Measurement of Moisture Sorption Isotherm by DVS Hydrosorb

Y R Kurniawan¹,², Y A Purwanto², N Purwanti² and S Budijanto³
¹ Center for Appropriate Technology Development, Indonesian Institute of Sciences, Indonesia
² Department of Mechanical and Biosystem Engineering, Bogor Agricultural University, Indonesia
³ Department of Food Science and Technology, Bogor Agricultural University, Indonesia

E-mail: yorizkl@gmail.com

Abstract. Artificial rice made from corn flour, sago, glycerol monostearate, vegetable oil, water and jelly powder was developed by extrusion method through the process stages of material mixing, extrusion, drying, packaging and storage. Sorption isotherm pattern information on food ingredients used to design and optimize the drying process, packaging, storage. Sorption isotherm of water of artificial rice was measured using humidity generating method with Dynamic Vapor Sorption device that has an advantage of equilibration time is about 10 to 100 times faster than saturated salt slurry method. Relative humidity modification technique are controlled automatically by adjusting the proportion of mixture of dry air and water saturated air. This paper aims to develop moisture sorption isotherm using the Hydrosorb 1000 Water Vapor Sorption Analyzer. Sample preparation was conducted by degassing sample in a heating mantle of 65°C. Analysis parameters need to be fulfilled were determination of Pₒ, sample data, selection of water activity points, and equilibrium conditions. The selected analytical temperatures were 30°C and 45°C. Analysis lasted for 45 hours and curves of adsorption and desorption were obtained. Selected bottom point of water activity 0.05 at 30°C and 45°C yielded adsorbed mass of 0.1466 mg/g and 0.3455 mg/g, respectively, whereas selected top water activity point 0.95 at 30°C and 45°C yielded adsorbed mass of 190.8734 mg/g and 242.4161mg/g, respectively. Moisture sorption isotherm measurements of artificial rice made from corn flour at temperature of 30°C and 45°C using Hydrosorb showed that the moisture sorption curve approximates sigmoid-shaped type II curve commonly found in corn-based foodstuffs (high-carbohydrate).

1. Introduction
Artificial rice, also called rice analogues, is made from local carbohydrate sources besides rice and wheat flour. This rice was created in response to the problem of the availability of rice as the staple foods. The high consumption of rice that is not offset by increase in rice productivity has the potential to flooding of imported rice in market. In addition, increasing consumption of food made from wheat flour that in fact is made from imported wheat makes out the local carbohydrate sources such as cassava, corn, sweet potatoes and so on [1].

IPB as a leading agricultural education institution has been researching and developing artificial rice. Artificial rice produced mini-plant scale and has been spread on the market. The artificial rice is
produced using extrusion technology and is made from the main ingredients of corn flour and sago as well as some other additives. The fabrication process of artificial rice using extrusion process passes several stages commonly used by other extruded products i.e. formulation, extrusion, and drying. After process of drying, artificial rice is packed and stored before it is distributed.

One of the most influential food properties in production process of artificial rice is moisture sorption isotherm. Sorption isotherm is relationship between water activity with moisture content of food materials at certain temperature and pressure (equilibrium moisture content). The pattern of water sorption isotherm shows interaction between food with water molecules contained therein and the water molecules in surrounding air. Equilibrium moisture content because material lost water (desorption) can be useful for drying process analysis, and equilibrium moisture content that occurs due to material adsorb water (adsorption) to determine storage method.

Study of measurement sorption isotherm generally still using the traditional method of saturated salt slurry method, no exception for Indonesia. This method has disadvantages of long period of measurement time and periodic handling of samples. Nowadays, there is new method, well-developed method, that is humidity generating method or better known as Dynamic Vapor Sorption (DVS) method. DVS technique is performed using instrument that utilize divided flow technology. This technology allows the instrument to generate sorption isotherm in relatively short period of time. User selects the desired relative humidity or relative humidity series using the program computer. Relative humidity is automatically controlled by mass flow controller, dry air flow and wet air flow, by mixing them in right ratio will yield selected relative humidity. Sample is conditioned in desired relative humidity, then mass or volume of sorption is measured. The instrument is automatically programmed to cycle between humidity levels, and keeps the humidity constant in each level until equilibrium is reached [2][3].

There are already some commercially available brands as mentioned by Mermelstein [3]: Dynamic Vapor Sorption (UK), IGA-Sorp (England), VTI and Q5000SA (USA), Cisorp Water Sorption Analyzer (UK), SPS Moisture Sorption Analyzers (Germany), Hydrosorb™ 1000 Water Vapor Sorption Analyzer (USA), AquaSorp Isotherm Generator (USA). This DVS method has a number of advantages compared to the saturated salt slurry method. The equilibrium time is around 10 to 100 times faster than the standard method. The DVS instruments are automated and use computer interface thereby reducing need for supervision work of the slurry methods and maintaining relative humidity over the duration of the experiment.

