Water-Polysaccharides Interactions During Apples Drying Process

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SUMMARY: In this work the state of water in samples of a food (apple) during the drying process was analyzed.
Low resolution NMR, differential scanning calorimetry (DSC) and sorption measurements were performed on differently dried samples.
It was possible to correlate the NMR proton relaxation time to the water activity aw=P/P_0, in order to have an independent method for measuring this parameter. The calorimetric curves showed the thermal transitions of different water populations and the sorption measurements on dry apple gave the fraction of water tightly bond to the structure, which resulted about 30%.

Introduction

Water, as the main component of food and biological material, plays a predominant role in determining their shape, structure, physical and chemical properties.
It also is a major control component in mass transfer, spoilage reactions both enzymatic and non-enzymatic and rates of microbial survival and growth.
Most of the unit operations used in food processing have as a goal either the removal of water to stabilize the material (as in drying and concentration) or its transformation into a non active component (as in freezing).
Dehydrated foods have been always widely used; natural drying is, in fact, one of the few preservation techniques available since the origin of human civilization. The first dried foods were mainly protein based products, while in recent times the processing of vegetables gained importance, due to the interest of the consumer towards ready to use dishes including different ingredients.
So a better understanding of water relations with the food would be very helpful especially in product development and process design.
An important index of how successful we are controlling product degradation rate is the equilibrium water activity[1], a_W, defined as the ratio of the equilibrium vapour pressure of the system, P, and the vapour pressure of pure water at the same temperature, P_0.
This parameter is, in fact, a general measure of water availability that determines microbial growth and enzymatic activity, rather than water content itself.
The aim of this work is to analyze the state of the water in food during a drying process. The food here analyzed is apple, already widely used to study drying processes[2-3].

 CCC 1022-1360/99/$ 17.50+.50/0

This analysis is executed by NMR, DSC and sorption measurements.
Low resolution NMR is proving to be a powerful technique for studying the state of water in foods under a wide variety of conditions and materials[4].
So it is useful in monitoring a drying process since the relaxation properties are related to the mobility of water and to its state in the system.
The differential scanning calorimetry (DSC) is able to reveal all those phenomena during which heat transfers occur, such as phase transitions.
From DSC measurements it is possible to have interesting information about the number, the nature and the temperature of the thermal events.
Sorption measurements consist in the dispersion of a penetrant (water) in a solid matrix. The equilibrium concentration and the distribution of the sorbed penetrant depend on thermodynamic factors regulating the interactions between the water and surroundings.

EXPERIMENTAL

Material

Stark delicious apples have been used during the experiments due to their availability throughout the entire year and their fairly constant quality .
The composition of stark delicious apples is reported in table 1.

COMPONENT	g/g (wet basis)	g/g (dry basis)
Water	0.844	5.41
Dry matter	0.156	1
Soluble sugar	0.1218	0.781
Cell matter	0.0342	0.219

Table 1. Chemical composition of Stark Delicious apple

NMR Experiments

NMR measurements were performed at 60 MHz by a STELAR low resolution spectrometer with a variable temperature control.
They were executed on fresh samples and on treated ones, dried at different water contents.
The drying process was carried out in an oven with a temperature and humidity control system; the process conditions were T=50°C and R.H.=15%.
The proton longitudinal (T_1) relaxation time was measured using saturation recovery (SR) sequence.

NMR relaxation times were measured in order to investigate the mobility of the water molecules and their interactions with the surroundings.

In addition, the intensity of NMR signal as a function of the temperature was measured.

DSC experiments

The thermal analysis was carried out over the temperature range -80÷30°C, using a METTLER TA 3000 DSC instrument.

Runs were conducted on samples of about 10 mg at a heating rate of 5°C/min.

All the samples having a water content lower than 40% were prepared working from the dried ones and exposing them at a water pressure of $1.9 \cdot 10^{-2}$ atm for different times.

The samples with higher water contents were obtained from the fresh ones, dried under vacuum for different times.

Sorption experiments

Sorption of water was measured by a microgravimetric method, using a quartz spring balance, having an extension of 1,4 cm/mg.

Sorption of dried samples was measured at a temperature of 25 °C as a function of vapour activity a =P/P_0, where P is the actual pressure to which the sample was exposed and P_0 is the saturation pressure at the temperature of the experiment.

RESULTS AND DISCUSSION

Figure 1 shows the H^1NMR normalised signal as a function of the temperature for differently dried samples.

The signal, in practice, gives information about the bond water fraction and the amount of liquid or non-freezing water at any temperature, that can be measured from its reduction in the amplitude[5]. The filled circles data, obtained for the distilled water, show almost null signal below the temperature of 0°C, being the water completely freezed and therefore motionless, and maximum unitary signal above 0°C, corresponding to the presence of the liquid state of water characterised by a very high mobility.

