

# Solid-State $^{13}\text{C}$ -NMR and Study of the Subproducts Obtained from Corn Industry

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**ABSTRACT:** The two types of commercial corn flour subproducts from the Brazilian corn industry containing starch with low fat and with fat were investigated by solid-state NMR techniques to improve their uses. From the NMR techniques used, it was characterized that after a treatment the quantity of fibers decreased. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1680–1685, 2002; DOI 10.1002/app.10547

**Key words:** solid-state NMR; subproduct; corn flour; characterization

## INTRODUCTION

Starch is the principal food-reserve polysaccharide in plants and serves as the main source of carbohydrates. The waste subproducts of the Brazilian corn flour industry, which contains starch, low protein, and low fiber quantity, need to be carefully analyzed to obtain more information on its composition, chemical components, and molecular dynamic to improve its quantity of gluten protein and fibers and to find a new commercial application. It is known that starches typically contain ca. 25% of amylose and 75% of amylopectin. However, the origin of the food reserve is a dominant factor that is responsible for the ratio between both polysaccharide forms. With this knowledge, it is possible to use nuclear magnetic resonance (NMR) to investigate and identify the components, because this method directly provides the composition, without having previous

treatment.<sup>1</sup> For this purpose, we have chosen different NMR techniques,<sup>2–10</sup> including  $^{13}\text{C}$  solution, magic angle spinning (MAS), cross-polarization with magic angle spinning (CPMAS), variable contact time (VCT), and delayed contact time (DCT).

The main purpose of this work was to characterize two types of subproducts from the corn industry (with low and normal quantities of fat) by using NMR spectroscopy, and by employing solution and solid-state techniques.<sup>1</sup> After those procedures, a milled treatment was done. Then, we applied the solid-state NMR to implement the changes in the subproduct compositions.<sup>2</sup>

## EXPERIMENTAL

### Sample Preparation

The commercial subproduct from the Brazilian corn industry (Rio de Janeiro, Brazil) was received and analyzed as received and also after being milled at 35 mesh.

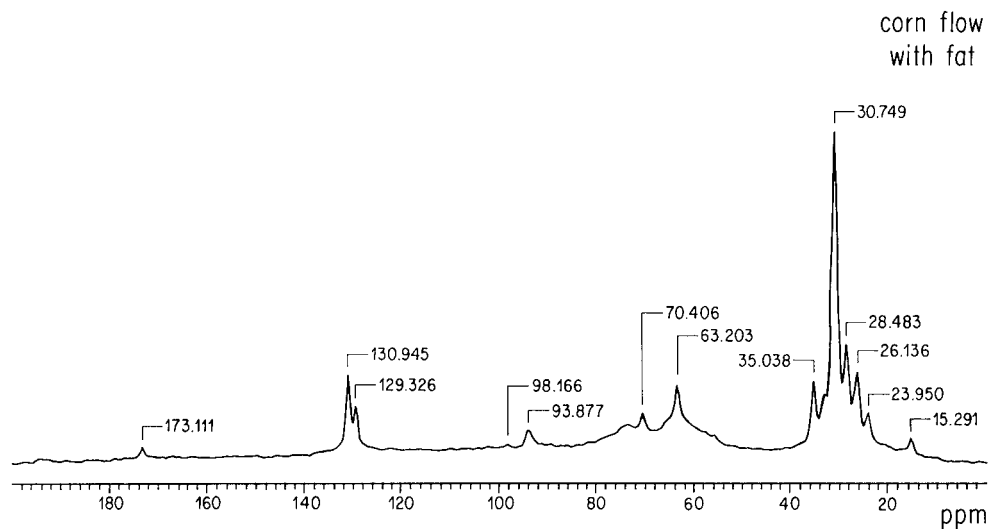
### NMR Measurements

All solution  $^{13}\text{C}$ -NMR spectra were obtained on a Varian Mercury 300 and the solid spectra on an

