CHAPTER 3

Lessons Learned from 150 Years of Pulping Wood[†]

CARL HOUTMAN

USDA, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726, USA
Email: choutman@fs.fed.us

3.1 History

The invention of the Gutenberg printing press in 1440 started a steady increase in demand for paper. Until the mid-1800s, most paper pulp was made by collecting, cleaning, and beating discarded linen and cotton rags. Collection of rags was such a large and organized industry that companies were regulated by the government and workers had unions. Henry Mayhew described a grand banquet of the fraternal order of chiffonniers (rag-pickers).[1] As literacy and printing technology improved, demand for paper outstripped supply, and the search for alternative sources of fiber began in earnest. For example, Jacob Christian Shäffer, a noted clergyman and amateur botanist, in 1765 began releasing a six-volume treatise on new papermaking fibers.[2] He explored the use of a wide range of natural materials to make paper and he bound samples of the paper in his books to demonstrate their quality. Ultimately Shäffer started his own paper company.

[†]The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

Energy and Environment Series No. 19
Lignin Valorization: Emerging Approaches
Edited by Gregg T. Beckham

Published by the Royal Society of Chemistry, www.rsc.org

Many early materials for papermaking were naturally fibrous, but René Antoine Ferchault de Réaumur noted, as part of his extensive study of insects, "[Wasps] teach us that paper can be made from the fibres of plants without the use of rags and linen."[2] Specifically, he was referring to wasps that collect fibers from surfaces of wood to make their nests. Around 1800, Matthias Koops obtained two patents related to making paper without using rags.[3] While the exact process he used is unclear, he claimed to make paper from wood. He likely used a combination of chemical and mechanical action to fiberize the material. While Koops' business failed, others took his ideas and started making commercial quantities of ground-wood. Ground-wood pulp is made by pressing logs against rotating stone cylinders and releasing fibers by mechanical action. The short fibers produced by this method provided a smooth surface for printing, but the addition of longer rag fibers was still required to give the paper sufficient strength.

In his efforts to isolate the substance we now know as cellulose from wood, Anselme Payen used nitric acid to remove the "matière incrustante de bois", which we now call lignin.[4] While the elemental analysis experiments performed in 1838 were not intended to lead to alternate pulp fibers, they were among the first examples of chemical pulping of wood. In chemical pulping, a portion of the lignin is removed by chemical action, liberating the fibers. In 1864 Charles Watt and Hugh Burgess received US patent protection for their discovery of soda (sodium hydroxide) cooking of wood to make pulp.[5] While this patent was later determined to be invalid by a case appealed to the US Supreme Court,[6] the described process produced pulp from hardwoods. The search for other methods of chemical pulping continued because soda cooking made weak paper and could not be used with softwoods. Around the same time, Benjamin Tilghman noticed that both hardwood and softwood exposed to sulfurous acid became fibrous.[7] Difficulties in developing materials that could withstand corrosive process conditions and difficulties with process control made Tilghman abandon his experiments, but other engineers, inspired by his work, went on to develop the sulfite process.[8] In a typical sulfite process, the sulfurous acid is partially neutralized. The hydroxides or carbonates of calcium, magnesium, sodium, and ammonia have all been used as bases. Calcium carbonate was the first base used. Because of the low cost of limestone and sulfur, the spent cooking liquors were sewered. As environmental and cost pressures grew, the "magnefite" process was developed using magnesium oxide as the base. Magnesium oxide can be recovered by evaporating and then burning the spent cooking liquor. While the sulfite process continues to be practiced today, it has several limitations; recovering and recycling the cooking chemicals is inefficient, the sulfite pulp makes weaker paper than the kraft process, and the process does not work well with dense hardwoods and resinous softwoods.

The next advance in chemical pulping came with the discovery by Asahel Eaton[9,10] that sulfide in soda pulping liquor enhanced the pulping rate and resulted in stronger fibers. With the subsequent discoveries of an efficient

Table 3.1 Characteristics of commercially practiced chemical pulping processes in North America.

