Determination of Vapor Pressure in Vapor-Induced Puffing

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Water vapor pressure for cornstarch and popcorn grits at a temperature of between 100 and 180°C was determined by measuring vapor pressures generated at various moisture contents in a heated, closed system. At a higher temperature, fugacity of water increased with increasing temperature probably because of melting or partial melting of starch. The apparent heat of sorption for cornstarch changed significantly with moisture content and temperature. Noncondensible gases were produced by heating popcorn grits to temperatures above 150°C. It is not accurate to estimate vapor pressure based on the heat of sorption or extrapolation of currently used empirical isotherm equations to a temperature above 100°C. Vapor pressure inside popcorn at the instant of popping are roughly 758 to 827 kPa (110 to 120 psia).

Introduction

Vapor pressure or heat of sorption vs. moisture content data in the temperature and moisture content ranges involved in puffing of starch-based products can provide understanding about how vapor pressure changes inside pores during puffing. Vapor pressure affects growth of pore and setting of porous structure during puffing. The porous structures strongly affect the texture and quality of products.

Methods for determining vapor pressure or water activity, a_w, based on the use of saturated aqueous salt solutions between 10 and 80°C have not been standardized for higher temperatures. High-temperature isotherms or vapor pressure, however, can be obtained by measuring temperatures and steam pressures generated when samples with known moisture content are heated in microretorts or closed systems.

At equilibrium, the internal vapor pressure, P_i, within particles is given by:

$$\phi = \frac{f}{P_i} \tag{1}$$

where f is the fugacity or saturated vapor pressure of water at the particle temperature and ϕ is the fugacity coefficient of water at that temperature and the local moisture content. If water-sorption-isotherm plots or equations were available for puffy materials at temperatures of interest, vapor pressure during puffing could easily be estimated or calculated. Unfortunately, isotherms are not available in the temperature range usually needed, 100 to 200°C. A review of isotherms listed in the survey of Wolf et al. (1983) shows that the maximum temperature reported for sorption isotherms of corn is 68°C.

Use of isotherm equations, for example, the Henderson equation or the Chung equation (ASAE Standard, 1985), in which temperature is considered as a variable, to predict a_w at temperatures of interest involve considerable extrapolation. The reliability of the predicted a_w is doubtful. For instance, the desorption and adsorption isotherms of the Chung equation were based on only two temperature levels, 22 to 25°C and 50°C (Chung and Pfost, 1967). For yellow dent corn containing 12% d.b. (dry basis) moisture, the Henderson equation predicts $a_w = 0.87$ at 180°C; the Chung equation yields $a_w = 0.82$ at the same conditions.

Heats of sorption, ΔH_s (kJ/kg), can also be used to predict P_i or a_w at a higher temperature, T_2, from P_i or a_w values at a lower reference temperature, T_1, for the same moisture content (Labuza, 1968; Iglesias and Chirife, 1976; Loncin, 1980; Labuza et al., 1985), that is,

$$\ln\left(\frac{P_{i2}}{P_{i1}}\right) = \left(\frac{18.02 \cdot \Delta H_s}{R}\right)\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \tag{2}$$

$$\ln\left(\frac{a_{w2}}{a_{w1}}\right) = \left(\frac{18.02}{R}\right)(\Delta H_s - \Delta H_v)\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \tag{3}$$

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where ΔH_v is the latent heat of vaporization per unit mass of water; $R = 8.314$ kJ/(kg·mol·K). Labuza et al. (1985) reported that the Clausius-Clapeyron equation predicted a_w quite well for fish flour and corn flour in the temperature range of 25-65°C, but ΔH_s may change quite radically at higher temperatures. van den Berg (1981) found that using measured heats of wetting and Eq. 3, the calculated a_w agreed with a_w obtained from sorption data for the 2-67°C range. Using $(\Delta H_s - \Delta H_v) = 640$ kJ/kg and a_w for 8% d.b. moisture content at 340 K, Eq. 3 yields $a_w = 0.83$ at 187°C (460 K), which was somewhat closer to the a_w from the Chung equation than that from the Henderson equation. However, van den Berg noted that ΔH_s and sorption behavior tended to shift above 100°C. At higher temperatures, changes in chemical composition and physical structure may affect ΔH_s values.