Most of the above mentioned DVS instruments work gravimetrically by measuring mass changes per unit of time, and partly volumetrically by measuring pressure changes. Hydrosorb™ 1000 analyses by vacuum-volumetric system and figure 1 shows the instrument. Hydrosorb™ 1000 is better known as apparatus for measuring surface area and porosity. This paper aims to develop moisture sorption isotherm using the Hydrosorb™ 1000 Water Vapor Sorption Analyzer.
2. Materials and methods

2.1. Materials and equipments
Artificial rice samples were rice analogues manufactured by FITS Mandiri, Taman Kencana Science Park, Bogor, Indonesia. Artificial rice made from corn flour, sago, glycerol monostearate, vegetable oil, water and jelly powder was developed by extrusion method. The artificial rice has been sold commercially. Equipment were used in this study: Differential Scanning Calorimeters DSC 60 Shimadzu, Water Vapor Sorption Analyzer Quantachrome Hydrosorb™ 1000, desk computer, drying oven, 10 mL measuring cylinder, desiccator, and analytical balance.

2.1.1. Moisture content and bulk density Clean empty cup is dried in an oven at temperature of 100±5°C until it weighs constant (1 hour). The cup is cooled in desiccator for 30 minutes and weigh (W_o). Two to three grams of sample are weighed in the cup (W_1). The cup containing the sample is dried in a drying oven at temperature of 103-105°C to constant weight. The cup containing the dried sample is cooled in the desiccator for 30 minutes and weigh (W_2). Weight-loss is calculated as moisture content (m) using equation (2.1).

\[ m(\%) = \left( \frac{W_1 - W_o}{W_1 - W_o} \right) \times 100\% \]  

(2.1)

Bulk density is total granules mass occupying a particular volume unit. Rice analogues sample was poured into a certain known volume from a fixed height and mass of samples occupying the volume as determined. Ratio was calculated as g/mL [4].

2.1.2. DSC Analysis. Thermal characteristics of artificial rice were analyzed by using DSC 60 Shimadzu, Tokyo, Japan. The artificial rice were ground into flour and about 3 mg was weighed in a special sample container (pan cell no. 20153090). Distilled water 10 μL was added using a micropipette and then the pan cell was sealed tightly. The pan cell containing sample and the distilled water were rested for 2 hours at room temperature to achieve equilibrium. The pan was then heated from 40°C to 120°C with heating rate of 5°C/min[5].
2.2. Apparatus Hydrosorb 1000

Hydrosorb is innovation in moisture sorption characterization and works automatically to rapidly measure adsorption and desorption isotherms of water, including BET surface area calculations and heats of adsorption. Adsorbent temperature is thermostatted in the range 12-47°C or 12-85°C using thermal jacket controlled by temperature circulator bath with accurate water vapor dosing performed by special, heated (100°C) manifold design. Hydrosorb-1000 is the constant-volume variable-pressure (cvvp) apparatus and volumes of charging and dosing were calibrated by charging nitrogen gas (N2) with purity of 99.99%. The standard volume had been calibrated by liquid filling method using distilled water[6]. The integrated control system provides real-time status, graphical data review and reporting functions via built-in color monitor and printer port.

Control system of the Hydrosorb among others:

1. Computer
   The main parts of computer include computer controls, TFT display monitor and keypad. In the computer controls there is a button to activate Hydrosorb computer and set up the display monitor. TFT monitors displays the status of Hydrosorb operation, and to the right of the monitor is a keypad. Alternatively, standard keyboard can be connected to the computer via connection jack on the lower right of the keypad.

2. Panel and port
   There are main power switch and serial port in rear panel. Main power switch controls power across instrument including oven manifold and computer. When the button is ON, the power is supplied to Hydrosorb, although the computer and the oven might be switched off. RS-2232 serial port serves to relate Hydrosorb to an external PC for control, enhanced data reduction and reporting capabilities using HydroWin software. Gas connection connects high-purity nitrogen supply. Gas regulator must be set to deliver 10 psig (70 kPa). Vacuum pump is connected to back of Hydrosorb via vacuum fitting using vacuum hose.

3. Degasser
   Degassing of sample is performed insitu using built-in heating mantle. Main components are heating mantle and temperature control. Temperature control regulates the temperature of the heating mantle. Degasser is also equipped with thermocouple, LED temperature display, and power switch.

