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Update on LPMOs

LPMOs (lytic polysaccharide monooxygenases) were discovered by NMBU scientists in 2005 (1) and their enzymatic mechanism was elucidated in 2010 (2). The discovery of LPMOs was considered a breakthrough for enzymatic degradation of biomass because it had been thought earlier that only glycoside hydrolytic enzymes like cellulase and chitinase were responsible for degradation of non-edible woody plant biomass and chitin. This article gives a short review of recent discoveries with LPMOs, at Ås and internationally.

It is estimated that photosynthesis worldwide captures about 15 TW hours (terrawatt hours) of energy as biomass every year. This number, if it could be fully exploited, represents approximately 10% of total energy consumption yearly from all sources, including hydroelectric, natural gas, oil, coal and nuclear. In fact, estimates suggest that up to 30% of current petroleum usage in the USA could be offset based on second generation biofuels from non-edible woody plant biomass.

Several LPMOs have been described from at least 13 bacterial and 6 fungal sources (3). LPMO substrates include cellulose, chitin (the original LPMO, reference 1), xylan, xyloglucan, glucomannan and starch. LPMOs catalyze a metal- and reductant-dependent oxidative reaction, leading to chain cleavage internally in long polysaccharide chains that boost the activity of classical glucoside hydrolases by creating new chain ends upon which these enzymes can act.

Crystal structures of at least 4 LPMOs have been determined. Surprisingly, the enzyme lacks either a groove or a tunnel to accommodate the polysaccharide substrate. Rather, it appears that substrate is bound to a flat surface via aromatic sidechains. The enzyme also contains a single Cu atom, coordinated in a 'histidine brace', that transfers electrons to O2, generating reactive intermediates.

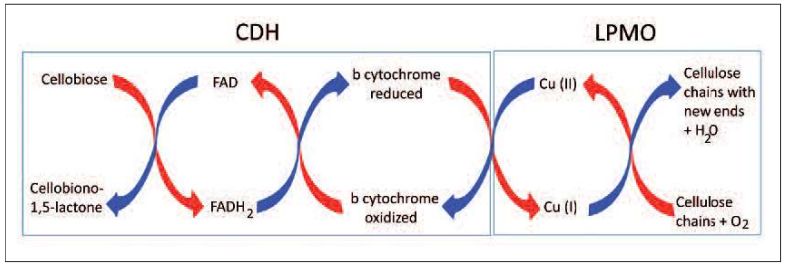

Figure 1. Model for cellulose oxidation by CDH plus LPMO

The current model for cellulose degradation (Fig. 1) is that cellobiose dehydrogenase (CDH) catalyzes the conversion of cellobiose to cellobiono-1,5-lactone with concomitant reduction of FAD to FADH2. Upon re-oxidation of FADH2 back to FAD, electrons are shuttled from CDH via its cytochrome domain to LPMO, reducing Cu(II) to Cu(I). A recent PNAS (USA) paper (4), published by the NMBU group and partners, used NMR and isothermal titration calorimetry to study interactions of LPMO from the fungus Neurospora with CDH and polysaccharide substrates, identifying sites on the LPMO around the copper-site that bind both substrate and the CDH. It also showed that the heme b cytochrome domain interacts directly with LPMO's copper site, confirming the model in Fig. 1. Apparently, all electrons necessary for the LPMO reaction are present in the enzyme before the polysaccharide substrate binds.

Even though production of second-generation biofuels on an industrial scale from woody-plant biomass has not been accomplished yet, the science of biomass degradation has changed significantly during the last 15 years. It is expected that the cocktail of components for the future in industry will include cellulases, -glucosidases, CDH and, of course, LPMOs.

Gustav Vaaje-Kolstad and Vincent Eijsink.

References

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