

images that were obtained resulted in a semi-quantitative picture (as shown) of the three-dimensional composition of the biomass. As expected, cellulose (green dots) mostly appeared in the gelatinous layer whereas lignin (red dots) was principally observed in the secondary cell wall. AP

BIOFUELS

Converting the biomasses

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Generating biofuels from waste biomass eliminates the competition between biofuels and food sources for arable land. Waste biomass contains a mixture of chemically similar components such as cellulose and hemicellulose, but current approaches require these sugars to be separated before they can be turned into useful feedstocks. This separation step can account for up to 30% of the capital costs required to set up a biofuel production plant. Simultaneous conversion of these different components would alleviate the need for costly and complicated pre-treatment steps while still maximizing the yield of useful products.

To address this problem, James A. Dumesic and colleagues at University of Wisconsin-Madison in the USA have developed a method of simultaneously processing hemicellulose and cellulose in a single reactor. Using maize stover (the leaves and stalks left behind after harvesting) as the feed, either an open reactor or a batch reactor can be used to transform a mixture of cellulose and hemicellulose into useful chemical feedstocks. In the open reactor, hemicellulose is converted to furfural and levulinic acid is formed from cellulose. Furfural has a lower boiling point than the solvent or other products, enabling it to be continuously removed by distillation. The process is similar when configured as a batch reaction, however the furfural is also converted — through furfuryl alcohol — to levulinic acid and so no separation is required.

Catalytic reduction of levulinic acid gives gamma-valerolactone, which is also used as the solvent in both processes, and therefore simplifies the separation of the product downstream. Another added benefit is that gamma-valerolactone also solubilizes the degradation products that are typically formed while converting lignocellulose into chemical feedstocks, which is particularly useful to prevent the build-up of solid residue in a continuous flow reactor. The processes give a comparable amount of liquid fuel, in terms of useable energy content, as does the fermentation of maize stover to ethanol. Furthermore, the products can be used as precursor chemicals or processed downstream into liquid fuels. RJ

ANTIOXIDANTS

Working shifts

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In response to infection, activated white blood cells known as phagocytes undergo what is known as an ‘oxidative burst’, during which they generate large amounts of reactive oxygen species to combat the invading pathogen. The enzyme myeloperoxidase is also generated and this catalyses the reaction of hydrogen peroxide with Cl^- to produce HOCl — a highly potent cytotoxic oxidant. Overproduction of HOCl, however, can have harmful effects. Carnosine is a naturally produced dipeptide — made up of β -alanine and L-histidine — that is able to scavenge HOCl and protect against damage caused by its excessive production. Now Leo Radom, Amir Karton and colleagues from the University of Sydney, have studied the mechanism by which this occurs.

Carnosine contains four nitrogen atoms, two of which can be chlorinated on reaction with HOCl. To effectively trap the chlorine, the carnosine must react to form the stable thermodynamic product in which the nitrogen atom of the primary amine group in the alanine residue is chlorinated. However, the kinetics of the reaction favours the formation of the less stable product, in which chlorine reacts with one of the imidazole nitrogen atoms of the histidine ring. Using *ab initio* and density functional theory calculations, Radom, Karton and colleagues show that an intramolecular Cl shift may occur, which transforms the initially formed kinetic product into the more stable thermodynamic product.

They explore the potential energy surface for the shift reaction and see that the migration occurs through three intramolecular steps: a proton shift that positively charges the imidazole ring, followed by the Cl shift from the imidazole ring to the amino end of the molecule, followed by a subsequent amino proton shift. Radom, Karton and colleagues also calculated the free-energy barriers for this mechanism in molecules structurally similar to carnosine, inserting or removing CH_2 groups to effectively lengthen or shorten the molecule. Shortening the molecule increases the free-energy barrier for Cl transfer, whereas lengthening it by one or two CH_2 groups has the opposite effect. The changes are related to the ease with which the transition state for chlorine transfer can form and provides a design principle for making improved HOCl scavengers. GA

Written by Gavin Armstrong, Stephen Davey, Russell Johnson and Anne Pichon

blogroll

Real-time chemistry

Chemists and proteins tell all, exposing their inner workings.

Tweeting chemists around the world will always remember the seventh of November as the inaugural ‘RealTimeChem’ day. The event was hosted by Jason Woolford (http://twitter.com/doctor_galactic), who blogs at Doctor Galactic and the Lab Coat Cowboy, and saw chemists of all kinds tweeting about their daily lives in chemistry (<http://go.nature.com/5J2LS8>). All interpretations of ‘doing chemistry’ were represented, including teaching, writing, going to meetings and of course pictures of reactions, extractions and chromatography. For a sampling of some of the contributions, check out Woolford’s compilation of his 24 favourite tweets (<http://go.nature.com/HYeTTw>).

Woolford explained that the seventh of November was chosen to honour Marie Curie’s birthday (<http://go.nature.com/kDsymx>) but he stressed that every day can be #RealTimeChem day (the official hashtag for RealTimeChem; <http://go.nature.com/VaYrbA>). He subsequently wrote of the importance “in this modern age of social media in particular that chemistry continues to engage with the masses and chemists are able to pass on their knowledge, enthusiasm and general love of their subject onto others in an entertaining way” (<http://go.nature.com/iJt1cQ>).

Meanwhile, Derek Lowe at In the Pipeline highlights a very literal interpretation of RealTimeChem (<http://go.nature.com/Ptge7u>). He discusses the use of ultra-short (100 ps) X-ray pulses to watch the tertiary structure of a protein change in response to a stimulus. Lowe describes the technique — picosecond time-resolved Laue crystallography — and its potential applications as “the sort of thing we chemists need to really understand what’s going on at the molecular level, and to start making our own enzymes to do things that Nature never dreamed of.”

Written by Adam Azman, who blogs as ‘azmanam’ at <http://www.chemistry-blog.com>