Oxidative Cleavage of C–C Bonds in Lignin

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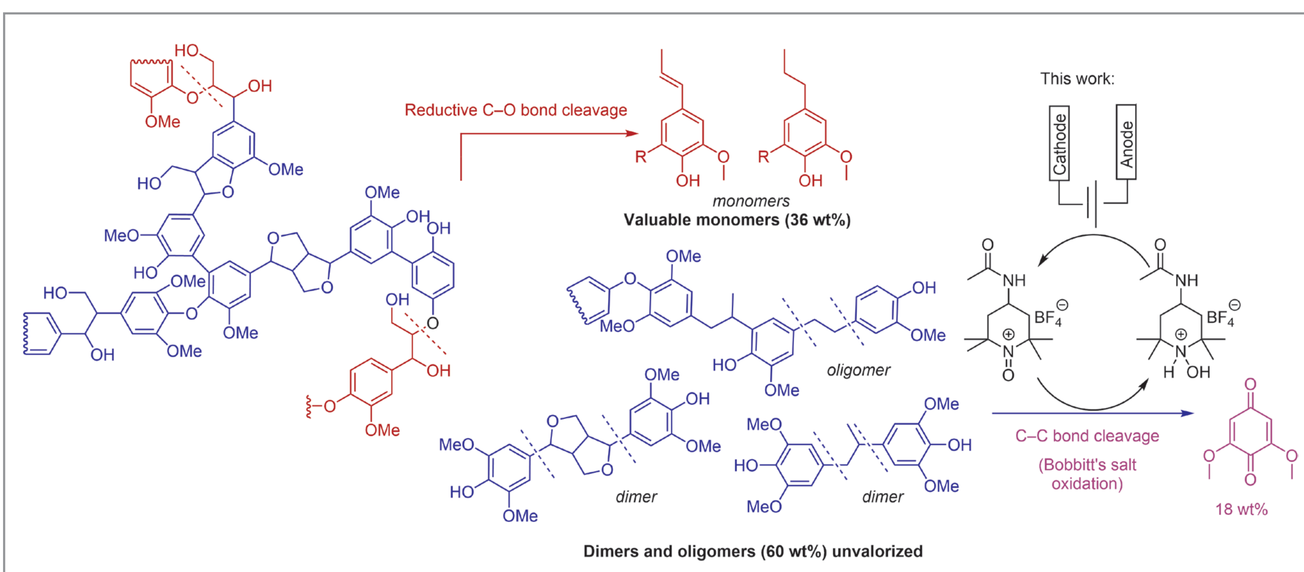
Lignin – which is second only to cellulose as the most abundant organic material on earth – is a complex water-insoluble polymer, composed largely of phenylpropane units which are generally linked through ether bonds (predominantly the aryl-aryl ether-type). Lignin is present mostly in plants' cell walls, representing a key constituent in the support tissues of all terrestrial plants. Industrially, the conversion of cellulose and hemicellulose into fuels and chemicals leaves lignin as a byproduct. To date, relatively few uses have been found for lignin, other than as a fuel. Professor Joseph S. M. Samec, from Stockholm University (Sweden), has a longstanding interest in lignin chemistry, within the group's broader research interests in green chemistry and biomass conversion. "In 2018 we had a whole day seminar in our research group and tried to think of research problems within our field that needed addressing further by the community of lignin chemistry. It's as true now as it was then that lignin chemistry was mainly focused on cleaving β-ether bonds (Scheme 1)," explained Professor Samec. He continued: "These bonds are prevalent in lignin; however, methods that can cleave 100% of these bonds still limit the yield to around 40% of desired aromatic monomers.[1] To enable higher yields, one would need to cleave C–C bonds, which requires pressures and temperatures found in oil refineries (above 360 °C and 60 bars). Thus, there was an obvious unexplored research direction, albeit very challenging."

