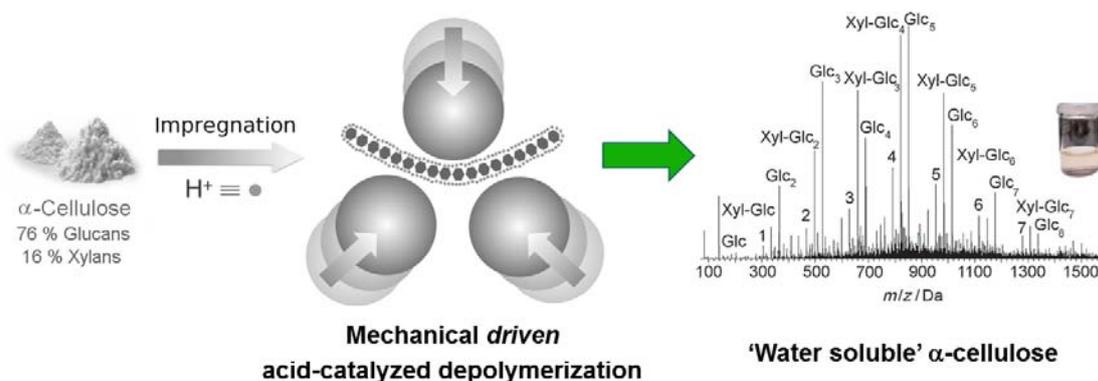


2.3.6 Research Area “Deep Depolymerization of Lignocelluloses by Mechanocatalysis”

(R. Rinaldi and F. Schüth)

Involved: N. Meine, J. Hilgert, M. Kälström, M. D. Kaufman Rechulski

Objective: The utilization of lignocelluloses (*e.g.* wood, grass, crops residues and several others) shows great potential as part of the solution for decreasing the dependence of modern societies on fossil resources. In spite of this, the direct conversion of these renewable carbon sources by chemical and biotechnological processes is hindered by their complex polymeric nature. In plant biomass, three polymers – cellulose, hemicellulose and lignin – form a complex composite that creates the plant cell walls. The composite structure is highly recalcitrant so that chemical or enzymatic processes for hydrolysis of cellulose suffer from low efficacy due to harsh reaction conditions and high byproduct formation in case of the chemical methods, or high costs and long reaction times for the enzymatic methods. Thus, there is an overwhelming need for novel processes to convert the whole plant biomass, forming fermentable sugars and technical sulfur-free lignins. In this group of projects, we aim at the development of energy- and solvent-efficient processes for ‘deep’ depolymerization, thus leading to full substrate conversion into ‘water-soluble lignocellulose.’



Scheme 1. The pathway towards full conversion of (ligno)cellulosic materials into ‘water-soluble lignocellulose.’ The substrate is impregnated with catalytic quantities of H_2SO_4 or HCl and then mechanically treated in a planetary ball mill. ESI-MS spectrum of water-soluble products obtained by milling H_2SO_4 -impregnated α -cellulose for 2 h. For clarity, products containing a levoglucosan unit (LG) are represented by numbers (n), where the composition is LG-Glc_n . The m/z values correspond to $[\text{M}+\text{Na}^+]$. Insets show the appearance of products from cellulose.

The real significance of processing ‘aqueous solutions of wood’, instead of slurries, lies in the prevention of accumulating the highly recalcitrant lignocellulosic residues on

solid catalysts, thus enabling the development of highly efficient processes for biomass valorization by solid catalysts, which is also studied in this area.

Results: Mechanical forces have been exploited for the past few hundreds of years as a first step in wood pulping and conversion of lignocellulose. Usually, conventional mechanical pretreatments (*e.g.* ball milling) are applied to lignocelluloses in order to comminute the substrate and disrupt the crystalline domains of cellulose. As a result, the raw material becomes more amenable for the chemical or biochemical conversions. In fact, moderate hexitol yields ($\sim 70\%$) can be obtained from cellulose conversion in the presence of Ru/C catalysts only,

if cellulose is pretreated for 2 to 4 days prior to the catalytic reaction. Similar experiences in other types of conversions (*e.g.* enzymatic saccharification) created a common notion that the effective pretreatment of cellulosic materials by ball milling is always time consuming, and thus very energy intensive for large-scale purposes.