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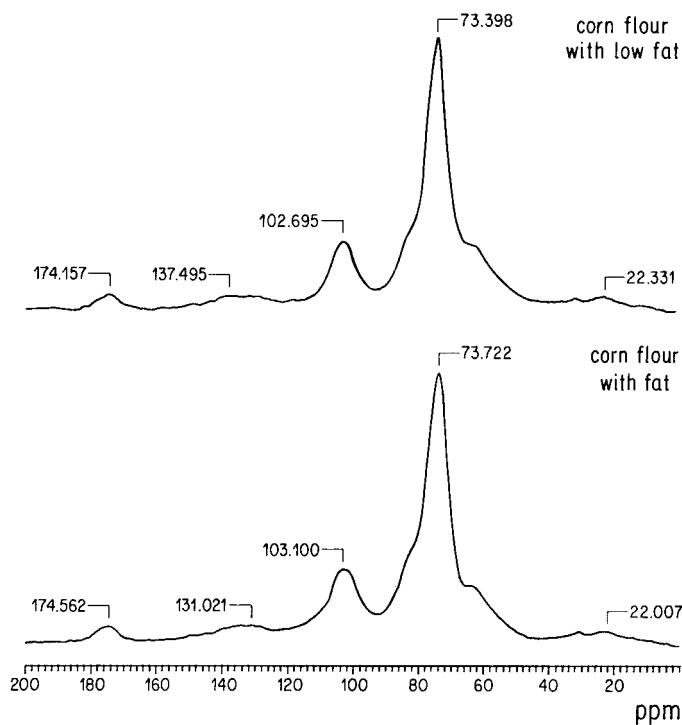
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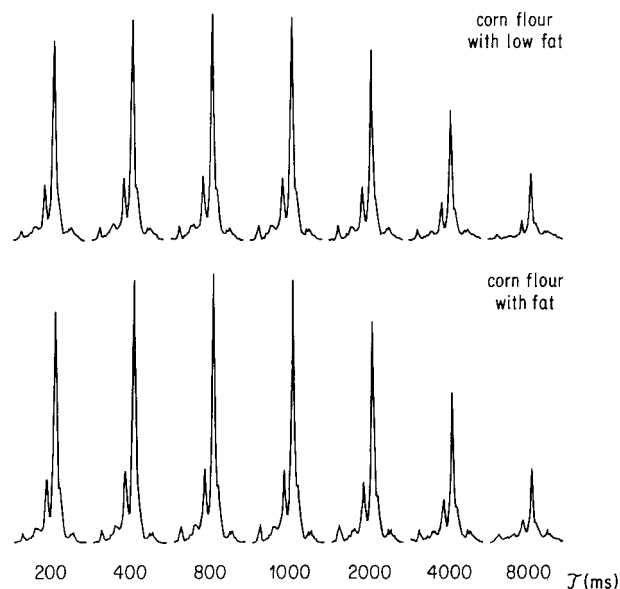
**Figure 1** MAS  $^{13}\text{C}$ -NMR spectrum of corn flour with fat.

Inova 300 spectrometer, operating at 75.4 MHz for  $^{13}\text{C}$ . The solution  $^{13}\text{C}$ -spectra were obtained under qualitative conditions by using deuterium oxide. All solid NMR experiments were obtained at ambient probe temperature with gated high-power decoupling. A zirconium oxide

rotor of 7 mm diameter was used to acquire the NMR spectra at rates of 6.2 kHz. The  $^{13}\text{C}$ -NMR spectra were carried out by using MAS, CP-MAS, and VCT with a range of contact times established from 200 to 8000  $\mu\text{s}$ . Proton  $T_{1\rho}$  values were determined from the intensity de-



**Figure 2** CPMAS  $^{13}\text{C}$ -NMR spectra of the subproduct.



**Figure 3** Distribution form of CPMAS  $^{13}\text{C}$ -NMR spectra of both subproducts.

decay of  $^{13}\text{C}$  peaks with increasing contact times and also from the delayed contact-time experiment with a spin locking  $\tau$  varying from 200 to 8000  $\mu\text{s}$ .