Examples of oxidative cleavage of aryl–C bonds can be traced back to the works of Joseph Bozell,[2] where Co-salen catalyzed oxidation of *p*-substituted phenols led to the formation of *p*-benzoquinones. "Oxidative cleavage of C–C bonds in lignin to generate simple and valuable products – e.g. derivatives of *p*-benzoquinone – seemed a very attractive, yet challenging approach, as an oxidation of phenols is generally complex and unselective,"[3] explained Professor Samec, who noted that oxidation of lignin and lignin model compounds using TEMPO and its derivatives were comprehensively investigated by Stahl's group.[4,5] "However, the main focus of these studies was on the β-ether bonds, and the fate of other types of linkages was largely unaddressed," commented Professor Samec, adding: "As we were interested in the cleavage of other types of bonds in lignin structure (C–C bonds) which remain intact during the vast majority of lignin depolymerization methodologies, we performed our studies on the residual 'unvalorized lignin', possessing no β-ether bonds, and the corresponding model compounds."

4-Substituted TEMPO-derivatives, such as 4-acetamido-TEMPO, are oxidants that are relatively cheap and easy to



Scheme 1 The novel oxidative cleavage of C–C bonds in lignin

handle. Moreover, the oxidant can be regenerated electrochemically. Professor Samec said: “Initial results on the lignin model compounds were very promising, as we observed a facile formation of 2,6-dimethoxy-*p*-benzoquinone at room temperature, using Bobbitt’s salt – an oxidized form of 4-acetamido-TEMPO. However, in order to achieve high selectivity, we had to go through optimization of reaction conditions and mechanistic studies. The mechanism shed light on the importance of having a nucleophilic reagent present to prevent condensation reactions and also significant difference in reactivity of mono-methoxy and dimethoxy phenolic models. Even though upon optimization of the reaction conditions the product was generated in high selectivity from both the model compounds and ‘unvalorized lignin’ (lignin possessing no β-ether bonds), usage of a stoichiometric amount of oxidant was still a disadvantage. We joined forces with Prof. Mats Johnsson at Stockholm University in order to re-oxidize the reduced form of Bobbitt’s salt. Fortunately, this collaboration worked very well, and together we were able to perform the reaction in a catalytic fashion, where the reduced form of the oxidant was isolated from the reaction mixture and subjected to electrochemical oxidation. We were able to perform five consecutive cycles with a minimal loss in conversion.”

Professor Samec concluded: “We are very excited about these results, not only that we can cleave C–C bonds in lignin but also that we generate dimethoxybenzoquinone, which is a precious fine chemical, in near perfect selectivity using benign reaction conditions. We hope these results will inspire more scientists to continue developing benign methods for other C–C bonds in lignin and other polymers.”

Matteo Zanda

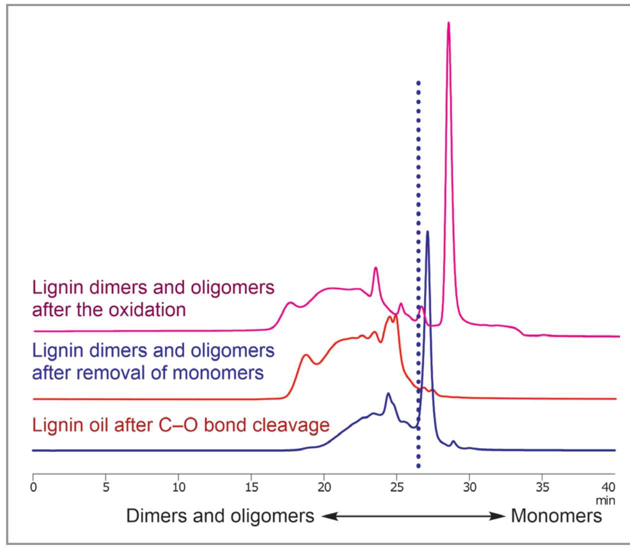


Figure 1 HPLC analysis of treated lignin samples. See Scheme 1 for the structures of monomers, dimers and oligomers.

