Effect of pretreatments and enzymatic deconstruction on the surface of biomass: Chemical image analysis.

Abstract

Lignocellulosic biomass pretreatment is an essential process in order to increase the conversion of biomass to ethanol product. Pretreatment biomass by reducing recalcitrance is known to stimulate more acceptable biomass to cellulose enzyme which is multi-step heterogeneous reaction via liquid-solid interface. Understanding what changes occur in biomass during pretreatment, therefore, can elucidate leading factor of recalcitrance, especially on the surface of biomass where most is to be an interfacial layer during enzymatic deconstruction.

Herein, we employed Time-of-flight secondary ion mass spectrometry (TOF-SIMS) to illustrate the chemical imaging of pretreated/deconstructed biomass. TOF-SIMS has been used to achieve the major component images (e.g. cellulose and lignin) on the surface of poplar stem and their semi-quantitative variation which is to be compared to bulk composition data by HPLC before and after pretreatment. Pretreated biomass represents relatively more cellulose appearance on the surface of poplar stem compared to bulk composition data, which should imply there is chemical interface. Understanding what changes occur in biomass during pretreatment, therefore, can elucidate leading factor of recalcitrance.

1. Enzymatic sugar release & Bulk analysis

Tension Wood sample demonstrated a remarkable 3-fold increase in cell wall digestibility with respect to the Normal Wood and Opposite Wood samples. However, bulk glucose content is only 25% difference between TW and NW. What recalcitrance factors are mainly affecting?

2. TOF-SIMS & CARS application for biomass (surface analysis)

CARS lignin image

- Linearity: The coherent signal generated in the non-linear CARS process is thousands times stronger.
- Quantitative: CARS signals are linearly dependent on the analyte concentration that allows relative quantification.
- Multiplexing: Multiple-channel CARS signals can be acquired to allow simultaneous imaging of major chemical species in biomass, such as lignin and cellulose.

3. Chemical image analysis using TOF-SIMS & immune-fluorescence microscopy

- Promoted biomass shows different chemistry between surface and bulk. After 160°C pretreatment, bulk glucose content is similar to starting sample, but, cellulose content on the surface relatively increases double compared to starting sample. Relative surface data can be used to predict optimal pretreatment conditions with Minimum point of cellulose and maximum point of lignin on the surface. This result is well corresponding to Bulk sugar & Lignin contents (TOF-SIMS analysis is in dynamic equilibrium compared to bulk analysis.)

Conclusions

- TOF-SIMS and CARS has been successfully applied to generate chemical image for surface characterization of biomass.
- 2D & 3D TOF-SIMS analysis provides:
  - Spatial distribution (xy plane) of major components (cellulose & lignins).
  - Semi-quantitative chemical information such as relative ion intensity or linear profiling.
- Pretreated biomass has different chemistry between surface and bulk. More cellulose (TOF-SIMS data) and xylan (immune-fluorescence data) are brought on the surface at initial stage of pretreatment. Lignin is localized at cell corner then disappears during pretreatment. Severe pretreatment (160°C 150min) compared to 120min. pretreated sample results in lignin increase and cellulose decrease without total weight change.

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