Process	Kraft	Acid-sulfite	Mg-sulfite	Neutral-sulfite
US production[14] (1000 tons per year)	42 107 (93.2%)	0 (0%)	207 (0.5%)	2827 (6.3%)
Chemicals	NaOH, Na_2S	H_2SO_3, $NaHSO_3$	H_2SO_3, MgO	Na_2SO_3, Na_2CO_3
Temperature (°C)	165–175	120–150	150–160	160–180
Time (h)	1–3	3–6	2–4	0.5–1
Yield (%)	45–50	48–51	50–52	70–80
Wood	Hardwoods and softwoods	Hardwoods	Hardwoods	Hardwoods and some softwoods

recovery cycle by Carl Dahl[11] and a recovery boiler by George Tomlinson,[12] kraft pulping has become the dominant method of producing chemical pulp today (Table 3.1). As was described by Kleppe,[13] the reasons kraft pulping dominates North American chemical pulp production are:

1. It has an efficient recovery process.
2. All wood species can be pulped.
3. Modern bleaching can produce high brightness pulps.
4. Paper produced from kraft pulp is stronger than paper produced from other pulps.

Although kraft pulping has many advantages, release of sulfur compounds, environmental impact, and capital intensity continue to present challenges to paper companies. Over the last 50 years, extensive research, pilot testing, and commercial trials have been conducted on solvent pulping. This class of processes has become known as ''organosolv''. Muurinen[15] has reviewed the wide range of solvents with acids and bases that have been tested. One of earliest organosolv process was proposed by Kleinert and Tayenthal,[16] but it took 40 years to develop a complete process.[17] Over the years, many processes have been trialed but none has remained in use longer than five years.[18] Complete processes based on methanol (Organocell and ASAM), ethanol (Alcell), acetic acid (Acetosolv), and peroxyformic acid (Milox) have all been tested on at least the pilot-scale.[15] The economic performance of all these processes depends on obtaining high recovery rates of solvent. The majority of solvent losses occur during pulp washing and solvent recovery. While kraft mills burn their black liquor to recover cooking chemicals and energy, all organosolv processes must include more complex separation unit operations. Recovered lignin is a by-product of these processes. Sales of recovered lignin could offset some of the other costs, but, except for a few niche markets, organosolv lignin has not developed into a profit stream, yet.

3.2 Chemistry

3.2.1 Delignification Chemistry

Because lignin is biosynthesized by phenolic radical coupling with unsaturated side chains, coniferyl alcohol and sinapyl alcohol, see Figure 3.1, there are a significant number (55–66%) of monomers with ether linkages.[19,20] While carbon atom-centered radicals forming C–C bonds and rearrangements result in other linkages, ether bonds are dominant targets of pulping chemistry.[21] Ether cleavage can be catalyzed by both acids and bases, and practically every acid and base has been explored as a pulping chemical. Once the lignin is fragmented, it must be dissolved in pulping liquor before it can be washed out of fibers. If the pulping liquor is aqueous, introduction of charge groups by sulfonation (sulfite pulping) or phenol deprotonation (kraft pulping) facilitates dissolution. Alternatively one can introduce organic solvents to help solubilize lignin fragments. For example, as mentioned above, Kleinert and Tayenthal patented an organosolv process.[16]

In all pulping processes, there is a balance between lignin fragmentation and condensation. C–C bonds can be formed under both acidic and basic conditions. While it is still a matter of active research, there appears to be a range of electrophilic and nucleophilic reactions, and subsequent rearrangements[19] that can form new bonds. Addition of hydrosulfide anion (HS^-) to kraft liquors likely serves the role of inhibiting these condensations by competing in addition reactions. The critical role that condensation reactions play in limiting the production of small lignin fragments has been shown by the effectiveness of thioacidolysis,[22] an analytical method for determining lignin composition. More recently, addition of formaldehyde to biomass pretreatment[23] produces a soluble lignin fraction with ''near theoretical'' yields of the monomeric subunits.

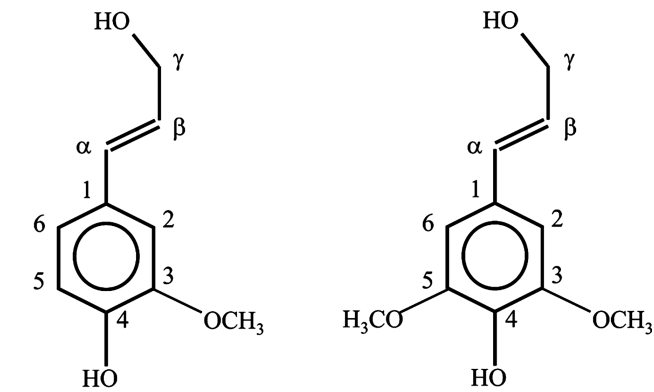

Figure 3.1 Nomenclature of lignin monomers.