‘One-pot processes’ that combine acid catalysis with mechanical forces thus have not yet been extensively explored for the depolymerization of lignocelluloses. We were the first to demonstrate the full conversion of lignocellulose into ‘water-soluble lignocellulose’ can easily be achieved by mechanocatalysis within milling durations as short as 2 h.^[23] We found that the simple impregnation of substrate fibers with catalytic quantities of a strong acid (*e.g.* HCl, H₂SO₄) holds the key for the high efficiency. This strategy alleviates the contact problems faced by the experiments performed in the presence of a solid acid. As a result, water-soluble oligosaccharides are formed in quantitative yield within milling duration of 2 h. Most interestingly, lignocellulosic substrates (*e.g.* sugarcane bagasse, beechwood, pinewood) are also fully converted into ‘water-soluble lignocelluloses’ within 2 to 3 h (Fig. 1). Remarkably, the method also solubilizes lignin, giving a red-brownish color to the solution products obtained from beechwood (Fig. 1).

Because the mechanical process does not destroy the acid catalyst, no additional acid is required in a subsequent step (taking place in aqueous phase) to hydrolyze the soluble

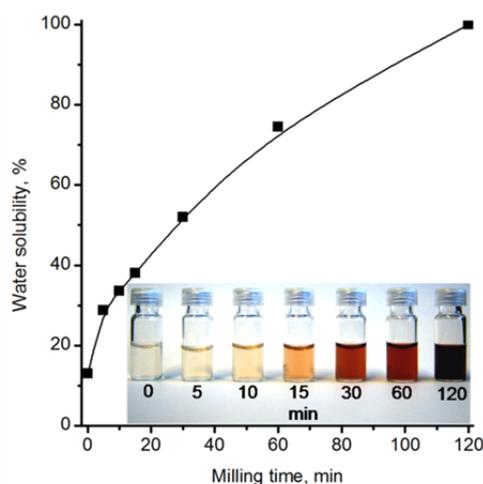


Fig. 1. Formation of water-soluble products (oligosaccharides and lignin fragments) as a function of milling time. Reaction conditions: H₂SO₄-impregnated beechwood (1 g, 0.8 mmol H₂SO₄ per gram of substrate) milled in a planetary mill at 800 rpm for the indicated duration.

oligosaccharides. This fact offers an attractive and inexpensive alternative to enzymatic hydrolysis. In fact, oligosaccharides undergo hydrolysis at temperatures as low as 130 °C for 1 h, forming 91 % glucose, 8 % glucose dimers and 1 % HMF relative to the glucan fraction, and 96 % xylose and 4 % furfural relative to the xylan fraction.^[23] Such high yields in monosaccharides with such a low degree of byproduct formation using such a simple process are unprecedented.

Even more impressive are the results for the saccharification of ‘water-soluble beechwood. The reaction starting with a 10 wt% aqueous solution of depolymerized beechwood (pH 1, at 140 °C for 1 h) also resulted in high yields of monosaccharides (84 % glucose and 89 % xylose, relative to the glucan and xylan fractions, respectively).

However, the saccharification led to an unexpected result – the precipitation of a *sulfur-free* lignin (Fig. 2). The separation of lignin from the monosaccharide solution becomes thus feasible by simple filtration.

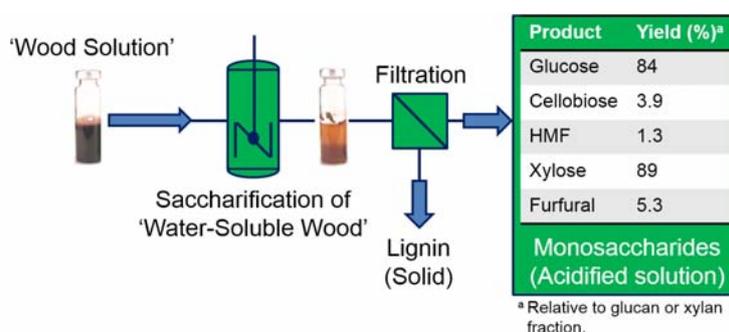


Fig. 2. Fractionation of beechwood into fermentable sugars and sulfur-free lignin by saccharification of ‘water-soluble beechwood.’