Thermal treatment of dry starch ultimately leads to depolymerization. At elevated temperatures, depolymerization of starch is accompanied by evolution of gases produced by various thermally induced reactions. Since most puffing processes are performed at temperature higher than 100°C, thermal decomposition may significantly affect sorption equilibria as well as puffed product quality attributes such as color and odor. Therefore, thermal decomposition must also be considered when measuring equilibrium vapor pressures in closed systems.

Appreciable decomposition of starch, to produce gases and lower molecular weight residues, occurred at 200°C at atmospheric pressure (Tomasik, 1989). Decomposition of starch in the 200 to 500°C range shows two maxima in yields of gaseous products evolved, roughly 250 and 400°C. In the first, CO_2 and CO in a 2:1 ratio are produced, and the second, CH_4 and unsaturated hydrocarbons (C_nH_{2n}). Thermal decomposition of starch could occur at temperature below 200°C because of high vapor pressures that developed in puffing processes. Color changes due to thermal decomposition of starch depend on the time and temperature of roasting. The chemical nature of colored products from cornstarch seems to be closely related to the colored compounds of caramel.

The objective of this study was to determine water vapor pressures developed inside starch-rich materials in temperature and moisture content ranges of interest in puffing, and to provide better information about how vapor pressure changes inside pores during puffing.

Materials and Methods

Cornstarch and popcorn grits were used to study high temperature sorption isotherms. Pure cornstarch was supplied by Best Foods, CPC International, Inc., Englewood Cliffs, NJ. Popcorn used in this study was commercial yellow popcorn "Bonnie Lee" distributed by Weaver Popcorn Co., Inc., Van Buren, IN. After purchase, they were stored in airtight glass bottles at room temperature before further treatment. Samples were slowly dehydrated or rehydrated to provide desired moisture contents, and equilibrated in sealed glass containers at least 72 h at room temperature. Samples whose moisture content had been adjusted were kept in a refrigerator at 4°C at least one week before testing and mixed every day by turning the container upside down 20 times. Before each test, samples were equilibrated at room temperature 24 h. Popcorn grits were prepared by grinding 30-g of popcorn in a coffee mill for 5-10 s. The moisture contents of cornstarch and popcorn grits were determined with replications by the official AOAC oven method (drying a 5-g sample at 130±3°C for 1 h).

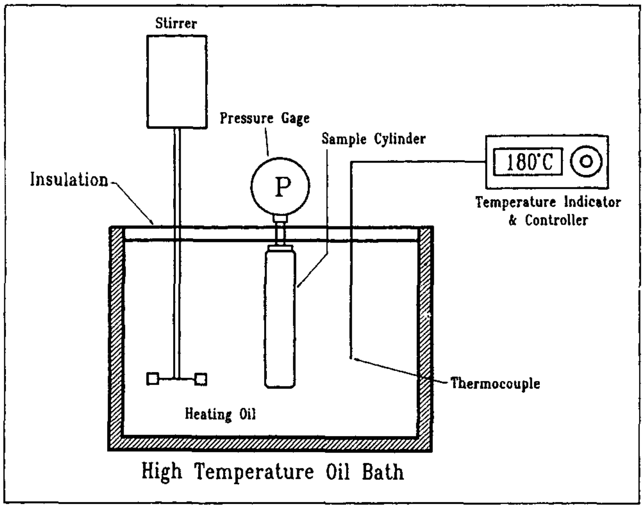

Figure 1. Apparatus used to measure equilibrium vapor pressures of starch-rich materials at high temperature.

Since it was difficult to determine vapor pressure developed inside starchy materials at temperatures and moisture contents of interest in puffing, samples were put in a heated, closed 50-mL stainless steel cylinder with attached pressure gage and total pressures were measured in duplicate at different temperatures and moisture contents (see Figure 1). 20-mL sample whose volume and density had been previously measured using a pneumatic pycnometer (stereopycnometer, Quantachrome Corp.) was put inside the sample cylinder and sealed tightly. Then, the cylinder was heated to the desired temperature in an oil bath (Fisher, HI-TEMP Bath, Model 160). Four different temperatures (100, 125, 150 and 180°C) were tested.