4. Oven
   Water for analysis is stored in the water reservoir in a vial glass installed inside the oven. The oven functions to heat the water vapor dosing system and has been equipped with temperature controller and oven power switch. The appropriate operating temperature has already been set to 100°C. Adjacent to the water reservoir, there are needle valve settings for N2 inlet, vapor source inlet, and fine vacuum inlet that have been pre-set at factory and need to be adjusted periodically.

5. Analysis station
   Sample cell is mounted on sample station secured by bulkhead fitting. Sample cells are available with 3 diameters choice conforming sample size, outside diameters of stem 6, 9, and 12 mm. Bulkhead fitting equipped with Viton O-ring, adaptersleeve and retainer ring, serves to keep the sample cell with a vacuum firm seal to the bulkhead on the analysis port. Dewar is used in conjunction with external water bath circulator (figure 2) and functions to thermostat the sample cell at the desired isothermal temperature. The bath circulator allows analysis at different temperature.
Figure 2. Dewar and steps to use [6][7].

Significant components in the Hydrosorb system are manifold and three-way valve[8]. Working principle of the system is preceded by pressure conditioning (using vacuum pump) in the Hydrosorb and sample cell. After the pressure has stabilized, water vapor is supplied to the manifold until the desired relative pressure is reached. Then, the water vapor is channeled into the sample cell so that the vapor occupy the sample cell. As water molecules adsorb on the sample, the pressure in the sample cell will drop until the relative pressure reaches equilibrium. Pressure change that occur at equilibrium will be calculated to obtain the volume/mass of adsorbed water vapor. Three-way valve plays key role of monitoring the pressure in the manifold and in the sample cell alternately.

3. Results and discussion
Determination of water sorption curve was carried out at 30°C and 45°C. At temperature 30°C, the measurement was carried out by adsorption at water activity of 0.05-0.95 by an increase of 0.05 steps, and at temperature of 45°C was performed by adsorption and desorption at water activity of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.85, 0.9, and 0.95. Measurement using DVS Hydrosorb can only be done for one sample, thus for analysis with different sample must be resetting.

3.1. Material characterization
Preliminary measurement should include moisture content, density, and glass transition point. The density value will be input in filling the parameters of sample when initiating the analysis, whereas from the measurement of moisture content using oven method, it can be estimated the moisture content after sample preparation stage or before the start of the analysis. The glass transition point becomes degassing temperature limit. The degassing temperature, as a general guideline, must be kept below glass transition point to prevent undesirable changes in the structure of the material. Valuable glass transition point information can be collected from thermal analysis, particularly DSC (differential scanning calorimetry) and TGA (thermogravimetric) analysis.
The bulk density was 0.58 g/mL, while the sample moisture content of measurement at the sorption temperatures of 30°C and 45°C were 14.74% db and 14.39% db, respectively. The result of the thermal characteristic test in DSC was thermogram presented in figure 3. The thermogram shows the presence of two melting curves at temperatures around 75°C and 93°C. It means the gelatinization temperature is at the top of the first melting curve at 75.37°C and has curve peak point/melting point of 93.74°C. There is no shift that can indicate glass transition point. Herawati et al. [9] stated that determination of glass transition point using conventional linear heating in DSC was very difficult. Glass transition temperature of instant artificial rice was determined by isothermal relaxation method in DSC. The result of analysis using Gordon-Taylor formula approach predicted glass transition temperature 75.5°C.

3.2. Sample regeneration

Each sample should be degassed before performing an analysis to remove unwanted contaminants or vapors in the sample. Degassing is executed in-situ by placing approximately 0.5 g of sample in the sample cell and then dried in the heating mantle. The degassing variables are temperature and time. The proper temperature of degassing varies depending on the chemical structure of the material and the desired dryness state. The degassing time varies according to the initial moisture level, porosity and temperature used. To improve sample preparation capability, additional instruments can be used for flow outgassing and vacuum outgassing.

The temperature used for artificial rice degassing was 65°C. Determination of degassing temperature was based on Herawati et al.[9] which states that the glass transition temperature of instant artificial rice made from corn flour is 75.5°C. The degassing temperatures used are still relevant to the conditioning of samples performed on the research of sorption isotherm by Wulandari and Soekarto [10] which dried material up to 2% moisture content by heating the sample at oven temperature of 70°C. During the degassing process, water spots stick to the sample cell wall indicating the water contained in the material is gradually released. Degassing can be stopped by disappearance of water spots on the sample cell wall.
3.3. Sample analysis

After completing all parameters in the “Start Analysis” window (figure 4), the user can click “Start” box to commence analysis. Sample analysis progress can be monitored in continuation window. The total analysis time might be hours or days depending on the quantity and type (hydrophobic, hydrophilic, porous or non-porous) of sample. The results of water sorption isotherm analysis of the artifical rice at temperature of 30°C and 45°C are presented in figure 5. The sorption isotherm at 30°C was measured at 19 points of adsorption taking place for approximately 25 hours, whereas at temperature of 45°C was analyzed at 26 points of adsorption-desorption for about 36 hours.

