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The diffusion of calcium ion into the organic layers studied by a differential photoacoustic system

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Abstract. Kinetics of water and calcium ion diffusion into biological layer (pericarp) exposed to different thermal treatments was investigated using the novel concept of differential photoacoustic cell (DPC). The latter enabled the real time measurements of amplitude and phase of PA signals originating from the reference and test samples. The uptake of calcium ion and water into kernel during the cooking of maize occurs predominantly through the pericarp. This process affects the physiochemical properties of kernel causing the corresponding changes of the signal and the phase of PA signal in time. The novel concept of DPC including temperature profiles is an excellent tool to study in-situ kinetics and thermal properties of material.

1. INTRODUCTION

Photoacoustic (PA) technique is widely used to investigate properties of materials [1]; in particular, the non contact and non invasive character of PA make this technique very useful in studies of thermo physical, optical and structural properties of matter. Both, the photothermal and PA technique, rely essentially on sensing the temperature fluctuations in a given sample generated as a result of non-radioactive de–excitation processes, following the absorption of modulated radiation. In the conventional PA instrument, the absorbing sample, enclosed in an air-tight cell is usually exposed to a chopped beam of radiation. As a result of a periodic heating due to absorption, the pressure of air inside the cell oscillates at the same modulation frequency; this is detected by a microphone coupled with a PA cell. The PA method was used to study kinetic processes such as a permeability of water vapor in biodegradable films [2], ceramics (3) and alkaline cooked corn [4]; all of these studies were performed using the single PA cell characterized by its own "instrumental figure" (i.e calibration factor needed for the quantitative measurements). The experimental conditions may however uncontrollably change during the experiment affecting thereby the instrumental figure. Unless timely detected such changes could lead to erroneous interpretation of measured data.

Due to the existence (mainly in Mexico) of nixtamalization process (NP) studies of water and water-calcium ions are important. The NP implies alkaline cooking (at temperatures between 72º C and 92 ºC) and steeping (0 to 24 h) of maize using calcium hydroxide. This application of NP increases steadily in the USA as well as worldwide due to the general spread of Mexican and Mesoamerican foods and nixtamalized products (for example corn flour, tortillas, tacos and tortillas chips). Traditional NP implies the simultaneous entry of water and calcium into kernel during the cooking [6]. According to Fernandez et al [6] diffusion of the calcium ion during the cooking time takes place only in pericarp generating thereby physicochemical changes. The removal of hemicelluloses and lignin is a major effect of such treatment on pericarp. This in turn increases permeability of pericarp and as a consequence facilitates the transfer of alkali solution into corn kernel [5].

The amount of calcium and the speed at which this substance penetrates in whole kernels (pericarp, endosperm and germ) during the nixtamalization are very important. This is due to the fact that the interaction between calcium hydroxide and different kernel components determine both, physicochemical and sensorial characteristics of the products. Reports on the extensive studies the objectives of which were to determine (using atomic absorption spectroscopy) calcium ion content and its distribution in kernel (pericarp, germ and endosperm) and water uptake (gravimetry) [7] can be found in specialized literature. However, there are no reports on studies describing in-situ simultaneous diffusion process of water and water-calcium ions. In this paper the concept of a Differential Photoacoustic Cell was proposed and used for the first time to study kinetic process in organic layers (corn pericarp is a good example).

2. EXPERIMENTAL SETUP

2.1 Differential photoacoustic cell (DPC)

The experimental set-up used and the differential Photoacoustic cell (DPC) used in this study are shown in Fig. 1. The COHERENT Compass 415M laser emitting at 532 nm was used as the excitation source. The radiation of the laser was modulated (from 5 Hz to 1 kHz) by means of the acoustic-optic modulator (ISOMET model 232A-2). Modulation frequency of 45 Hz was used to study the kinetics

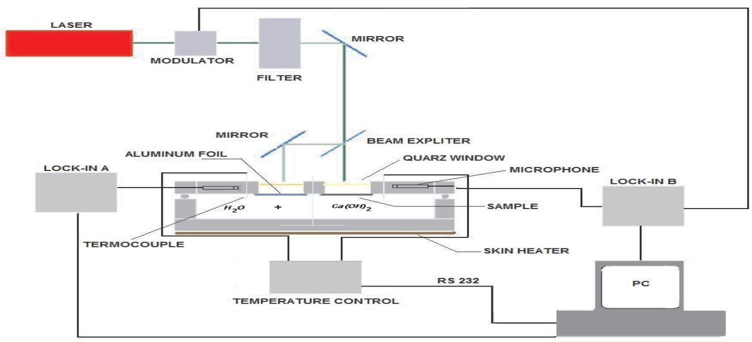


Figure 1. Differential photoacoustic cell (DPC) used to study the temperature dependent diffusion of water and water–calcium ions.

of diffusion process (water, water-Ca ions). The beamsplitter divides (60/40) the incoming radiation in two separate beams; each of them is focused into apart PA cell. One cell acts as the reference chamber while the other chamber serves to accommodate the test gas. Each of the two PA cells (machined from an aluminum plate) is a cylinder 4 mm in diameter and 1.5 mm long. Water reservoir was a cylinder was 7.8 cm in diameter and 5 cm deep. An "O" was used to provide a seal between differential PA cell (DPC) and the reservoir. The output signal (depends on the amplitude and phase) from each PA cell was amplified (OPAM-TL084) and connected to SRS 830 lock in amplifiers. To study kinetics of water and calcium hydroxide as a function of temperature (72, 82 and 92ºC), DPC was heated in a controlled fashion using a Watlow-96, 1/16 DIN temperature controller and two T-type thermocouples (G302986, Watlow) located at the center of DPC (see Fig. 1).