Calibration was required because partial pressure increased due to the gases initially present in the headspace. The apparent total pressure, P_t, was the sum of the vapor pressure, P_v, and the air pressure, P_a plus the systematic error, E_s:

$$P_t = P_v + P_a + E_s \tag{4}$$

Errors occurred when the ideal gas law was used to calculate P_a at elevated temperatures. These probably occurred because of heating the Bourdon pressure gage. To determine P_v from measured values of P_t, the air pressure inside the heated capsule was accounted for. The system was calibrated by using pure water at each temperature. At constant temperature, the equation for calibration is:

$$P_{st} - P_{sv} = P_a + E_s = \alpha \tag{5}$$

for actual measurement is:

$$P_v = P_t - \alpha \tag{6}$$

where P_{st} is total pressure at T (°C) during standardization tests; P_{sv} is saturated vapor pressure of water. α was a function

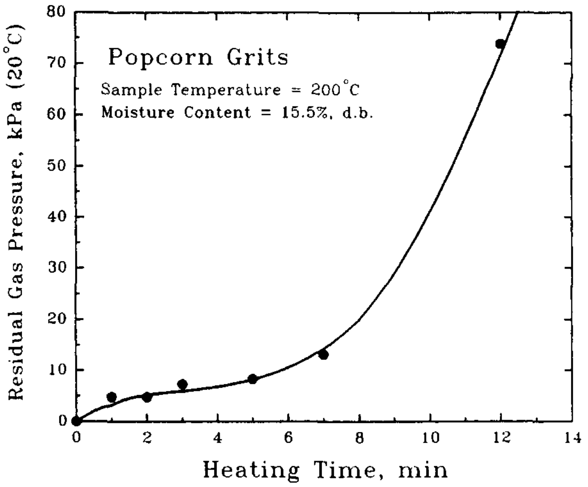

Figure 2. Residual gage pressure (at 20°C) generated by thermal decomposition of popcorn grits 200°C.

of temperature and sample volume, which increased as temperature increases. Constant volumes of sample and headspace were used. Since Dalton's law of partial pressures is reasonably valid, it can be assumed that P_a and α remain constant at constant temperature and headspace volume. For 20-ml sample volume, the values of α were -28, -74, -141 and -195 kPa at 100, 125, 150 and 180°C, respectively.

Total pressure was recorded at successive times until equilibrium was reached, that is, no further change in total pressure. This usually took about 60 min when measuring high equilibrium vapor pressure. Moisture evaporates from foods during heating. Based on the temperature and vapor pressure, the specific volume of vapor, v, was estimated from the superheated steam tables.

$$W_{ds}\cdot(M_i-M_e)=\frac{V_h}{v} \tag{7}$$

$$M_e=M_i-\frac{V_h}{W_{ds}\cdot v} \tag{8}$$

where M_i = initial moisture content of starch (d.b.); M_e = equilibrium moisture content of starch (d.b.); W_{ds} = weight of dry solid, gram; V_h = volume of the head space, cm^3. The volume of head space was roughly 33 cm^3. For this volume, the sample volume used, and typical v in the temperature ranges used, the sample moisture content did not change by more than 0.4%.

Calibration for noncondensible gases

Total pressures usually equilibrated after 1 h heating during measurements of equilibrium vapor pressures. If total pressure continued to rise and exceeded the vapor pressure of water, as occurred at 150 and 180°C with popcorn grits, heating was stopped at a time at which pressure normally equilibrated. The popcorn grits became progressively browner and developed a progressively stronger, burned odor during the course of heating. The cylinder was cooled to room temperature, and the residual gage pressure, which indicated that noncondensible gases had been produced, was measured. Therefore, the partial pressure of noncondensible gases, P_g, was accounted for estimating the vapor pressure:

