Conference paper

Ivan Kumaniaev, Elena Subbotina, Maxim V. Galkin, Pemikar Srifa, Susanna Monti, Isara Mongkolpichayarak, Duangamol Nuntasri Tungasmita and Joseph S. M. Samec*

A combination of experimental and computational methods to study the reactions during a Lignin-First approach

<https://doi.org/10.1515/pac-2019-1002>

Abstract: Current pulping technologies only valorize the cellulosic fiber giving total yields from biomass below 50 %. Catalytic fractionation enables valorization of both cellulose, lignin, and, optionally, also the hemicellulose. The process consists of two operations occurring in one pot: (1) solvolysis to separate lignin and hemicellulose from cellulose, and (2) transition metal catalyzed reactions to depolymerize lignin and to stabilized monophenolic products. In this article, new insights into the roles of the solvolysis step as well as the operation of the transition metal catalyst are given. By separating the solvolysis and transition metal catalyzed hydrogen transfer reactions in space and time by applying a flow-through set-up, we have been able to study the solvolysis and transition metal catalyzed reactions separately. Interestingly, the solvolysis generates a high amount of monophenolic compounds by peeling off the end groups from the lignin polymer and the main role of the transition metal catalyst is to stabilize these monomers by transfer hydrogenation/hydrogenolysis reactions. The experimental data from the transition metal catalyzed transfer hydrogenation/hydrogenolysis reactions was supported by molecular dynamics simulations using ReaXFF.

Keywords: biomass valorization; catalytic fractionation; ICGC-8; lignin; Lignin-First; ReaXFF.

Introduction

Our current utilization of fossil resources for transportation, chemicals, energy production, materials creation, medicines, computers, etc. is not sustainable because of the worldwide threats that we have to face such as climate change, resource depletion, and political instability. Even though biomass is a potentially renewable source of carbon [1] current biorefineries, such as pulp mills, have been developed at a time when fossil energy was considered endless and thus, are rather inefficient. Indeed, less than 50 wt% of the lignocellulosic biomass ends up as valorized products and more than 50 % is burnt at a low value to produce heat. Inspired by Hibbert's early work devoted to characterize lignin from a structural point of view [2–6], a methodology termed “Lignin-First” has been recently resurrected by several groups of scientists (for instance, Kou [7],

Article note: A collection of invited papers based on presentations at the 8th IUPAC International Conference on Green Chemistry (ICGC-8), Bangkok, Thailand, 9–14 September 2018.

***Corresponding author: Joseph S. M. Samec**, Stockholm University, Organic Chemistry, Stockholm, Sweden, e-mail: joseph.samec@su.se

Ivan Kumaniaev, Elena Subbotina, Maxim V. Galkin and Pemikar Srifa: Stockholm University, Organic Chemistry, Stockholm, Sweden. <https://orcid.org/0000-0001-6543-7674> (M. V. Galkin)

Susanna Monti: University of Pisa, Faculty of Natural Science and Mathematical Physics, Pisa, Toscana, Italy

Isara Mongkolpichayarak: Chulalongkorn University, Faculty of Science, Bangkok, Thailand

Duangamol Nuntasri Tungasmita: Chulalongkorn University, Chemistry, Bangkok, Thailand

Fig. 1: Traditional pulping versus Lignin-First approach.

Zhang [8], Abu-Omar [9], Rinaldi [10], Sels [11] and our group [12]) with the aim and ambitious plan of introducing this revised procedure as an alternative to current pulping (Fig. 1). Recently, a few reviews describing all the processes and ideas behind them have been published [13–17]. In summary, the methodology combines an organosolv pulping with transition metal catalysed (transfer) hydrogenolysis/hydrogenation reactions. The combinations of these processes yield a solid pulp residue, an aqueous phase consisting of hemicellulose, and a lipophilic fraction with depolymerized lignin. It should be noted that alternative strategies to the transition metal catalyzed reductive stabilizations such as capping reactive intermediates by ethylene glycol [18] or preventing their formation by blocking the reactive sites prior to depolymerizations have also been reported [19].

