STRUCTURE AND FUNCTION OF LYTIC POLYSACCHARIDE MONOOXYGENASES (LPMOS) AND OTHER REDOX ENZYMES INVOLVED IN BIOMASS PROCESSING

Vincent G.H. Eijsink, Norwegian University of Life Sciences (NMBU), Faculty of Chemistry, Biotechnology and Food Science, P.O. Box 5003, N-1432 Ås, Norway
Vincent.eijsink@nmbu.no
Bastien Bissaro, NMBU, Norway & INRA, UMR792, Ingénierie des Systèmes Biologiques et des Procédés, F-31400 Toulouse, France

Key Words: Cellulose, monooxygenase, hydrogen peroxide, copper, cellulase

The discovery of Lytic Polysaccharide Monooxygenases (LPMOs) has revolutionized our understanding of biomass conversion in Nature and has been instrumental for the development of economically sustainable lignocellulose biorefineries. LPMOs are mono-copper redox enzymes that attack the most recalcitrant parts of biopolymers such as crystalline cellulose and chitin. LPMOs employ the power of redox chemistry to cleave glycosidic bonds that are not easily cleaved by hydrolytic enzymes. By doing so, they make the substrate more tractable to the action of canonical enzymes such as endo- and exo-cellulases. LPMOs are abundant in Nature, for example in the secretomes of wood-decaying fungi. Despite their importance in both Nature and the biorefinery, several aspects of these intriguing enzymes remain unclear. The catalytic mechanism of LPMOs is of particular importance because the enzymes display a unique active site architecture that is employed to catalyze a challenging chemical reaction on a substrate that is embedded in a crystalline lattice. Deeper insight into this mechanism may have wide-reaching consequences, not only for biomass processing but also, perhaps, in developing enzymatic or other catalytic systems for difficult reactions, such as controlled oxidation of methane and other alkanes. Using a variety of experimental approaches, we are studying LPMO function, addressing issues such as the structural basis of oxidative regio-selectivity and substrate specificity, routes and mechanisms for electron delivery, the roles of appended carbohydrate-binding domains, and the determinants of catalytic activity and stability. Knowledge gained from these fundamental studies is being used to optimize biomass conversion processes, whereas translation of this knowledge to other fields is also being explored. In this presentation, I will review recent work in the field and present our latest results. Special attention will be paid to recent research in our group that has led to the proposal that LPMOs may not be true monooxygenases. Based on our recent results, we have proposed that hydrogen peroxide, rather than molecular oxygen, is the preferred co-substrate of LPMOs. While this paradigm-shattering proposal may not yet have found wide acceptance in the field, we have already demonstrated that the controlled administration of hydrogen peroxide during biomass degradation by LPMO-containing commercial cellulolytic enzyme cocktails leads to drastically improved LPMO activity and more efficient saccharification. These recent findings also shed new light on the interplay between LPMOs and other redox enzymes in the secretomes of biomass degrading microorganisms.