$$P_t=P_v+P_g+P_a+E_s \tag{9}$$

P_g strongly depended on temperature and heating time. At 100 and 125°C, the residual gage pressure after heating was zero. To determine pressure contributions caused by noncondensible gases, excess gage pressures present after the cylinder was cooled to room temperature were recorded. These excess pressures were multiplied by the absolute temperature ratio (T/T_{room}) to calculate the partial pressure of noncondensible gases at the test temperature. This pressure, P_g, along with α, was subtracted from the total gage pressure measured at T to determine the vapor pressure. P_g equaled 81 kPa at 150°C after 2 h heating; and 124 kPa at 180°C after 30 min heating. Figure 2 shows the residual gage pressures at room temperature which were produced by heating of popcorn grits with 15.5%, d.b. moisture content at 200°C. The moisture content apparently did not affect the value of P_g. Since noncondensible gases formed for popcorn at 150 and 180°C (Table 1) although they did not form for cornstarch, the reaction involved is likely one between protein and starch. Popcorn contains 79.9% carbohydrate and 13.2% protein (Watt and Merrill, 1975).

Table 1. Noncondensible Gas Pressure, P_g, When Popcorn Grits with Various Moisture Contents were Heated at 150 and 180°C

Moisture %, Dry Basis	Temperature 150°C*	180°C**
7.2	75.8±2.8 kPa	49.6±5.5 kPa
11.5	79.3±3.4 kPa	134.4±4.8 kPa
15.5	77.2±3.4 kPa	134.4±5.5 kPa
20.7	79.3±3.4 kPa	120.7±4.1 kPa
26.0	75.8±2.8 kPa	120.7±6.2 kPa
35.2	96.5±4.8 kPa	141.3±6.2 kPa

*Samples were heated at 150°C for 2 h.
**Samples were heated at 180°C for 30 min.

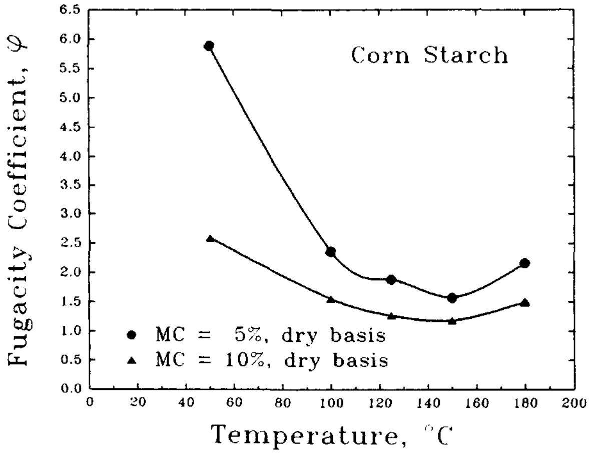

Figure 3. Fugacity coefficient of water vs. temperature for cornstarch at constant moisture content.

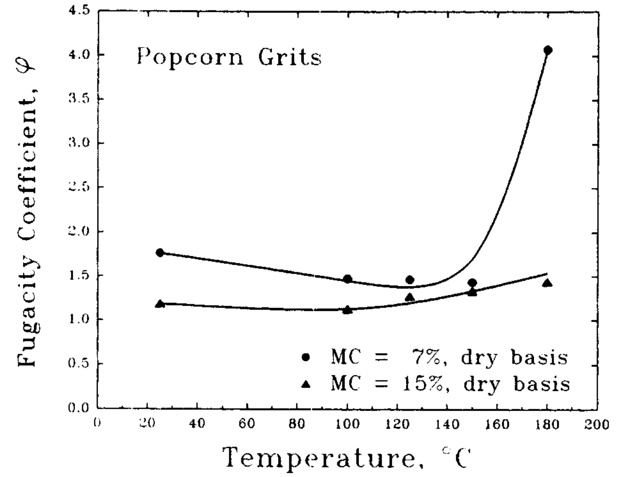

Figure 4. Fugacity coefficient of water vs. temperature for popcorn grits at constant moisture content.