We have developed, in a first approach, a redox neutral lignin depolymerization where hemicellulose operates as an inherent hydrogen donor [11, 20]. Its advantages are: (1) avoiding hazardous, explosive, high pressure, capex intensive infrastructure, and usually fossil fuel-derived hydrogen gas; (2) no addition of other hydrogen donors or trapping agents; (3) no regeneration or other post-treatments, or separation of spent trapping or reducing agents. Up until recently, Lignin-First reactions have been carried out by means of batch autoclaves, where biomass, solvent mixtures, catalyst, and hydrogen or hydrogen donors have been blended together. This reaction set-up leads to complex product mixtures and tedious purification challenges, especially because the heterogeneous catalysts and cellulose pulp are difficult to separate. Another disadvantage of batch processes is that the solvolysis and the reactions performed by the catalyst cannot be either optimized or studied separately. Sels's research group handled the separation of these two processes in space by employing the catalyst in a basket without observing any deviation in reactivity [22]. This clearly showed that the solvolysis yields lignin derivatives that could be transformed by the catalyst that was separated from the rest of the biomass. The group of Roman-Leshkov and our group obtained a separation of the solvolysis and transfer hydrogenolysis/hydrogenation reactions in both space and time by applying a flow-through technology [21, 23, 24]. Besides solving the purification issues of catalyst and cellulose, this experimental set-up enabled us to optimize and study the two processes separately.

Results and discussion

The flow-through set up consists of one percolation chamber, in which the lignocellulosic biomass is placed. The chamber is connected to a reactor charged with palladium on charcoal (Pd/C) (Fig. 2). The percolation

Fig. 2: The flow-through set up for catalytic lignin fractionation.

chamber is connected to the reactor with Pd/C through a three way valve which allows to collect a sample of the reaction mixture after the first (solvolyis) step and to study the products independently. The solvent is preheated prior to entering the system. Back pressure regulators connected to the outlets maintain the required pressure in order to keep the solvent in a liquid phase. The solvent mixture ($\text{MeOH}:\text{H}_2\text{O}:\text{H}_3\text{PO}_4$) is pumped through the heating coil and through the percolation chamber where extractions and solvolyis occur. Then the solvent fraction containing extracted wood components is led out and either collected and analyzed, or transferred to the next heating coil and then to the Pd/C reactor. The Pd/C reactor is responsible for transfer hydrogenation and hydrogenolysis reactions. The product mixture from the reactor with Pd/C is then collected and analyzed. This set-up assembly guarantees that both the solvolyis and hydrogenolysis/hydrogenation reactions can be studied separately in real time.

Different lignocellulose fractionation methods result in isolated lignin with high molecular weight (from 5 to up to 30 kDa) [13]. Thus, before these studies, it was accepted that lignin was released predominantly as oligomers from the wood matrix and then transformed by the catalyst through hydrogenolysis reactions targeting the $\beta\text{-O-4'}$ bond. Using the batch methodology, this processes were difficult to study mainly because the solvolyis and transfer hydrogenolysis reactions occurred simultaneously and the intermediates were not isolated. Previous studies have revealed that formation of allylic alcohols (and their fast recondensation at longer reaction times) during the treatment of wood in $\text{MeOH}:\text{H}_2\text{O}$ has been observed [25]. In addition, Rinaldi and coworkers observed high concentrations of monophenolic compounds formed during the solvolyis reaction at the very beginning of the transformation. These findings suggested that the solvolyis involved more complex processes than the release of the oligomers solely [10].

The flow-through set-up provided an opportunity to get a better insight into the nature of the extraction process. Rapid cooling of the reaction mixture from the percolation chamber allowed us to study the solvolyis in real time. We found that monophenolic compounds comprising mostly of coniferyl and sinapyl alcohols could be isolated in above 20 % yield related to the initial Klasson lignin content (Fig. 3, top). Thus, about 50 % of the theoretical yield of monomers can be obtained by means of metal-free solvolyis which is therefore responsible not only for the extraction but also for partial depolymerization of the lignin. To explain this, we proposed a mechanism which involves partial reduction of lignin with hemicellulose and/or methanol. The role of hemicellulose as an internal hydrogen donor was confirmed with a model reaction of isoeugenol reduction. Isoeugenol and Pd/C were mixed under the typical Lignin-First approach conditions with and without xylose. In the presence of xylose, reduction of isoeugenol to propylguaiacol was faster (39 % conversion as compared to 7 % conversion within 10 min).