## RESULTS AND DISCUSSION

### Chemical Analysis

The starch obtained from the corn sample was chemically analyzed after being milled. It contained 53% polysaccharides, 10% protein, and 22% fibers.

### Solid-state NMR

Solid-state NMR gave a lot of information, which was available because anisotropic interactions had more direct effects on spectra. Solid-state

**Table I**  $T_1^{\text{H}\rho}$  Values, as a Function of Chemical Shift, Measured by DCT

Subproduct of Corn Flour	$T_1^{\text{H}\rho}$ (ms) $\delta$ (ppm)	
	103.1	73.3
With low fat	3.9	3.9
With fat	3.3	3.9

**Table II**  $T_1^{\text{H}\rho}$  Values, as a Function of Chemical Shift, Measured by VCT

Subproduct of Corn Flour	$T_1^{\text{H}\rho}$ (ms) $\delta$ (ppm)	
	102.3	73.3
With low fat	5.2	5.1
With fat	4.4	4.9

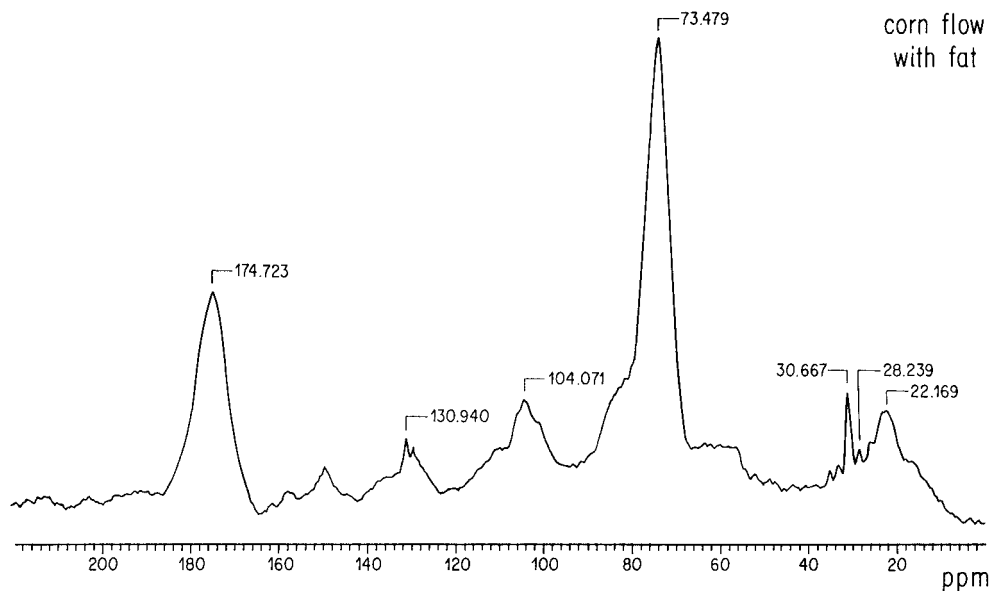
NMR is also very adequate to be applied to amorphous and heterogeneous materials, such as starches. By applying different techniques, we obtained responses of components presented in different domains.

The MAS  $^{13}\text{C}$  was acquired by using a short delay time (0.3 s) between  $90^\circ$  pulses to detect specifically the mobile region (liquid-like), a mobile domain presented in the sample. No NMR signal from starch was detected, which indicates that in these samples the starch does not have a mobile region, as expected in this time of scale, because of its rigidity. Therefore, the sample from corn flours showed signals derived from triacylglycerols (Fig. 1) that, probably, are those from  $\text{C}_{16}$ – $\text{C}_{20}$ , saturated (palmitic) and unsaturated (oleic, linoleic).