Results and Discussion

Figures 3 and 4 show fugacity coefficient of water vs. temperature at constant moisture content for cornstarch and popcorn grits, respectively. At low moisture contents (< 11%, d.b.) and temperature below 180°C, the fugacity coefficient of water, ϕ, for cornstarch decreased with increasing temperature; but ϕ increased as temperature increased in the 150–180°C range. Similar changes occurred for popcorn grits at 7% moisture content. At 15% moisture content, ϕ vs. temperature behavior for popcorn was somewhat dissimilar. The chemical composition and physical properties of cornstarch and popcorn grits changed at 180°C. For cornstarch with 5% and 10% moisture contents, an endothermic phase transition occurred at 180°C (Wu, 1991). This may be the reason why the fugacity coefficient of water increased at 180°C. The phase transitions of popcorn grits behaved differently from cornstarch. A phase transition occurred at 180 and 160°C for popcorn samples with 7% and 15% moisture contents, respectively. Therefore, the fugacity coefficient of water for sample with 15% moisture started to increase at lower temperature.

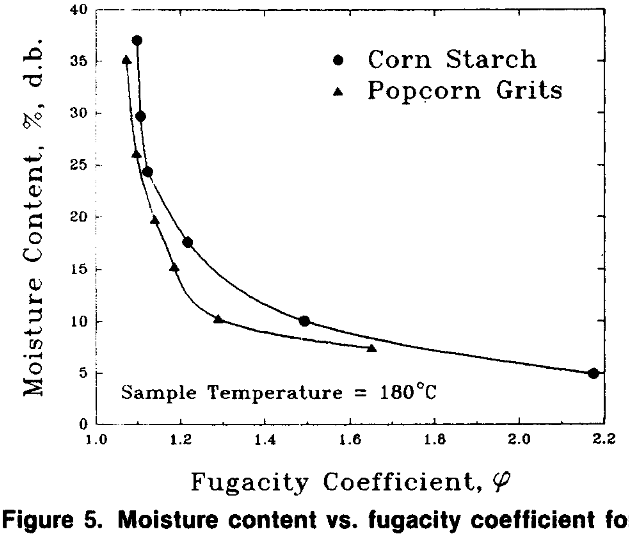

Figure 5. Moisture content vs. fugacity coefficient for cornstarch and popcorn grits at temperature of 180°C.

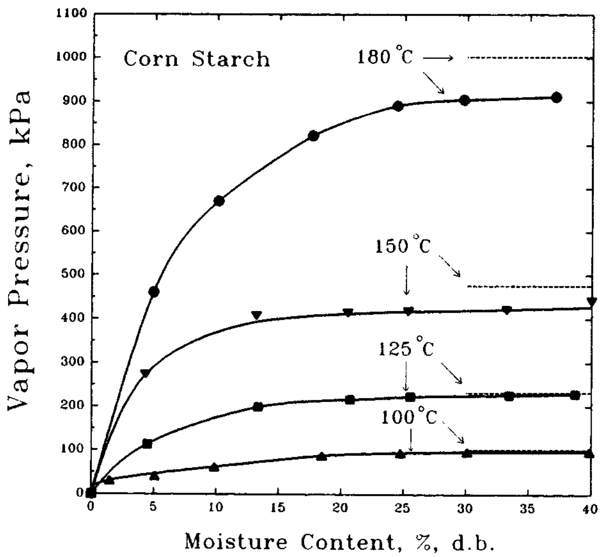

Figure 6. Vapor pressure vs. moisture content of cornstarch at various temperatures.

Dash lines represent saturated vapor pressures of pure water at various temperatures.

Cornstarch samples became sticky but remained white after heating to 150°C. At 180°C, the color of cornstarch changed gradually to brown, like caramel, and some of the starch turned into sticky liquid. Popcorn grits at 180°C became sticky and dark brown. Browning of popcorn grits at high temperature may be caused by the Maillard reaction (nonenzymic browning) which takes place during the processing of protein foods containing reducing carbohydrates or carbonyl compounds (Eriksson, 1981; Cheftel et al., 1985).

Moisture content vs. fugacity coefficient of water for cornstarch and popcorn grits at a temperature of 180°C are compared in Figure 5. Below 100°C, the isotherms of cornstarch and popcorn grits showed the typical sigmoid shape, and a_w increased with increasing temperature at constant moisture content. The isotherms behaved differently at higher temperatures, and were similar to the adsorption isotherms of sugar and sugar alcohols. The isotherms of sugar alcohols were characterized by breakpoints, at which the products began to dissolve, and a_w decreased with increasing temperature because of the increases of water solubility (Weisser, 1985). For cornstarch and popcorn, water adsorbed at low water activities did not initiate melting or partial melting; at higher temperature and water activity, it did.