However, while the solvolyis afforded relatively high yields of monomers, oligomers with molecular weight averages of 5 kDa were also observed (Fig. 4, orange). Mild reaction conditions do not allow for all $\beta\text{-O-4'}$ bonds cleavage where more stable non-terminal $\beta\text{-O-4'}$ bonds stay intact. Monophenolic compounds

Fig. 3: The study of the solvolysis process over time. The GPC diagram shows that the monomer fraction at retention time of 25 min is large both at t_1 (25 % delignification at 18 min) t_2 (75 % delignification at 36 min), and only at t_3 (95 % delignification at 60 min), oligomer region (~ 5 kDa M_w) becomes dominating. Reprinted from ref 14b, published by Royal Society of Chemistry with a Creative Commons Attribution-NonCommercial 3.0 Unported License (<https://creativecommons.org/licenses/by-nc/3.0/>).

Fig. 4: Relative abundance of species during the solvolysis process with (green line) and without (orange line) a transition metal catalyst. Reprinted from ref 14b, published by Royal Society of Chemistry with a Creative Commons Attribution-NonCommercial 3.0 Unported License (<https://creativecommons.org/licenses/by-nc/3.0/>).

are unstable under fractionation conditions and tend to repolymerize [26, 27]. We could conclude the observations made by Rinaldi's group that monophenolics were observed in the beginning of the reaction. However, at 75 % conversion, monophenolic compounds were still observed in the reaction mixture, likely due to a rapid dispatch from the reaction zone and rapid cooling (Fig. 3, middle).

While the solvolysis itself gives rise to high yields of monophenolic compounds, the yields of monophenolics are increased to 37–40 % relative to Klason lignin content when the solvolysis was followed by the transition metal catalyzed transfer hydrogenolysis/hydrogenation reactions. Furthermore, the monophenolic compounds from the solvolysis are transformed to less reactive species. Moreover, the organosolv lignin obtained at the first step was depolymerized further. The reaction mixture of the transition metal catalysis step was analyzed by means of GPC. Produced compounds were found to correspond to species with molecular weights of monomers, dimers, and trimers (Fig. 4, green). This implies that lignin is partially cleaved during solvolysis and the depolymerization is completed when the metal catalyst comes into play.

Noteworthy, we found that while the solvolysis was a fast process where above 95 % delignification occurred after an hour, the operation of the Pd/C catalyst was significantly slower (Fig. 5). Even after 3 h,

Fig. 5: Interaction between the substrates and products that have been identified from both the solvolysis and the hydrogenation/hydrogenolysis reactions. Reprinted from ref 14b, published by Royal Society of Chemistry with a Creative Commons Attribution-NonCommercial 3.0 Unported License (<https://creativecommons.org/licenses/by-nc/3.0/>).

products from the hydrogenation/hydrogenolysis reactions were still present in the eluting solvent. This was intriguing and stimulated a new investigation focused on the interactions of substrates and products with the catalyst (identified from both the solvolysis and the hydrogenation/hydrogenolysis reactions).

With this aim in mind, we opted a combination of experimental and theoretical descriptions. From an experimental point of view, we studied the adsorption of products of the solvolysis and hydrogenation/hydrogenolysis reactions over the Pd/C catalyst surface [28]. As shown in Fig. 6, compound **1** represents oligomer, including dimeric species. Compounds **2–7** have all been isolated and verified from solvolysis or hydrogenation/hydrogenolysis. These compounds were individually mixed with Pd/C in different concentrations and the Langmuir adsorption isotherms were measured.