The absence of sulfur in these lignin precipitates distinguishes these materials from technical lignins obtained by current pulping processes (*e.g.* kraft and sulfite processes, which may contain up to 10 wt.% sulfur). Furthermore, it is conducive to advanced utilization of the lignin precipitates for the production of high value products (*e.g.* chemicals, fuel additives and carbon fibers).

We also demonstrated the deep depolymerization as a unique entry-point process for efficient production of sugar alcohols from cellulosic substrates.^[34]

Under low-severity

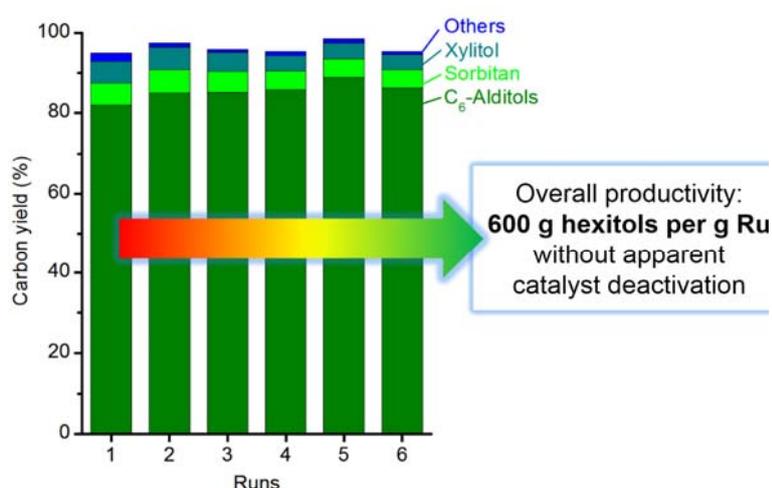


Fig. 3. Recycling of Ru/C. Reaction conditions: 500 mg depolymerized microcrystalline cellulose, 10 mL water, 100 mg Ru/C, 50 bar H₂ (r.t.), at 160 °C for 1 h.

conditions, 94 % yield of hexitols was obtained from the depolymerized microcrystalline cellulose, in the presence of a pre-activated Ru/C, by a batch reaction at 150 °C for 1 h. Noteworthy, such a high yield was achieved in an overall time of only 3 h, that is, *24-36 times faster* than the best examples reported so far. Indeed, a commercial Ru/C catalyst was fully compatible with the presence of H₂SO₄ in the reaction medium. The catalytic activity of Ru/C was fully maintained throughout six runs at 160 °C for 1 h each, as seen in Fig. 3. In the recycling experiments, the cumulative productivity achieved about 600 g of hexitols per g of Ru. As the catalyst is still highly active at the sixth reaction run, this value will be much higher in an extended recycling test.

In a joint research project with J. A. Dumesic (U. Madison-Wisconsin), we also demonstrated the high-yield production of furfurals starting with mechanocatalytically depolymerized substrates.^[41] This reaction is conducted in a biphasic reactor containing an organic phase (4-propylguaiacol) and an aqueous salt phase comprising the sugar oligomers. Short reaction times are possible with the use of microwave heating and limit the extent of degradation reactions. Remarkably, at a conversion of glucans of 94% or higher, the isolated yield of HMF reached 60 and 69% in the experiments beginning with water-soluble products from beechwood and sugar cane bagasse, respectively. These yields are remarkably high, as similar studies have reported HMF yields of ~35% when starting from pinewood. Full conversion of xylose with high selectivity for furfural was achieved for the lignin-containing substrates. Again, the current yields of furfural (74 – 84 %) are also higher than those previously reported for the direct processing of solid lignocellulosic substrates (~ 65 %).

One may argue that milling would not be a feasible solution on the scale required for bulk processing of lignocellulosic biomass. Amidst the several conditions studied for the mechanocatalytic depolymerization, we found good correlations of the estimated energy dose, transferred to the substrate, with the achieved solubility of the products. Table 1 compares the milling energy input required for full conversion of the substrate into water-soluble products with the substrate energy content. Most importantly, we have found that the method would be, indeed, already feasible on a kilogram-scale, as indicated by the lower energy demand of the method (by a factor of 0.3-0.7) relative to the substrate energy content.

Table 1. Comparison of the energy demand for the milling process at several method scales.