Figure 4. Window of “Start Analysis” [11].
Figure 5. Water sorption isotherms of artificial rice at 30°C and 45°C.

Water sorption curve expressed in water activity ($a_w$) in abscissa and adsorbed mass (mg/g) in ordinate. Selected bottom point of water activity 0.05 at 30°C and 45°C yielded adsorbed mass of 0.1466 mg/g and 0.3455 mg/g, respectively, whereas selected top water activity point 0.95 at 30°C and 45°C yielded adsorbed mass of 190.8734 mg/g and 242.4161 mg/g, respectively. By converting adsorbed mass unit from mg/g to g/100g, it will be retrieved curves illustrating the relationship between water activity ($a_w$) with the equilibrium moisture content (% dry basis) which are more commonly encountered in water sorption isotherm curve. At the lowest water activity (0.05), samples of artificial rice show different levels of moisture content, which at the analysis temperature of 30°C by 0.02% and at temperature of 45°C by 0.04%. At the highest water activity (0.95), the equilibrium moisture content at 30°C and 45°C were 19.1% and 24.2%, respectively.

The characteristic of moisture sorption isotherms showed the increase in equilibrium moisture content is positively correlated with the water activity at fixed temperature [12]. The higher the relative humidity level the more water is adsorbed by the artificial rice. Initially the rapid increase in equilibrium moisture content occurs in the first layer ($a_w < 0.5$), known as monolayer moisture. In this layer, single water adsorption occurs on the material. The second layer occurs above the monolayer until activity water of about 0.7-0.8, known as multilayer moisture showing the water adsorption transition from free state to chemically bonded state. The third layer is an area with rich of free water content [13][14].

The research of moisture sorption isotherm of instant artificial rice and commercial rice by Herawati [15] showed that the pattern of moisture content graphic of commercial rice is higher than instant artificial rice. Measurement of equilibrium moisture content using saturated salt solution resulted in moisture content of 28.8% db and 28.1% db for paddy rice and instant artificial rice at water activity 0.97, respectively. At the lowest water activity 0.08, equilibrium moisture content were 5.3% db and 4.6% db for paddy rice and instant artificial rice, respectively. The experimental artificial rice used glycerol mono-stearate and vegetable oil which are hydrophobic component, while the instant artificial rice used glycerol mono-stearate. The hydrophobic components are thought to affect the material’s binding capacity to water. Hydrophobic component factor and addition of alginate hydrocolloid of instant artificial rice are suspected to be the cause of higher equilibrium moisture content than experimental artificial rice at various levels of water activity.
Curves of moisture sorption isotherm of experimental artificial rice close to type II, resembling sigmoid shape or like the letter S. Labuza [16] classifies moisture sorption isotherm curves into 3 types, namely type I is Langmuir type, type II is sigmoid or S-shaped curve and type III (Flory-Huggins) which is shaped like the letter J. The moisture sorption isotherm curve has a sigmoidal shape in many foods, although for foods with high sugar content or low soluble molecules having sorption curve in the form of J. J-shaped curves are typical of products holding small quantities of water at lower αw levels and higher quantities of water at high αw values. Dry food ingredients generally include sorption isotherm of type II. Corn and its derivative products such as corn flour, corn starch, corn snack, tortilla, instant artificial rice belong to the group [17][18][19][20][21][22]. The type II sorption isotherm curve is due to the accumulative effect of hydrogen bonding, Raoult law, capillaries, and the interaction between the surface of the material and the water molecule. The type II sorption curves are common pattern in amorphous food systems. The carbohydrates and starches used are mostly amorphous materials.

Moisture sorption isotherm curve at 45°C is presented by adsorption and desorption so that it appears hysteresis. In many cases, the adsorption and desorption curves do not coincide so that hysteresis phenomena are discovered. In this state, the adsorption process produces a lower equilibrium moisture content than the desorption process. Large hysteresis size occurs in multilayer areas. Material characteristics affect the size of hysteresis [10].