The temperature dependent instrumental figure of DPC was recorded by heating the system using the profile applied in nixtamalization process. The normalized PA signal was calculated as a ratio of the amplitudes of PA signals obtained at a given instant from the sample (corn) and reference sample (in this case the aluminum foil) respectively. On the other hand, the relative phase of the PA signal at a given instant is defined as the difference of phases between the two signals reference minus sample

2.2 Sample preparation

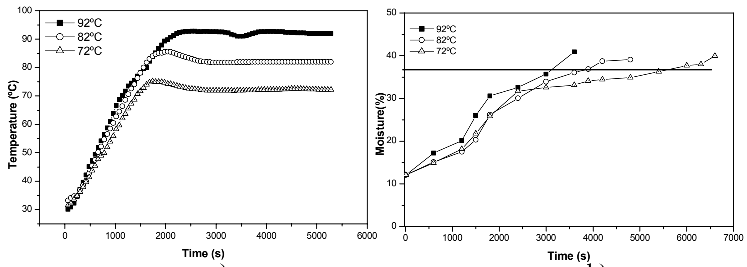
Corn (quality protein maize (QPM-H366)) grain, typically 3.56mm long and 2.12mm thick were used to study kinetics of water and water-calcium hydroxide. Kernels were grinded using type 800 abrasive papers. The face corresponding to a location of germ was grinded until remaining kernel became 1 mm thick. The kernel (pericarp and endosperm) was then attached to the cell using vacuum grease; the other cell was sealed with aluminum foil 76 μm thick.

The samples were prepared by cooking in the pan 20gr of whole maize kernel in 40ml of distilled water and 2% $Ca(OH)_2$ of the weight of the corn (reagent powder, Fermot, Monterrey, NL, Mexico). The first maize kernel sample was heated (rate 2.5ºC/min) from ambient temperature to 92ºC and held at 92ºC for 25 minutes. Another maize kernel was heated at the same rate until 82ºC and maintained at this temperature for 40 minutes. Finally, the third sample of maize kernel sample was brought to 72ºC (rate 2.5ºC/min) and kept at 72ºC for 65 minutes. The PA signal recorded during the cooking process originated from a corn kernel placed in the PA cell inside the pan.

The 30-20, AACC 1983 method was used to measure variation of moisture content in time for samples exposed to cooking step at three different temperatures (72, 82, 92ºC).

3. RESULTS

Figure 2 (a) shows the time dependent temperature for the system consisting of corn and $Ca(OH)_2$. The moisture content plotted as a function of time is shown in Fig. 2 (b). The combined uptake of water and calcium ion by corn is temperature dependent and in addition not linear.



a) b)

Figure 2. The temperature profile of the pan (a) and the moisture content of corn plotted as a function of the cooking time (b).

The continuous trace (Fig. 2b) at 36 % moisture content indicates that cooking step is completed. According to literature data [4, 6] it is possible to remove pericarp at this stage. Figure 3 shows the amplitude of PA signal obtained for three different corn kernels that were exposed to"varying temperature treatment" during cooking step of nixtamalization process. The penetration of water and calcium during initial cooking stages is in this case influenced by temperature, and pH factor of the cooking solution (nejayote). It is clear that when temperature increases, the amplitude of the signal soon begins to increase too indicating rapid entry of water into pericarp. The two peaks are associated with physicochemical changes caused by the thermo alkaline treatment taking place in pericarp. According to R. Gonzalez et al. (2004) the changes in pericarp observed in Fig. 3 can be related to the removal of hemicelluloses and lignin. This increases permeability of pericarp and facilitates the entry of alkaline solution into corn kernel.

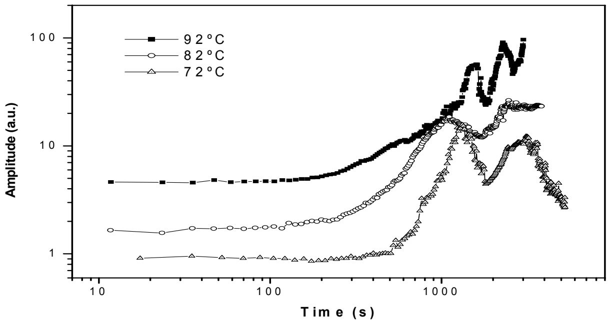


Figure 3. Time dependent normalized PA amplitude at three different temperatures. The plots were obtained during the cooking step.

4. CONCLUSION

The temperature Differential Photoacoustic Cell (DPC) is a new and useful device for studying the kinetics of water and calcium ion diffusion into corn kernel. The results suggest that the uptake of water and calcium by the kernel under same $Ca(OH)_2$ saturating conditions is temperature dependent. This finding was also confirmed by the experimental evidence gained by the independent measurements (gravimetry) of moisture content during the cooking step.

Acknowledgments

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