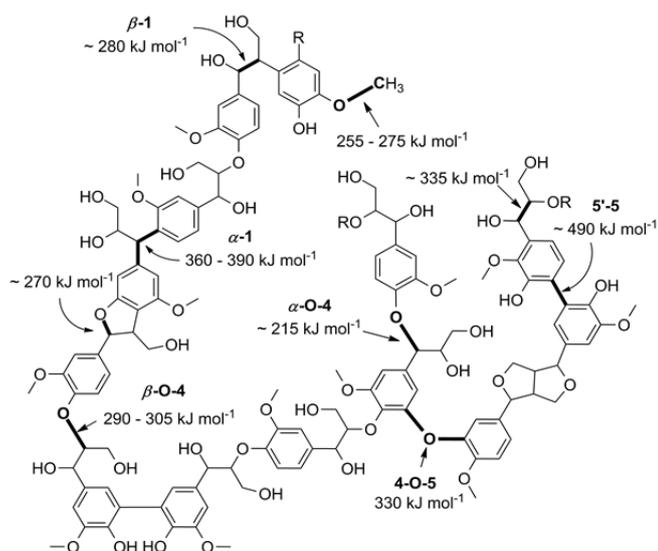
Method scale (g)	Milling energy input / substrate energy content*
2	49
40	7
100	1
1000	0.3-0.7

* Values estimated considering an average energy content of dry wood of 18 MJ/kg.

2.3.7 Research Area “New Catalytic Methodologies for Valorization of Lignin” (R. Rinaldi)

Involved: X. Wang, P. Ferrini, G. Calvaruso, N. Ji, H. J. Estevez-Riveira, J. Geboers

Objective: Lignin occurs alongside hemicellulose and cellulose in the plant cell walls. Chemically, lignin is a network polymer made of phenylpropenyl units (*i.e.* coumaryl, syringyl and coniferyl alcohols) that are randomly connected by C—C and C—O bonds (Scheme 1). This biopolymer corresponds to up to 30 % of the plant biomass composition and 40 % of the energy content of lignocellulose. Hence, to find outlets for technical lignins is clearly required for lignocellulose utilization to become carbon economic and energy efficient. At the first sight, the structural model of a native lignin suggests that this



Scheme 1. Example of lignin structure depicting some of the primary inter-unit linkages and the corresponding average values of bond dissociation enthalpy.

feedstock could serve as a raw material for the production of phenols. In this context, hydrogenolysis of aryl alkyl ethers is a reaction receiving increasing attention because of the large fraction of lignin subunits connected by such ether bonds (Scheme 1). However, the lack of catalytic methodologies able to transform the polymeric lignin into solely a class of monomeric products present a major barrier to exploit the potential of this feedstock to the fullest. In this group of projects, we aim to establish a world-class laboratory on catalysis for lignin valorization. The mission of this laboratory, supported by the Alexander von Humboldt Foundation through the Sofja Kovalevskaja Award 2010 given to Rinaldi, is to contribute to the foundations for the rational design of catalytic systems for efficient lignin conversion. Accordingly, we rely on two main strategies to develop catalysis for lignin conversion. First, to understand the solvent effects on the hydrogenolysis/hydrogenation of lignin in the presence of Raney Ni and other Ni catalysts. Second, to design reaction pathways for the molecular simplification of lignin feeds (organosolv lignin and biogenic phenols from bio-oil) based on catalytic hydrogen transfer.

Results: Solvents play an important role in catalytic hydrogenations. So far, however, there has been almost no discussion on the influence of solvents in the catalytic hydrogenolysis of lignin or related model compounds. Aiming to ultimately assess the solvent effects on the hydrogenolysis of lignin, we first examined the influence of several solvents in a model reaction using diphenyl ether, a substrate comprising a very strong C–O bond (analogous to 4-O-5, Scheme 1). In the exploratory study, Raney Ni was chosen for several reasons. Unlike noble metals, which show usually a high chemoselectivity towards hydrogenation or hydrogenolysis, Raney Ni is a relatively less expensive material and a ‘promiscuous’ catalyst in regard to its chemoselectivity. Hence, Raney Ni is able to tackle the structural complexity of lignin, thus showing great potential for lignin conversion.