4. Conclusions
Thermal characterization of test material needs to be done to determine the degassing temperature. The degassing temperature used for experimental artificial rice was 65°C. Degassing can be completed after water spots on the sample cell wall have disappeared. The results of moisture sorption isotherm of aritificial rice made from corn flour at temperature of 30°C and 45°C using Hydrosorb showed that the moisture sorption curve approximates sigmoid-shaped type II curve commonly found in corn-based foodstuffs (high-carbohydrate). The content of hydrophobic material and hydrocolloid material in the artificial rice composition are thought to affect the water holding capacity so that it affects the moisture sorption isotherm curve.

References
[1] Budijanto S and Yuliyanti 2012 Study of preparation sorghum flour and application for analogues rice production J. Teknol. Pertan.13 177-86
[2] Yu X 2007 Investigation of Moisture Sorption Properties of Food Materials Using Saturated Salt Solution and Humidity Generating Techniques PhD thesis(Urbana: University of Illinois at Urbana-Champaign) p73
[3] Penner E A 2013 Comparison of the New Vapor Sorption Analyzer to the Traditional Saturated Salt Slurry Method and the Dynamic Vapor Sorption Instrument thesis (Urbana: University of Illinois at Urbana-Champaign) pp 15-6
[4] Singh N, Kaur L, Sodhi N S and Sekhon K S 2005 Physicochemical, cooking and textural properties of milled rice from different Indian rice cultivars Food Chem.89 253-59
[5] Gelders G G, Vanderstukken T C, Goeaert H and Delcour J A 2004 Amylose–lipid complexation: a new fractionation method Carbohydr. Polym.56 447–58
[6] Cevallos O R F 2012 Adsorption Characteristics of Water and Silica Gel System for Desalination Cycle thesis (Thuwal: King Abdullah University of Science and Technology)
[7] Hydrosorb Manual 2007 Hydrosorb 1000 Operating Manual(Boynton Beach: Quantachrome Corporation) p 23
[8] Seymour L 2006 Apparatus and Method for Water Sorption Measurement US patent 2006/0027014A1 pp 3-4
[9] Herawati H, Kusnandar F, Adawiyah D R, Budijanto S and Rahman M S 2014 Thermal characteristics and state diagram of extruded instant artificial rice Thermochimica Acta593 50-7
[10] Wulandari N and Soekarto S T 2003 Hysteresis phenomena of moisture sorption isotherm in amylose, amylopectin, protein and cellulose J.Teknol. dan Ind. Pangan14 21-8
[11] HydroWin Manual 2007 HydroWin 5.0+ Operation Manual (Boynton Beach: Quantachrome Corporation)
[12] Oliveira E G, Rosa G S, Moraes M A and Pinto L A A 2009 Moisture sorption characteristics of microalgae Spirulina platensis Brazilian J. Chem. Eng.26 189-97
[13] Widowati S, Herawati H, Syarief R, Suyatma N E and Prasetia H A 2010 Effect of moisture sorption isotherm to stability of “sweet potato rice” J. Teknol. dan Ind. Pangan21 123-8
[14] Menkov N D and Durakova A G 2007 Moisture sorption isotherms of sesame flour at several temperatures Food Technol. Biotechnol.45 96–100
[15] Herawati H 2015 Process Optimization, Moisture Sorption Isotherm Profile and Thermal Analysis of Instant Artificial Rice PhD thesis (Bogor : Bogor Agricultural University) pp 76-83
[16] Labuza T P 1984 Moisture Sorption: Practical Aspects of Isotherm Measurements in Use (St Paul : American Association of Cereal Chemist)
[17] Sukainah A, Tawali A B, Salengke and Laga A 2013 The effect of fermentation on adsorption isotherm corn flour and corn crackers Int. J. of Sci. and Tech. Research2 263-7
[18] Budijanto S, Sitanggang A B and Kartika Y D 2010 Shelf life study of tortilla using accelerated shelf life testing method and its mathematical modelling of moisture sorption isotherms J. Teknol. dan Ind. Pangan21 165-70
[19] Aini N, Prihananto V and Wijonarko G 2014 Moisture sorption isotherm of instan corn flour from four variety of corn Agritech34 50-5
[20] Palou E, Lopez-Malo A and Argaiz A 1997 Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks J. of Food Eng.31 85-93
[21] Peng G, Chen X, Wu W and Jiang X 2007 Modeling of water sorption isotherm for corn starch J. of Food Eng.80 562-7
[22] Oyelade O J, Tunde-Akintunde T Y, Igbeke J C, Oke M O and Raji O Y 2008 Modelling moisture sorption isotherms for maize flour J. of Stored Prod. Research44 179-85