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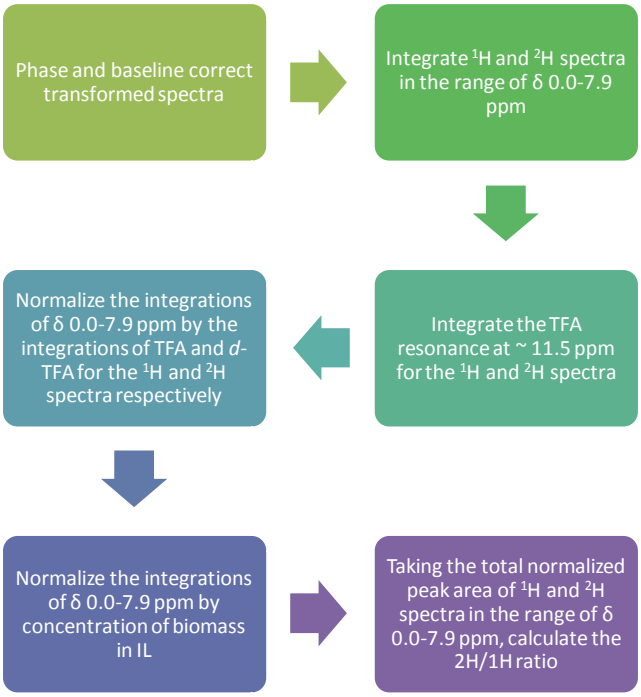
Supplementary Material

Supplementary Experimental

Solid State NMR Analysis

Solid NMR samples were prepared with dry ball-milled biomass added into 4-mm cylindrical ceramic MAS rotors. Solid-state NMR measurements were carried out on a Bruker Avance-400 spectrometer operating at frequencies of 61.4 (^{2}H) or 400.1 (^{1}H) MHz in a Bruker double-resonance MAS probehead under non-spinning conditions. ^{2}H NMR spectra were collected using a 1D 90-90 solid-echo sequence for deuterium wide-line observation accounting for the detector dead time delay, with an on-resonance 2.5 μs excitation pulse, echo delay of 20 μs, 8k data points, 0.5 us dwell time, 15-s recycle time, and 4k scans. ^{1}H NMR spectra were measured with an on-resonance 2.5 μs excitation pulse, 4k data points, 0.5 μs dwell time, 15-s recycle delay and 512 scans. To ensure the quantitative nature of the spectra, average spin-lattice times of glucose/glucose-d_7 mixture in the solid form (^{1}H 4.4 s and ^{2}H 1.2 s), D-kale in the solid form (^{1}H 2.1 s and ^{2}H 1.0 s) and D-kale dissolved in ionic liquid (^{1}H 0.8 s and ^{2}H 0.02 s) were measured using a saturation recovery experiment which in turn utilized a train of 64 pulses separated by 500 us to fully excite all nuclei present. We chose a saturation recovery experiment because of the difficulty in finding exact 90 and 180 degree pulses in these highly heterogeneous systems. The average ^{2}H relaxation during echo formation was measured on the glucose/glucose-d_7 (20 us) mixture and D-kale (126 μs) using a 2D 90-90 solid-echo sequence with variable delay times during the 90 degree pulses. ^{1}H spectra were baseline corrected and processed using 5 Hz exponential apodization, while ^{2}H spectra were saved as analog filtered data, baseline corrected and processed using 1 kHz exponential apodization.

Supplementary Figures



Supplementary Fig. 1. Flowchart describing the procedure for calculating the ^{1}H and ^{2}H solution spectra of D-labeled biomass by whole cell ionic liquid dissolution.

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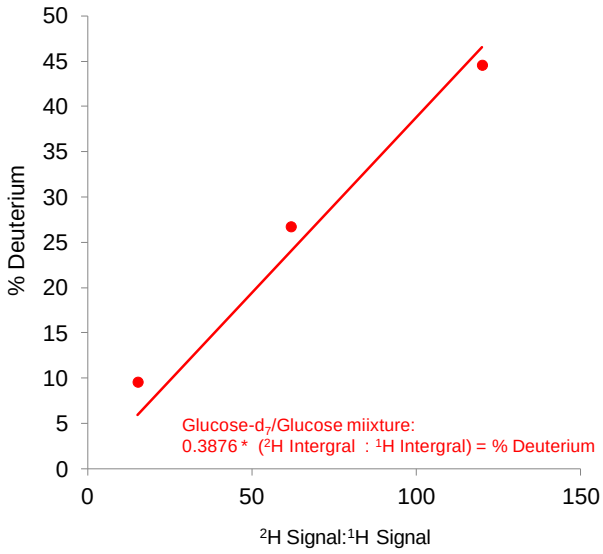

Supplementary Fig. 2. Calibration curve relating the % deuterium determined by the molar fraction of glucose/glucose-d_7 mixtures to the integral of the proton and deuterium spectra in a 4-mm MAS rotor.

Supplementary Discussion

For example, keeping in mind for every one TFA proton there is one TFA deuteron in the external standard, therefore the ^{1}H spectra indicated for every TFA proton there was 1.25 proton on the D-Kale sample in the deuterated solvent system likewise the ^{2}H spectra indicated for every TFA deuteron there was 1.69 deuteron on the D-Kale sample in the protonated solvent system. By mass, the concentration of the D-Kale in the ^{1}H spectra was .035 g of D-Kale in 1 g of deuterated solvent system and .045 g of D-Kale in 1 g of protonated solvent system for the ^{2}H spectra. After normalizing by the concentration of D-Kale in solution and the TFA/*d*-TFA ratio, the ratio of deuterons to protons in D-Kale is 17.8:35.7 or 33.2%.