Figure 2 shows the CPMAS  $^{13}\text{C}$ -NMR spectra of the subproduct, in nature, which presents broad resonance lines, which come from different positions in the glucose units, located at 62.8 ppm (C6;  $\text{CH}_2\text{—OH}$ ); 72.6 ppm (C2, 3, 5;  $\text{CH—OH}$ ) with a shoulder in 84.2 ppm (C4;  $\text{CH—O}$ ), and 103.4 ppm (C1 anomeric;  $\text{C—O}$ ), which derive from starch. Both subproducts present very similar line shapes, indicating that the fat content does not have an influence on the signal forms, and also, in chemical shift.

The analysis of the distribution form of the variable contact time (Fig. 3) shows that both subproducts probably have the same molecular dynamic behavior. The optimum contact time for the  $^1\text{H}$ – $^{13}\text{C}$  polarization transfer, for both types of corn reject, were the same (800  $\mu\text{s}$ ) and the decay starts at the same contact time. The  $^{13}\text{C}$  decays of corn flour with fat decays a little deeper than the corn flour with low fat, which is in agreement with MAS and CPMAS data.

The molecular dynamic and chain packing were analyzed by  $T_1^{\text{H}\rho}$ , which were measured by DCT and VCT. The values are listed in Tables I and II, respectively.



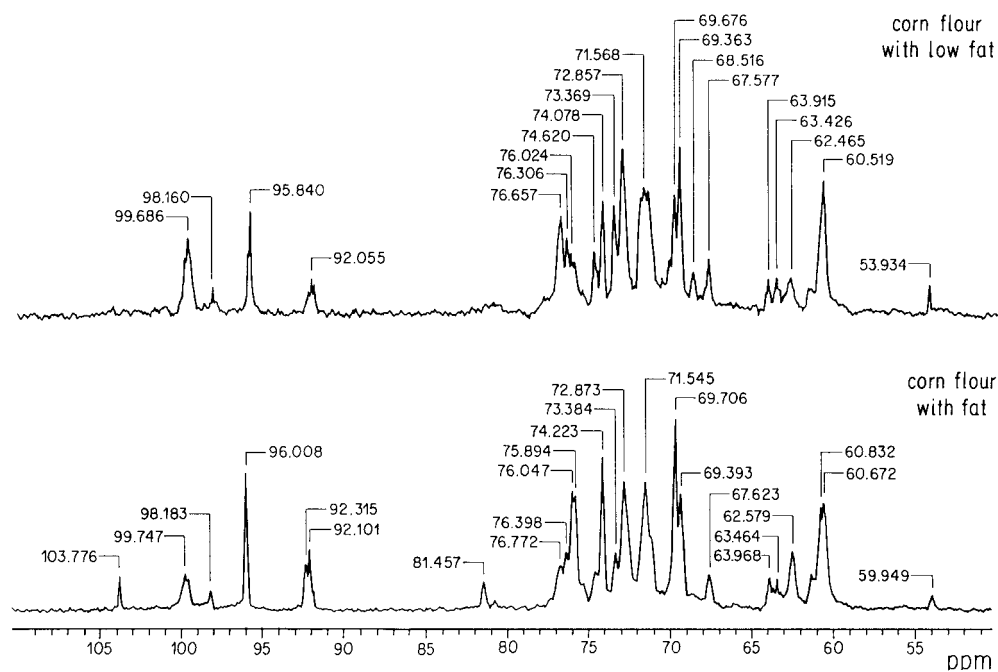
**Figure 4** CPMAS  $^{13}\text{C}$ -NMR spectrum with dipolar dephasing of corn flour with fat.

From the values of  $T_1^{\text{H}\rho}$  measured by DCT, it can be seen that both subproducts present one large domain that controls the relaxation process.