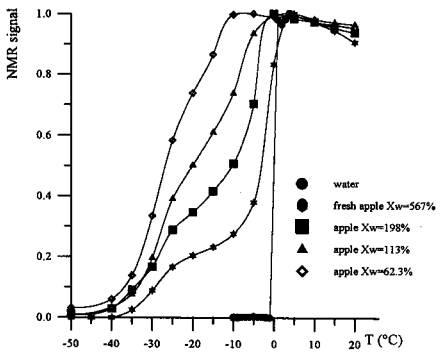

Fig. 1. NMR signal intensity versus temperature

Analyzing apples with decreasing water content, a different behaviour can be observed. Apple is, in fact, a complex system in which there is a solution of water and polysaccharides

and surely not pure water . The curves obtained for apples at different water content show an intermediate behaviour in the range -40°C ÷ 0°C. It can be noted that there is not a sharp transition in correspondence of the temperature of 0°C, like for pure water, but a smooth distribution of freezable water as a function of temperature, below 0°C. During the drying process the samples are subject to, the actual solution becomes gradually more concentrated and therefore the less the water content, the lower its mobility and the higher the interaction with the matrix.

Also from these curves it can be seen the shift of the freezing point for the samples at different water contents.

Fig.2a and 2b show the calorimetric curves from -80 to 30°C of samples with different water contents.

During these measurements the samples are first rapidly carried from 30°C to -80°C . As the cooling continues more ice will form reducing the volume of the residual solution and increasing its solute content.

After this rapid cooling, they are carried back to 30°C with a heating velocity of 5°C/min .

In the fig.2a empty circles refer to the fresh apple, which corresponds to a melting of ice at a temperature close to 0°C.

In the same figure, the others symbols refer to samples dried at different water contents. As expected, the less the water content of the sample, the lower its melting temperature, due to concentration effects.

Moreover in all the samples we observe an exotherm preceding the melting of the water.

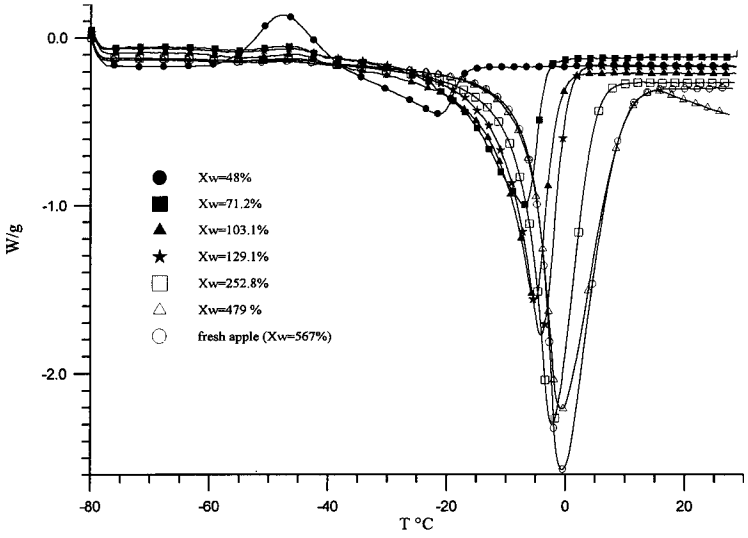

Fig. 2a. Differential scanning calorimetry traces for the samples with a water content Xw higher than 48% (water/d.m.)

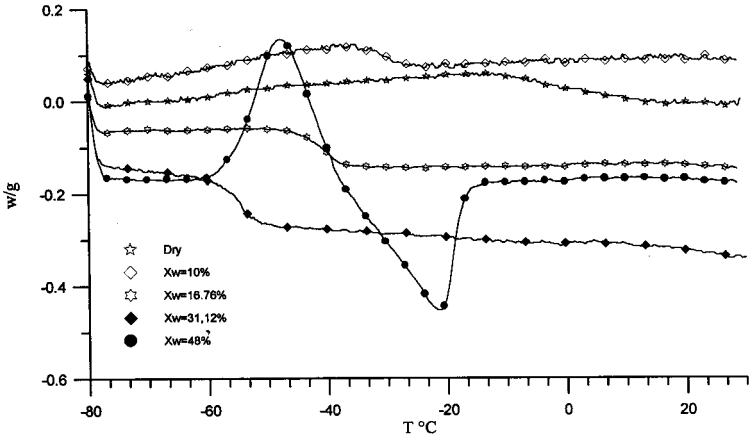

Fig. 2b. Differential scanning calorimetry traces for the samples with a water content Xw lower than 48% (water/d.m.)

