# SOLID STATE NMR STUDY OF CUMBARU FLOUR

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## Introduction

Starch is the most abundant storage carbohydrate in higher plants. It can be found in storage organs such as roots and tubers in a granular form. Size and shape of the storage starch granules are specific for each starch crop. Starch consists of two types of glucose polymers; amylose, an essentially unbranched α-1,4 linked glucose polymer and amylopectin, consisting of α-1,4 linked chains with α-1,6 branches. Common starches contain about 15–30% amylose. Native starch and starch derivatives are widely used in the manufacturing of food, paper, textiles, adhesives, pharmaceuticals and building materials. The physical properties of starches and, therefore, the applications, depend on the starch composition (amylose: amylo-pectin ratio, size and degree of branching of amylose and the relationship between structural characteristics and the physico-chemical properties of starch[1-2].

It is known that solid state nuclear magnetic resonance (NMR) spectra are sensitive to the form of crystalline solids and can therefore be readily used to study polymorphism and phase transitions. NMR is a substantial value for study both amorphous and heterogeneous materials, which are, of course, starch polysaccharide and other compounds. So, that, useful chemical and physical microstructure information can be obtained, particularly in the case of amorphous polysaccharide or other materials[3-5], because discriminating pulse sequences can be applied to obtain sub spectra of components in different domains. In spite of this NMR can provide detailed information on mobility at the molecular level over a wide range of rates and, in favourable cases can distinguish static from dynamics disorder and can produce direct data on interatomic distances.

The main purpose of this work was to evaluate the main chemical components and the molecular dynamic of cumbaru flour using solid state NMR techniques, such as: magic angle spinning (MAS), cross-polarisation magic angle spinning (CPMAS), cross-polarisation magic angle spinning with dipolar dephasing (CPMASDD), variable contact time (VCT), delayed contact time (DCT), and proton spin lattice relaxation time in the rotating frame ($T_1^H\rho$)[6-9]. The evaluation of NMR responses it is possible to get very much information on the behaviour of this type of sample.

## Experimental

### Sample

The cumbaru flour were obtained from the treatment of the fruit seed, after dehydrated and powder.

### NMR measurements

All solid state spectra were obtained on a VARIAN INOVA 300 spectrometer operating at 75.4 MHz for $^{13}C$. All solid NMR experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7mm diameter was used to acquire the NMR spectra at rates of 6.2 kHz. The $^{13}C$ NMR spectra were carried out in the cross-polarization mode with magic angle spinning. The MAS $^{13}C$ NMR main condition was to use a sort delay between 90 degrees pulses. For CPMAS $^{13}C$ NMR de delay time was 2s. The dephasing time was 40 μs. For the variable contact-time experiment, a range of contact time was established from 200 to 8,000 μs. Proton $T_1\rho$ values were determined from the intensity decay of $^{13}C$ peaks with increasing contact-times and by delayed contact-time experiment, where the range of spin-locking was 200 to 8,000 μs.

## Results and Discussion

The MAS $^{13}C$ NMR analysis of cumbaru flour, focusing only the mobile region showed signals located at 175 ppm (C=O); 103 ppm (C anomeric); 62 ppm ($CH_2$-OH); 28-14 ppm (aliphatic saturated) derived from the oil, probably a triacylglycerol and from polysaccharide.

The $^{13}C$ solid state NMR spectrum at the optimum contact-time of cumbaru flour showed signals from the most abundant components. Starch located at 103 ppm (C anomeric), 68 ppm (CH-OH) and 61 ppm ($CH_2$-OH), peaks from the oil at 172 ppm and 24 ppm and also weak peaks from the gluten proteins at 170 ppm and 26 ppm. The signals detected were broad, which shows that this can be a heterogeneous amorphous materials.

The CPMASDD $^{13}C$ spectrum showed the same signals related to the oil and polysaccharide presented in the flour, confirming that the signals already detected from the MAS and CPMAS techniques, which were derived from the oil, probably a triacylglycerol.

The variable contact-time experiment showed that the distribution form of the $^{13}C$ decays is typical for heterogeneous amorphous materials.

The proton spin-lattice relaxation time in the rotating frame, measured by both VCT and DCT experiments, showed that this flour has a molecular dynamic compatible to an amorphous material and heterogeneous material.

All NMR data corroborated and showed that the cumbaru flour is mainly constituted by a starch, triacylglycerol and gluten proteins, which indicates that this flour can be applied to food science.

## Conclusions

Based on the main purpose of this work, from the routine solid state NMR techniques was possible to evaluate the main chemical components presented in the cumbaru flour without any treatment. And the response of the molecular dynamic of cumbaru flour, which was monitored by MAS, CPMAS, CPMASDD and proton $T_1\rho$ indicated that general network mobility is due to the heterogeneity of the sample.


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