Figures 6 and 7 show vapor pressure vs. moisture content of cornstarch and popcorn grits at various temperatures. Based on the measured popping temperatures and moisture content during popping, that is, 14% is the start of popping, vapor pressures that produce vapor-induced puffing in popcorn are about 758 kPa (110 psia) when popcorn starts to pop. This pressure is much lower than the pressures used in puffing guns where 1,379 kPa is used in gun chambers (Fast and Caldwell,

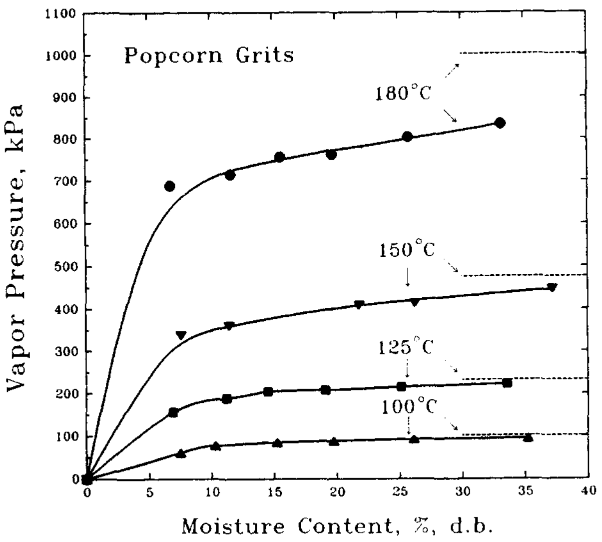

Figure 7. Vapor pressure vs. moisture content of popcorn grits at various temperatures.

Dash lines represent saturated vapor pressures of pure water at various temperatures.

1990). Popcorn had a higher expansion ratio than gun puffed cereals (Schwartzberg et al., 1990). However, the internal vapor pressure in cereal grains inside puffing guns may not reach the 1,379 kPa chamber pressure before puffing.

Based on Eq. 2, the experimental vapor pressure data of cornstarch and the sorption isotherm of cornstarch in the 25–50°C range (Shatton and Harb, 1965), apparent heats of sorption, ΔH_s, kJ/kg, were calculated in the 37–165°C range, and plotted in Figure 8. At low temperatures, apparent heats of sorption increased as moisture content decreased. At 5.3%, d.b. moisture content, ΔH_s decreased monotonically as temperature increased. Given the scatter in data this may also be true at 11% moisture content, or there may be a slight maximum as occurred at 17%. Below 140°C ΔH_s significantly exceeded ΔH_v at moisture contents less than 17%, d.b. At 150°C and higher, apparent ΔH_s fell below ΔH_v (2,050 kJ/kg at 170°C), and the deficit was greater for low moisture contents. Apparent ΔH_s was strongly affected by moisture content and temperature because of these reactions, that is, the chemical nature of the materials being heated was changing. Production of noncondensible gases during heating of popcorn grits also indicated chemical changes. Therefore, estimation of vapor pressure based on ΔH_s at high temperature was probably unreliable. Comparisons of estimated vapor pressure and experimental data at various moisture contents and temperatures are listed in Table 2. Direct measurement of vapor pressure in a closed system is probably preferable.

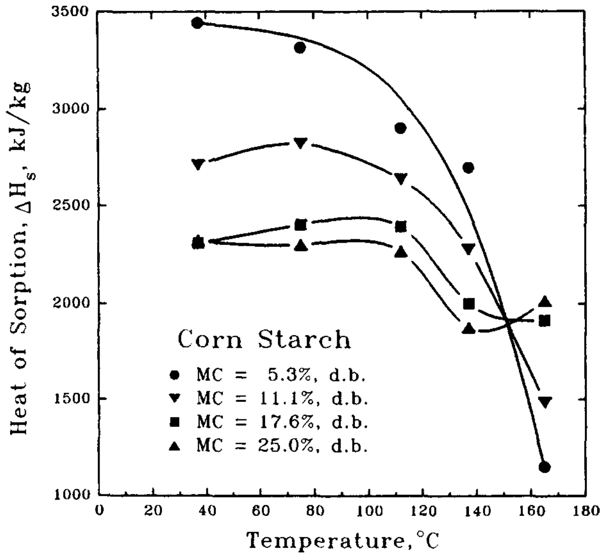

Figure 8. Estimated heat of sorption, ΔH_s, kJ/kg, of cornstarch at various temperatures.