As expressed by a solvent parameter called ‘donor number’, the Lewis basicity of the solvent was identified as one of the most important parameters accounting for the activity and selectivity of Raney Ni in the conversion of diphenyl ether. In non-basic solvents (*e.g.* 1,1,1,3,3,3-hexafluoro-2-propanol and alkanes), Raney Ni is an extremely active catalyst for hydrogenolysis and hydrogenation, as shown by the full conversion of diphenyl ether into saturated products. In basic solvents, however, Raney Ni is less active, but a much more selective catalyst for hydrogenolysis of the C—O bonds.

Lignin conversion can be performed even in solvents in which lignin is insoluble. Indeed, lignin starts to undergo thermolysis at temperatures as low as 160 °C. This non-catalyzed process brings aromatic fragments into solution and, consequently, enables the action of solid catalysts. Nonetheless, for high conversion of solid lignin, the process should be performed at temperatures above 250 °C, although such a requirement increases the energy demand of the process. We found that subjecting organosolv lignin to Raney Ni in methanol under an initial H₂ pressure of 7 MPa (*r.t.*) at 300 °C for 8 h is an effective strategy to produce a complex mixture of phenols from lignin. In turn, if saturates are the desired products, solvents possessing no Lewis basicity (*e.g.* methylcyclohexane) are the best choices for the lignin conversion.^[71]

Raney Ni is able to catalyze the reduction of many organic functionalities by transfer hydrogenation using 2-propanol as an H-donor. These reactions usually take place under reflux conditions. The transfer hydrogenations with Raney Ni have not

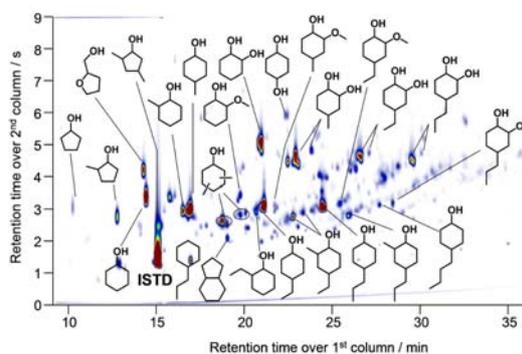


Fig. 2. GC×GC image of bio-oil processed by transfer hydrodeoxygenation using 2-propanol as solvent and H-donor at 160 °C for 3 h.

found extensive uses in organic synthesis due to the lack of chemoselectivity, very often leading to defunctionalization of complex molecules. This ‘disadvantage’ attracted our attention because the upgrade of highly functionalized phenols, such as those found for the lignin substructures or bio-oil, requires catalysts capable of simultaneously reducing several functionalities under low-severity conditions.

We demonstrated the transfer hydrodeoxygenation of the phenolic fraction of bio-oil to a mixture of cyclic alcohols and diols to be feasible under unprecedented low-severity conditions (*e.g.* 160 °C and autogeneous pressure).^[70] In spite of the importance of the aforementioned findings, we realized that the even in the best cases, the formation of mixtures of oxygenated products from lignin (*e.g.* phenols, cyclohexanols and cyclohexanones) still does not suffice for utilization of lignin by the chemical industry. This is because the cracking of the complex structure of lignin leads to very complex product mixtures having only low content of individual components. In effect, since the oxygenated lignin products have high boiling points (*e.g.* phenol, 182 °C), the product separation is very difficult to envision on such a large scale as needed for the lignocellulosic biorefinery. Thus, the complex mixture of oxygenated products would be mostly destined for low-value purposes. Alternatively, the conversion of lignin yielding

