = -\frac{1}{C}\ln\left[\frac{(T+B)\ln(a_w)}{-A}\right] \tag{2}$$

Modified Halsey (Iglesias and Chirife, 1976)

$$M = \left[-\frac{\exp(A+BT)}{\ln(a_w)}\right]^{\frac{1}{C}} \tag{3}$$

Modified Oswin (Oswin, 1946)

$$M = (A+BT)\left(\frac{a_w}{1-a_w}\right)^C \tag{4}$$

Peleg's model (Peleg, 1993)