The model **1** representing an oligomer has the strongest adsorption ($K = 7.0 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1}$). Noteworthy, this is still an underestimation since the model compound is itself a dimer while we were able to detect oligomers up to 9 kDa in the GPC (see Figs. 3 and 4). For the syringyl series, i.e. compounds **2**, **4**, and **6** an expected correlation between unsaturation and number of hydroxyl groups with the adsorption was observed ($K = 6.6, 3.4, 1.2 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1}$, respectively). This was not the case for the guaiacyl series, where all molecules showed a low affinity to the Pd/C. The latter observation is surprising, however, it can shed light on the results obtained from catalytic fractionation of guaiacyl rich species, such as spruce and pine that give lower yields of monophenolic compounds than observed from syringyl rich species such as birch. The main reason for the lower yields for guaiacyl species is the lower content of $\beta\text{-O-}4'$ interlinkages, however, the isotherm study shows that the guaiacyl species has a significantly lower affinity to the catalyst than the syringyl species. Thus, the guaiacyl species have a stronger propensity of being in solution where repolymerization reactions occur.

Reactive species from organosolv pulping

Identified products from transfer hydrogenolysis

Fig. 6: Model compounds that used for the study of adsorption isotherms.

We could then plot the Gibbs energy expressed through the thermodynamic constant of Langmuir adsorption ($\Delta G_{\text{ads}} = -RT \ln K + \text{const}$) to the measured maximum coverage of each molecule to Pd/C (Fig. 7). Surprisingly, a linear correlation ($r^2 = 0.89$) was observed. This trend may be explained by suggesting that α_0 is in inverse ratio to the characteristic surface area of each molecule, and the surface area is in its turn in a direct proportion with the Gibbs energy of adsorption.

As the products from hydrogenolysis/hydrogenation reactions had a lower affinity to the Pd/C than the substrates, we proposed that the hydrogen transfer reactions could be responsible for the reaction profile shown in Fig. 5. As the reactions on the Pd/C are hydrogen transfer reactions, a way to study whether this is a slow step is to measure the kinetic isotope effect. Thus, we evaluated the isotopic effect of Pd/C-catalysed hydrogenation of lignin model monomer isoeugenol **8**. Formic acid was used as a hydrogen source (Fig. 8) since it can be formed from the biomass under the pulping conditions [29]. A primary isotope effect of 5 was observed, which support that the hydrogen transfer is slower than the desorption of product **7** from the Pd/C surface.

From a theoretical point of view, we simulated the catalytic processes inside the Pd/C reactor by means of classical reactive molecular dynamics simulations in the methanol-water mixture used in the experiments after parametrizing all the interactions of the whole species present in the system against quantum chemistry calculations [30]. All the molecular components, their structure, dynamics and reaction mechanisms were satisfactorily reproduced. The new force field could be used to reproduce the behavior of lignin analogs inside the reactor. The simulation model and investigation plan is schematized in Fig. 9. Dimeric model **1'** (an analogue of **1**) and monophenolic compound **2** were selected. The palladium surface was modelled by both Pd(100) and a Pd(111) slabs. One of the major advantages of using ReaXFF is that also the dynamics, reactivity and effects of the solvent mixtures on the solutes can be reproduced realistically. The solvent is fundamental for both the solvolysis and transfer hydrogenation/hydrogenolysis steps. Interestingly, it was found that the solvent not only physisorbed on the Pd surfaces but also chemisorbed. Indeed, some methanol molecules released its hydrogens to the Pd surface. Even if this was observed experimentally, we propose that the main

Fig. 7: Correlation between thermodynamic terms of adsorption and the maximum coverage of each model compound on Pd/C. Reprinted with permission from *Ind. Eng. Chem. Res.* **58**, 6899 (2019). (Ref. 17). Copyright (2019) American Chemical Society.

Fig. 8: The kinetic isotope effects of **8** under the present of formic acid. Reprinted with permission from *Ind. Eng. Chem. Res.* **58**, 6899 (2019). (ref 17). Copyright (2019) American Chemical Society.

