Characterization of Lignocellulosic Biomass Using Solid-State NMR Spectroscopy

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Introduction

Lignocellulosic biomass has long been recognized as a feedstock for biofuel production.[1] The conversion of the biomass into the biofuel requires breaking down plant cell walls to release carbohydrates bound in the cell wall. The main obstacle in this process is the natural resistance of plant cell walls to releasing sugars (biomass recalcitrance), which is largely responsible for the high cost of biofuel production from biomass.[1] Thermochemical conversion platform for lignocellulosic biomass has received wide attention, due to its possibility on practical applications in the near future. There are several different thermochemical processes for the biomass, which include fast pyrolysis (~500°C), gasification (~900°C), and combustion (>1200°C). Understanding structural changes in biomass during the heat treatment is essential to optimizing the thermochemical processing condition for the production of high-quality biofuels. Solid-state NMR spectroscopy has proven promising for structural analyses of the non-crystalline materials. In this project, structural changes of woody biomass after heat treatments were investigated using ^{13}C DP/MAS and long-range dipolar-recoupled dephasing experiments.

Experimental

It was reported that aromatic structures develop during the thermochemical conversion. In order to investigate the degree of aromatic condensation, long-range dipolar-recoupled dephasing experiments[2] were carried out for the biomass treated at different heating conditions (500 and 700 ^{o}C under pure N_2 and mixture of N_2 and O_2 (7%)). The QCPMG detection scheme[3] was incorporated into the dephasing experiment for signal enhancement. The NMR experiments were performed on a 600 MHz solid-state NMR facility equipped with 3.2 mm MAS probe in the NHMFL (Tallahassee).

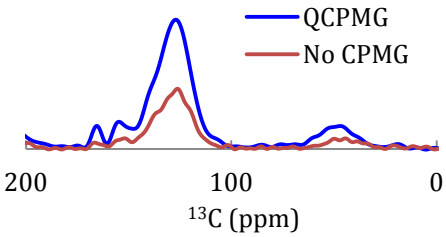

Figure 1. ^{13}C DP/MAS spectra with and without QCPMG detection scheme.

Results and Discussion

The QCPMG pulse sequence was implemented in the DP/MAS experiment, which enhances the signal to noise ratio by a factor of 2 (**Figure 1**). The QCPMG detection scheme was also used for the dephasing experiments (**Figure 2**). The NMR signal decreases during the dephasing time due to the ^{1}H-^{13}C dipolar interactions. The slower decay for the sample treated at higher temperature indicates weaker dipolar interactions, and thus larger average distance between the two nuclei. During the heat treatment, the aromatic sidechains of the lignin in the pant cell wall are fused and form a bigger aromatic cluster. Relative content of the non-protonated carbons inside the cluster would increase in a larger cluster, leading to the slower signal decay due to the weaker dipolar interactions. Thus, the slower signal change at higher temperature clearly suggests that the size of the aromatic cluster increases, leading to a higher degree of aromatic condensation. In addition, heat treatment in the presence of O_2 appears to produce a larger aromatic cluster at 700 ^{o}C (Figure 2).

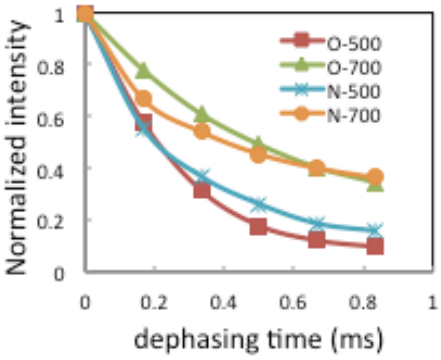

Figure 2. NMR signal changes for the non-protonated carbons under the recoupled ^{1}H-^{13}C dipolar interactions.

Conclusions

The solid-state NMR experiments demonstrated that the size of the aromatic cluster increases at higher temperature and in the presence of O_2. The more effective QCPMG detection scheme was also successfully implemented into the long-range dipolar dephasing experiment.

Acknowledgements

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References

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[2] Mao, J. D., *et al*., J. Magn. Reson. **161**, 217-227 (2004).
[3] Larsen, F. H., *et al*., J. Magn. Reson. **131**, 144-147 (1998).