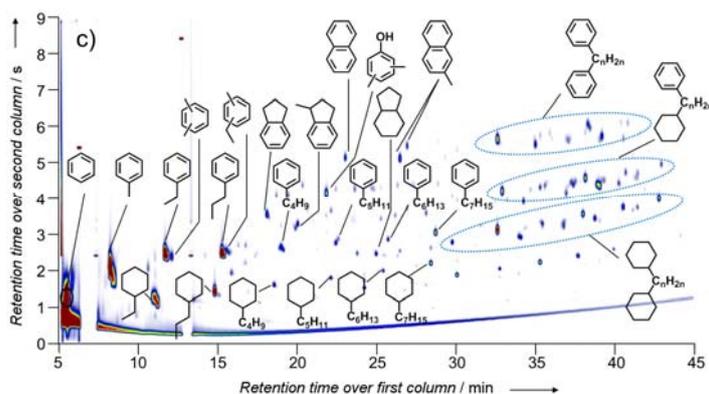
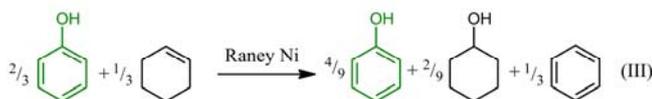
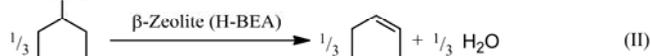
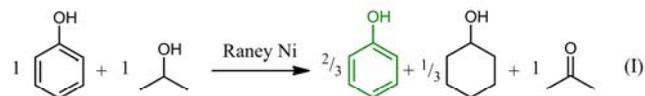


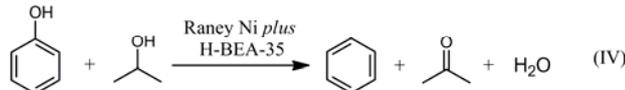
Fig. 3. GC×GC-MS of lignin products obtained from the tandem dehydroxylation of phenols. Reaction conditions: Raney Ni (0.6 g), H-BEA-35 (0.050 g), substrate (0.1 g), 2-PrOH (0.50 g), *n*-pentane (7 mL) processed at 160 °C for 2 h and sequentially at 240 °C for an additional 2 h.

Main reactions involved in the one-pot tandem conversion:



∴ propagation by (II) and (III) leads to full conversion of phenol

Overall reaction:



Scheme 2. Simplified pathway for the dehydroxylation of phenols to arenes by catalytic tandem reactions with concurrent use of Raney Ni and β -zeolite (H-BEA-35). The structure in green corresponds to the unconsumed phenol by (I) and (III).

arenes with low boiling point could greatly facilitate the fractionation and further processing of the arene mixtures into chemical commodities (*e.g.* benzene, toluene, ethylbenzene and xylenes) by conventional refinery and petrochemical routes.

In spite of the potential in lignin and bio-oil valorization, the dehydroxylation of phenols is a very challenging chemical transformation. In fact, the Ar—OH bond has a bond dissociation enthalpy of $465 \text{ kJ}\cdot\text{mol}^{-1}$, which is even higher than that of a C—H bond in methane ($439 \text{ kJ}\cdot\text{mol}^{-1}$). In organic synthesis, there are few methods available for phenol dehydroxylation. Typically, they require the derivatization of the Ar-OH group with an electron withdrawing group for weakening the C—O bond. As such, the derivatization enables the hydrogenolysis of the C—O bond with the use of Pd/C and H_2 , thus forming the corresponding arenes. It is understandably difficult to envision the utilization of these procedures on a large scale, since they generate stoichiometric quantities of waste.

We demonstrated a novel pathway as highly useful for the depolymerization of lignin and removal of its oxygen-containing functionalities in addition to dehydroxylation of phenols.^[73] The novel approach for phenol dehydroxylation (Scheme 2) consists in coupling (I) hydrogenation of phenol to cyclohexanol and (II) dehydration of cyclohexanol to cyclohexene with (III) dehydrogenation of cyclohexene to benzene. Under H_2 pressure, the combination of steps (I) and (III) in a one-pot procedure is impossible. However, steps (I) and (III) become compatible in a one-pot procedure when the reactions are performed by *H-transfer in the absence of H_2* . The conversion of phenol continues by the utilization of cyclohexene formed by (II) because the reaction (III) is thermodynamically more favorable than (I). Therefore, the formation of arenes occurs by the propagation of the reaction chain by (II) and (III). The one-pot procedure is carried out in the presence of Raney Ni and β -zeolite using 2-propanol solely as a starting H-donor, that is, in a molar ratio 2-propanol-to-phenol below 3. Applying the catalytic procedure to organosolv lignin (Fig. 3) resulted in an isolated yield of about 40 wt% colorless oil (78 % of the detected products are arenes, 18 % alkanes, and only 4 % are phenols). Similar results were obtained from the upgrade of the phenolic fraction of bio-oil. Overall, if one considers that the lignin has 70 % of C-content, and the products, 80 - 90 %, isolated yields of ca. 50 % corresponds to a very good carbon yield of ca. 70 - 80 %.