Fig. 9: Schematic representation of the catalyst reactor and the simulated system. IN: Molecule in solution at the beginning of the simulations. OUT: some of the identified products. On the right-hand side: Adsorbed fragments and Solvent molecules.

hydrogen source in the current system is decomposition of hemicellulose e.g. hexoses and further to formic acid. Dimeric species **1'** physisorbed by the ether linked aromatic ring and the benzylic alcohol function, which rapidly leads to a chemisorption in which the hydrogen of the benzylic alcohol is released to the palladium surface. The ether linked aromatic part has a strong adsorption to the Pd/C while the other aromatic ring has no connection to the catalyst. The C–O bond of the β –O–4' linkage is elongated and cleaved within 25 picoseconds. The syringol leaves the surface rapidly while the benzyl alcohol **9** is strongly adsorbed to the Pd/C. As **9** is never observed in the product mixture, we propose that it either dehydrates to compound **8** or undergoes a hydrogenolysis reaction to generate **6** (Fig. 10).

Fig. 10: The cleavage mechanism for β –O–4' ether linkage of **1'** on Pd (111) surface. Physisorption of **1'** to the surface (a). Chemisorption of **1'** leads to the release of hydrogen of the benzylic alcohol. The elongation of C–O bond of β –O–4' ether linkage was found to be a slow step (b). The syringol leaves the surface while another fragment maintains adsorbed to the catalyst (c). The benzyl alcohol **9** probably transforms to **6** or **8** before or after leaving the surface (d).

Fig. 11: Sample caption Mechanism for reduction of C=C bond of **2** on Pd (111) surface. Physisorption of **2** to the surface (a). Both the aromatic ring and the C=C bond chemisorb to the surface (b). Hydrogen that is present on the surface is ready to insert to the double bond (c). The saturated product **4** leaves the surface (d).

Compound **2** physisorbed to the palladium surface with first the aromatic ring, then the double bond and the hydroxyl group. Thus, the molecule formed a strong physisorption to the Pd/C. Both the aromatic ring and the double bond then underwent a chemisorption to the palladium, where the C=C bond was elongated from 1.35 Å to 1.45 Å. As there was hydrogen present on the surface of palladium, insertion of hydrogen to the double bond resulted in saturation of the double bond and the double bond was elongated to 1.55 Å. Product **4** is then detached from the palladium surface (Fig. 11).

Conclusions

The combined experimental and theoretical study gives new insights into the lignin first approach. We have reported a flow-through experimental set-up in which the solvolysis and transfer hydrogenation/

Scheme 1: Summary of chemical processes in the flow-through set-up for catalytic lignin fractionation in the percolation chamber as well as on the palladium surface. Left, up; hexose is dehydrated to levulinic acid and formic acid; left, down; end groups of lignin are peeled off by reducing sugars or formic acid. Right, up; Pd/C cleave internal β-O-4' linkages using formic acid; right down; sinapyl alcohol is reduced by Pd/C using formic acid.

hydrogenolysis reactions are separated in both space and time, thus allowing to study the individual roles of the solvolysis and transfer hydrogenation/hydrogenolysis reactions. It was found that solvolysis has a major role in not only delignifying the cellulose pulp, but also in the generation of monophenolic compounds. We propose that metal-free solvolysis is responsible for the reductive cleavage of some part of β -O-4' linkages, taking place before the Pd/C mediated transfer hydrogenation/hydrogenolysis reactions. The mechanism of this metal-free process is still not understood, however, reducing sugars from decomposition of hemicellulose probably play an important role [31]. Delignification of wood occurs at a faster rate than the catalytic stabilization of lignin derivatives due to their strong adsorption to Pd/C catalyst, and slow hydrogen transfer reactions on the palladium surface (Scheme 1).

Acknowledgements: We thank the Swedish Energy Agency for financial support.