Table 2. Estimated Vapor Pressure vs. Experimental Data

Heat of Sorption at 75°C		Moisture Content, % Dry Basis			
		5.3	11.1	17.6	25.0
ΔH_s, kJ/kg		3,317.4	2,821.2	2,403.3	2,300.2
50°C	P, kPa*	2.23	5.50	9.34	12.10
100°C	P, kPa*	42.88	70.71	89.24	97.96
	P_E, kPa**	44.20	69.60	81.14	95.82
125°C	P, kPa*	128.42	189.42	210.49	222.56
	P_E, kPa**	148.36	194.92	195.08	221.84
150°C	P, kPa*	313.98	405.76	410.19	417.09
	P_E, kPa**	431.50	483.27	422.80	465.14
180°C	P, kPa*	482.91	695.16	821.82	894.57
	P_E, kPa**	431.50	483.21	422.79	465.17

* Experimental results.

** Estimated vapor pressure by using Eq. 2 and the heat of water sorption at 75°C. Reference temperature, T_R is 50°C.

Evaluation of ΔH_s and ΔH_v in terms of vapor pressure vs. temperature behavior at constant moisture content is only valid for substances whose chemical composition remains the same. We showed elsewhere that dissolvable sugars were produced during the heating of starch and popping of popcorn. Dissoluble sugars were produced from starch by hydrolytic breaking of dissaccharides bonds. One molecule of water is removed for each bond broken. Such removal of water may be the reason why ϕ increases instead of decreases as temperature increases above 150°C. Further production of dissoluble sugars may very well account for the transition from solid-solvent ϕ vs. X behavior to meltable solid ϕ vs. X behaviors.

Conclusions

Pressures corresponding to temperatures and moisture contents occurring during puffing were estimated by measuring equilibrium water vapor partial pressures positive over cornstarch and popcorn grits containing various amounts of moisture at temperatures between 100 and 180°C. The water partial pressure vs. moisture content data were used to calculate sorption isotherms, and variations in partial pressure with temperature at constant moisture content were used to calculate apparent ΔH_s for water in cornstarch. These ΔH_s varied strongly with moisture content and temperature. The fugacity coefficient of water at constant moisture content decreased with increasing temperature in the 150–180°C range probably because of partial conversion of starch to sugar and sugar mixtures and melting or partial melting of starch. Estimation of vapor pressure based on heat of sorption or extrapolation of empirical temperature-dependent isotherm equations at temperature above 100°C was unreliable.

Based on a typical popping temperature, 185°C, and typical moisture contents immediately before popping (that is, 12 to 14%, dry basis), vapor pressure inside popcorn at the instant of popping were roughly 760 to 830 kPa (110 to 120 psia). However, the magnitude and change of the pressure difference, ΔP strongly affect the expansion of pore during puffing.

Notation

a_w = water activity
E_s = systematic error, kPa
f = fugacity of water, kPa
ΔH_s = heat of sorption, kJ/kg
ΔH_v = latent heat of vaporization per unit mass of water, kJ/kg
M_e = equilibrium moisture content, dry basis
M_i = initial moisture content, dry basis
P_a = air pressure, kPa
P_g = partial pressure of noncondensible gases, kPa
P_i = internal vapor pressure, kPa
P_t = total measured pressure, kPa
P_v = vapor pressure, kPa
R = gas constant = 8.314 kJ/kg·mol·K
T = sample temperature, °C or K
V_h = volume of head space, cm^3
W_{ds} = weight of dry solid, g

Greek letters

α = sum of air pressure, P_a, and systematic error, E_s, kPa
ν = specific volume of the superheated vapor, cm^3/g
ϕ = fugacity coefficient

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