In conclusion, the unprecedented high selectivity to arenes obtained under low-severity conditions provides a new route in stark contrast to emerging approaches for catalytic upgrade of bio-oil or other methods using H-transfer which are performed under extremely harsh conditions (5 – 20 MPa, 300 – 500 °C). Finally, even if the isolated

yield of the products is insufficient to give a suitable return in today's chemical industry, the mixture of arenes and aliphatics could very well serve as valuable bio-additives to synthetic fuels produced by the Fischer-Tropsch process, which lack aromatic and branched hydrocarbons required for high-performance of fuels for aviation or Otto-engines.

2.3.8 Research Area “Understanding the Mechanisms of Dissolution and Hydrolysis of Cellulose in Electrolytes”

(R. Rinaldi)

Involved: H. F. Nunes de Oliveira, A. Carvalho, N. Meine

Objective: Native cellulose is, for several reasons, often unsuitable for technical applications. Accordingly, the dissolution of cellulose is essential to reshape the natural fibers, thus providing materials with the desired properties. Furthermore, in solution, cellulose is not physically protected by its supramolecular structures, thus enabling the direct investigation of its chemical reactivity. In this group of projects, research into new solvents for cellulose and mechanisms of cellulose dissolution and hydrolysis have been performed.^[75]

Results: In 2011, a significant breakthrough was achieved by us,^[67] we introduced a novel class of solvent systems for cellulose (Fig. 1). We demonstrated organic electrolyte solutions, which contain just a minor mole fraction of ionic liquid (χ_{IL}), as better solvents for cellulose than the parent ionic liquids (ILs) themselves. These solutions are able to instantaneously dissolve cellulose in concentrations as high as 25 wt%. This

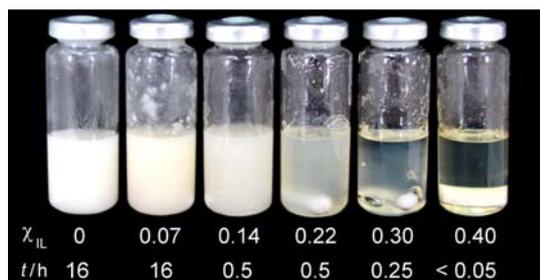


Fig. 1. Appearance of the mixtures containing microcrystalline cellulose (Avicel, 10 wt %), 1,3-dimethyl-2-imidazolidinone and 1-butyl-3-methylimidazolium chloride after stirring at 100 °C for the time indicated in the figure. Note that there is a magnetic bar at the bottom of the vials.

striking finding overcomes the major drawbacks that the dissolution of cellulose in neat ILs faces (*i.e.* the slow rate of dissolution, the high viscosity of the solutions obtained, the limited solubility of cellulose and not to mention the high costs of ILs). Indeed, the dissolution of cellulose in neat 1-butyl-3-methylimidazolium chloride (BMIMCl) is a process well-known to take more than 10 h.

Upon dissolving easily 10 wt% cellulose in few minutes (Fig. 1), the simultaneous use of BMIMCl and 1,3-dimethyl-2-imidazolidinone (DMI) brought enormous benefit to the process. Moreover, the use of 1-ethyl-3-methylimidazolium acetate (EMIMAcO) as IL in the solvent system allows instantaneous dissolution of cellulose at 100 °C. This feature enabled the determination of $\chi_{EMIMAcO}$ at which the dissolution of cellulose was achieved in the molecular solvents at 100 °C (Fig. 2).

fully converted into water-soluble oligosaccharides in the presence of a strong acid. The general mechanistic aspects of the hydrolysis of cellobiose strongly suggest that the hydrolysis of cellulose depends heavily upon conformational changes. Accordingly, we propose that mechanical forces serve to activate the 'latent state', i.e. the protonated cellobiose subunits occurring in the cellulosic chain, thus inducing the required conformational changes for the cleavage of the glycosidic linkage. Nonetheless, the reaction still requires a strong acid, which is conveniently provided by impregnation of cellulose with H_2SO_4 or HCl . Indeed, milling cellulose without additives leads mainly to the destruction of the crystalline domains. In this case, there is only little depolymerization, with very low yields of water-soluble products.