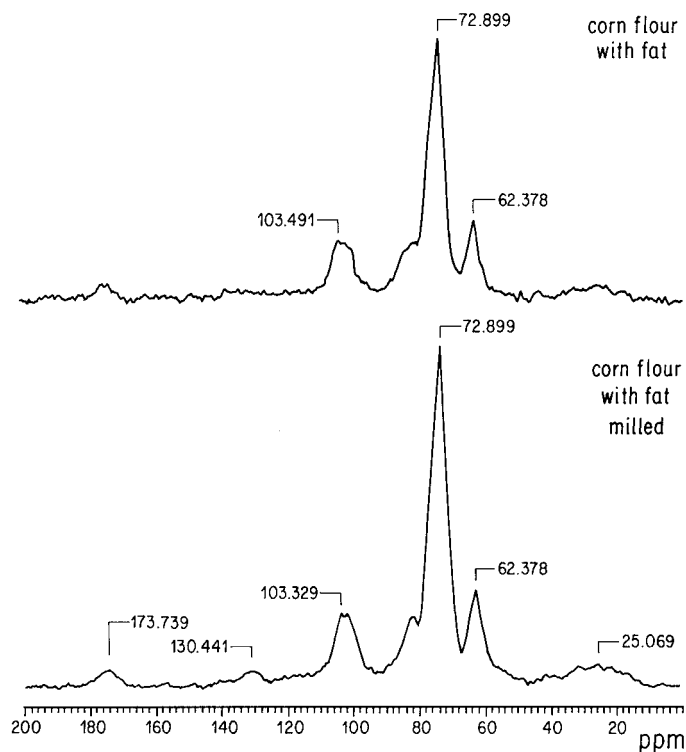
From the VCT, the  $T_1^{\text{H}\rho}$  parameter shows that there was not a significant difference in the chain packing or ordination, because of the fact that no

difference in the polarization transfer of intermolecular chains was detected.

When a dipolar dephasing technique was acquired, the spectrum (Fig. 4) shows signals from  $\text{C}=\text{O}$ ,  $\text{C}_1$ ,  $\text{CH}-\text{OH}$ , and methyl group, indicating the presence of starch and confirming the detec-



**Figure 5** The solution  $^{13}\text{C}$ -NMR spectra of the extracted of the subproducts.



**Figure 6** CPMAS  $^{13}\text{C}$ -NMR spectra of the subproduct before and after milling.

tion of carbonyl group that probably derives from the gluten and/or aggregated protein. It also showed that a rigid domain is presented.

### Solution NMR

To obtain more information on those polysaccharides, an extraction with water was carried out. This extraction occurred for 24 h at 25°C. Two phases were obtained; the material was filtered and the water solution was analyzed by solution  $^{13}\text{C}$ -NMR. The spectra of the solution extracted from both corn flours (Fig. 5) showed signals that probably derived from monosaccharides, disaccharides, and polysaccharides. Compared to HPLC, the information obtained by NMR was directly observed in the spectrum, without having previous treatment. Therefore, by using HPLC, more than one step is needed, and the type of polysaccharide was obtained indirectly. For this type of sample, the chromatogram is detected to the glucose (53%) and isomaltose traces.

The preceding study encouraged us to start developing a methodology to obtain more useful information on these types of samples.

Then, with an objective of separating the starch, protein, and fibers, the corn flour was

milled at 35 mesh, and the CPMAS  $^{13}\text{C}$  spectrum was recorded. By comparing this spectrum with the other spectrum, which was obtained before the milling (Fig. 6), the same NMR signals located at 62.3 ppm, 72.8 ppm with a shoulder in 84.2 ppm, and 103.4 ppm were detected. They presented a better resolution, and other signals located at 25.0, 130.4, and 173.7 ppm were more evident, suggesting that the treatment adopted was able to concentrate the starch fraction.

### CONCLUSION

The NMR techniques permitted us to generate a methodology of analysis that provided much information on the corn subproduct samples, which has contributed to the identification of their components, and the obtained results showed changes in the subproduct compound composition.

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