In fig. 2b the traces of the samples with lower water contents are reported.
In particular it can be observed that at water content lower than 48% H_2O/d.m. there is no melting of water, indicating that the water molecules are very tightly bond to the structure.
Concerning the water activity, due to its importance in food preservation, is very interesting to consider the possibility to have an alternative and independent way for measuring it[6].

Working from a new theory of water activity in heterogeneous porous systems[7-9] in which the observed activity is calculated as the volume average of a local varying activity determined by the differing proportions of bulk and bond water, we investigated the correspondence between NMR water relaxation rates and water activity.
We must underline that this theory is valid in conditions of fast exchange of water between the bulk and the bond state. The presence of this condition is derived from the monoexponential trend of the relaxation curves. Really, this theory is based on the assumption that there are several distinct states of water associated with biopolymers; it is usually sufficient to consider three states:

- structural or bond water, hydrogen bonded to proteins and polysaccharides;
- surface water , water whose dynamic state is perturbed by the surface;
- bulk water.

The relationship between the NMR relaxation rates in fast exchange regime and water activity is the following:

$$\gamma_{av} = \gamma_b + B/C\ (1 - a_{av})$$

where
$\gamma \sim$ relaxation rate
a ~ water activity

$B = m_0 (\gamma_s - \gamma_b) + m_1 (\gamma_{sw} - \gamma_b)$

$C = m_0 (a_b - a_s) + m_1 (a_b - a_{sw})$

m_0 ~ mass of surface water per unit mass of dry solid

m_1 ~ mass of structural water per unit mass of dry solid

and the subscripts sw, s , b refer to structural, surface, and bulk water and av to average.
Longitudinal relaxation time (T_1) was obtained as a function of the water content and reported in fig.3.

The water activity was measured by a Novasina hygrometer and reported as a function of water content (fig.4).

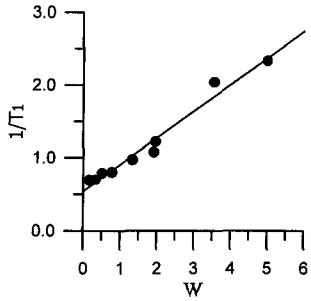

Fig. 3. The dependence of the water proton relaxation rate (s^{-1}) on the water content W (solid/water)

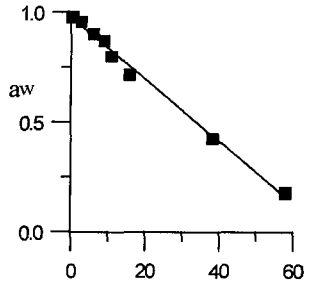

Fig. 4. The dependence of the water activity on the water content W (solid/water)

In fig.5 it is represented the dependence of the water proton relaxation rate (s^{-1}) on the water activity.
This linearity implies that NMR water proton relaxation time can be used to determine water activity independently of other methods.

The sorption curve of water vapour in the dry sample as a function of activity, $a=P/P_0$, is reported in fig.6.

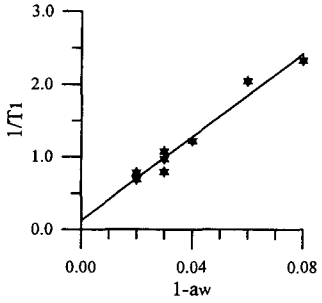

Fig. 5. The dependence of the water proton relaxation rate (s^{-1}) on the water activity

It shows two different zones: up to activity of 0.5 the sorption follows the "dual sorption mode", whereas at higher activities an almost linear dependence of sorption on pressure is evident. In the first zone the sorption is typical of systems in which the vapour strongly interacts with the substrates, progressively saturating specific sites of it.

We can associate this zone with the entrance of water, firmly associated to the structure.

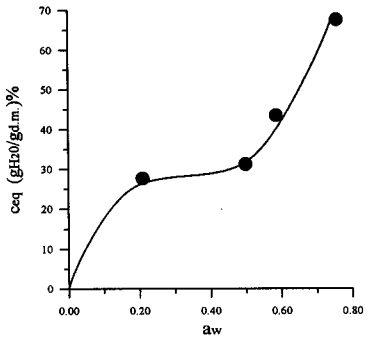

Fig. 6. The equilibrium concentration as a function of water vapour activity

From the fig. 6, the amount of water sorbed on specific sites of the matrix results of about 30% (H2O/d.m) well in agreement with literature data.

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This work was supported by Regione Campania and INFM – Italy.