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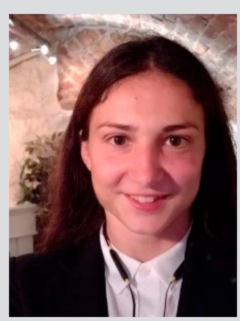

Dr. E. Subbotina

Elena Subbotina received her B.Sc. and M.Sc. degrees in organic chemistry from Lomonosov Moscow State University (Russian Federation) in 2014 and her Ph.D. in organic chemistry from Stockholm University (Sweden) in 2020 under the supervision of Prof. Joseph Samec. During her PhD studies she worked as a visiting PhD student in ITQ (Valencia, Spain) under the supervision of Prof. Avelino Corma. She is currently a postdoctoral fellow at KTH Royal Institute of Technology (Stockholm, Sweden) under the supervision of Prof. Lars Berglund and Prof. Martin Lawoko. Dr. Subbotina has received a Marie Curie fellowship and will go to Yale University (USA) and pursue a postdoc under the supervision of Prof. Paul Anastas. Her research interests include biomass valorization and bio-based materials.

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Thanya Rukkijakan was born and raised in Saraburi, Thailand. He obtained his B.Sc. in biochemistry from Kasetsart University (Thailand) in 2005 and worked as a scientist in microbiology at CPF (Thailand) PCL. In 2009, he started his M.S. in organic chemistry under the supervision of Assoc. Prof. Pitak Chuawong at Kasetsart University and received his Ph.D. in chemistry in 2018. During his doctoral studies, he participated in a research exchange program at Uppsala University (Sweden) supervised by Prof. Joseph S. M. Samec, and Nagoya University (Japan) supervised by Prof. Toshio Nishikawa. Since 2019, he has worked as a postdoctoral researcher in Prof. Joseph S. M. Samec's group at Stockholm University.

Dr. M. D. Márquez Medina

Maria Dolores Márquez Medina received her PhD in June 2019 at the University of Córdoba (Spain). Prior to this, in 2015 she spent time in the Christian Doppler Laboratory for Microwave Chemistry of Prof. C. O. Kappe at the University of Graz (Austria), and for four months in 2018 she had a doctoral stay at the University of Stockholm under the direction of Professor Joseph S. M. Samec, working in the field of catalysis. After completing her Ph.D., she worked in the CSIC catalysis and petrochemical center (ICP) to carry out a research project under the responsibility of the ENAGAS company. At present, she is developing her scientific work in the research group Supramolecular Analytical Chemistry Research Group (FQM-186) at the University of Córdoba. Her entire career has been focused on the use and transformation of plant waste using green chemistry.

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Xiaowen Yu was born in Baoji, Shaanxi, P. R. of China. She received her B.Eng. in polymer science and engineering from Beijing University of Chemical Technology (P. R. of China) in 2013 and Ph.D. in chemistry from Tsinghua University (P. R. of China) in 2018. She was a postdoctoral researcher at Stockholm University (Sweden) under the supervision of Prof. Mats Johnsson from 2018 to 2021. She will return to China and work as a professor in the State Key Laboratory of Crystal Materials, Shandong University (P. R. of China) in 2022. Her research interests include electrocatalysis and photo-electrolysis.

Prof. M. Johnsson

Mats Johnsson received his Ph.D. in 1993 from Stockholm University, Sweden. He has been guest researcher at CEMES/CNRS in Toulouse, France working with Prof. Jean Galy. He is now professor of inorganic chemistry at Stockholm University and has led several projects on ceramic materials, synthesis of ceramic whiskers, and synthesis and physical properties of low dimensional materials. His research has focused during the last few years on electrocatalytic water splitting and alcohol oxidation. He is Director of Studies at the Department of Materials and Environmental Chemistry at Stockholm University and he is actively involved in teaching.

Prof. J. S. M. Samec

Joseph S. M. Samec received his Ph.D. in 2005 from Stockholm University, Sweden. He was a visiting researcher for Professor Charles P. Casey at the University of Wisconsin (USA) in 2002. During 2006–2007, he joined the California Institute of Technology, USA as a postdoctoral researcher with Robert H. Grubbs (Nobel Laureate). In 2009, he started his independent research career at Uppsala University (Sweden) where he was promoted to associate professor in 2011. In 2015, he moved to Stockholm University and was then promoted to full professor in 2017. His research interest focuses on green chemistry in organic synthesis and biomass conversion and its applications. In 2013, he founded RenFuel AB, a spin-off company from his academic research that produces biofuels from lignin, and in 2020 he founded RenFuel Materials that produces lignin-based materials.