References

- [1] T. Scheper. *White Biotechnology*, p. 20, Springer-Verlag, Berlin (2007).
- [2] H. P. Godard, J. L. McCarthy, H. Hibbert. *J. Am. Chem. Soc.* **62**, 988 (1940).
- [3] H. P. Godard, J. L. McCarthy, H. Hibbert. *J. Am. Chem. Soc.* **63**, 3061 (1941).
- [4] H. P. Godard, J. L. McCarthy, H. Hibbert. *J. Am. Chem. Soc.* **63**, 3066 (1941).
- [5] J. R. Bower Jr., L. M. Cooke, H. Hibbert. *J. Am. Chem. Soc.* **65**, 1192 (1943).
- [6] J. M. Pepper, H. Hibbert. *J. Am. Chem. Soc.* **70**, 67 (1948).
- [7] N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu, Y. Kou. *ChemSusChem* **1**, 626 (2008).
- [8] C. Li, M. Zheng, A. Wang, T. Zhang. *Energy Environ. Sci.* **5**, 6383 (2012).
- [9] T. Parsell, S. Yohe, J. Degenstein, T. Jarrell, I. Klein, E. Gencer, B. Hewetson, M. Hurt, J. Im Kim, H. Choudhari, B. Saha. *Green Chemistry* **17**, 1492 (2015).
- [10] P. Ferrini, R. Rinaldi. *Angew. Chem. Int. Ed.* **53**, 8634 (2014).
- [11] M. V. Galkin, J. S. M. Samec. *ChemSusChem* **7**, 2154 (2014).
- [12] S. V. Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels. *Energy Environ. Sci.* **8**, 1748 (2015).
- [13] M. V. Galkin, J. S. M. Samec. *ChemSusChem* **9**, 1544 (2016).
- [14] R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. Bruijninx, B. M. Weckhuysen. *Angew. Chem. Int. Ed.* **55**, 8164 (2016).
- [15] T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser, B. F. Sels. *Energy Environ. Sci.* **10**, 1551 (2017).
- [16] Z. Sun, B. Fridrich, A. Santi, S. Elangovan, K. Barta. *Chem. Rev.* **118**, 614 (2018).
- [17] W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham, B. F. Sels. *Chem. Soc. Rev.* **47**, 852 (2018).
- [18] P. J. Deuss, M. Scott, F. Tran, N. J. Westwood, J. G. de Vries, K. Barta. *J. Am. Chem. Soc.* **137**, 7456 (2015).
- [19] L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J. S. Luterbacher. *Science* **354**, 329 (2016).
- [20] M. V. Galkin, C. Dahlstrand, J. S. M. Samec. *ChemSusChem* **8**, 2187 (2015).
- [21] M. V. Galkin, A. T. Smit, E. Subbotina, K. A. Artemenko, J. Bergquist, W. J. J. Huijgen, J. S. M. Samec. *ChemSusChem* **9**, 3280 (2016).
- [22] S. Van den Bosch, T. Renders, S. Kennis, S.-F. Koelewijn, G. Van den Bossche, T. Vangeel, A. Deneyer, D. Depuydt, C. M. Courtin, J. M. Thevelein, W. Schutyser, B. F. Sels. *Green Chem.* **19**, 3313 (2017).
- [23] E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham, Y. Román-Leshkov. *Joule* **1**, 613 (2017).
- [24] I. Kumaniaev, E. Subbotina, J. Sävmarker, M. Larhed, M. V. Galkin, J. S. M. Samec. *Green Chem* **19**, 5767 (2017).
- [25] E. Minami, S. Saka. *J. Wood Sci.* **51**, 395 (2005).
- [26] R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. Bruijninx, B. M. Weckhuysen. *Angew. Chem. Int. Ed.* **55**, 8164 (2016).
- [27] P. J. Deuss, M. Scott, F. Tran, N. J. Westwood, J. G. de Vries, K. Barta. *J. Am. Chem. Soc.* **137**, 7456 (2015).
- [28] I. Kumaniaev, J. S. M. Samec. *Ind. Eng. Chem. Res.* **58**, 6899 (2019).
- [29] I. Graça, R. T. Woodward, M. Kennema, R. Rinaldi. *ACS Sustain. Chem. Eng.* **6**, 13408 (2018).
- [30] S. Monti, P. Srifa, I. Kumaniaev, J. S. M. Samec. *J. Phys. Chem. Lett.* **9**, 5233, (2018).
- [31] C. Espro, B. Gumina, T. Szumelda, E. Paone, F. Mauriello. *Catalysts* **8**, 313 (2018).