The reduction in condensation reactions has also been correlated with lignin monomer subunit composition. Syringyl (S) is the 3,5-dimethoxy substituted subunit, while guaiacyl (G) is 3-methyloxy substituted (Figure 3.1). The reactive form of the lignin molecule is the phenolate, and the resonance delocalization of the negative charge increases the nucleophilicity of the carbons *ortho* and *para* to the phenol (positions 1, 3, 5).[24] For syringyl subunits, both the 3 and 5 positions are occupied by methoxyl groups, and thus reaction at this position is sterically hindered. The open 5 position in guaiacyl subunits bears a higher nucleophilicity and is more prone to compete with the other nucleophiles in the process, leading to irreversible condensed products.[21] Wood that is higher in S-lignin, *e.g.*, hardwood, is much easier to delignify both because there are fewer condensed linkages in the native lignin and because condensation reactions occur at a lower rate during pulping.[25]

3.2.2 Alkaline Pulping Chemistry

While the fundamental process chemicals of kraft pulping have not changed for 100 years, our understanding and ability to control the process has advanced. The reactions of lignin during alkaline pulping are a complex network of cleavages and condensations that occur both in the liquid phase and at solid–liquid interfaces. Delignification is often observed to proceed at a decreasing rate with higher extents.[13] The initial rapid reaction removes approximately 20% of the material in the secondary wall. Then bulk delignification proceeds through the secondary wall to the middle lamella and removes another 70% of the mass of material. Finally, the last 10% of the lignin reacts very slowly. The residual lignin is often enhanced in G-units and condensation products, and thus is only very slowly removed by hydrolysis. If white paper is desired, the residual material is removed by oxidative bleaching steps, which exhibit higher cellulose to lignin selectivity than kraft pulping.

Using a series of analysis methods, Prinsen *et al.* compared the lignin properties of residual and dissolved (black liquor) lignin during kraft and soda pulping[26] (Table 3.2). For comparison they also included similar analysis of milled-wood lignin (MWL). The MWL sample is the fraction of lignin soluble after ball-milling (20–30%). While it likely is significantly lower in molecular weight than native lignin, it can be used as a reference for the linkage types. The authors varied the cooking conditions to get samples with different extents of delignification for each type of pulping. Inspection of Table 3.2 shows that the lignin dissolved in the pulping liquor has a lower molecular weight, which is represented as estimated degree of polymerization (DP) in the table. The data in Table 3.2 show that the starting lignin has a significant quantity of ether linkages, 84%, the dissolved material has practically none, $<1\%$, and the major product of the hydrolysis is free phenolic hydroxyl groups. The C–C bonds are less dramatically affected.

Table 3.2 Properties of alkaline residual and dissolved lignin. Adapted with permission from P. Prinsen, J. Rencoret, A. Gutiérrez, T. Liitiä, T. Tamminen, J. L. Colodette, M. Á. Berbis, J. Jiménez-Barbero, Á. T. Martínez, and J. C. del Río, *Ind. Eng. Chem. Res.*, 2013, **52**, 15702.[26] Copyright 2013 American Chemical Society.

		Residual				Black liquor			
	MWL	Kraft		Soda		Kraft		Soda	
% Lignin	95.0	3.3	2.5	3.3	2.5	3.3	2.5	3.3	2.5
DP_n	17.5	12.2	11.9	13.5	12.7	8.3	8.1	8.2	7.8
DP_w	66.5	21.7	17.5	23.8	19.5	11.8	11.2	12.6	11.6
S/G	2.0	2.1	1.9	2.1	1.7	3.4	3.1	2.8	2.8
Ether linkages (%)	84	16	14	18	12	1	0	0	0
C–C bond linkages (%)	16	7	7	7	7	10	9	9	8
% Phenolic OH	13	34	41	43	45	79	88	81	85

As has been reviewed by Chakar and Ragauskas,[19] the dominant depolymerization mechanism is base-catalyzed hydrolysis of ethers. Upon deprotonation, the resulting phenolate can be converted into a quinone methide, which is likely the active intermediate for condensation reactions.

Over the last 10 years, there has been a growing appreciation of the importance of lignin–carbohydrate complexes (LCCs). It is now widely reported that almost all lignin isolates contain hemicellulosic sugars or their degradation products, covalently attached. Part of the reason for the slow identification is that the linkages, often esters, are rapidly broken under alkaline conditions.[27] In the context of chemical pulping, there seems to be a differentiation of types of lignin based on which hemicellulose is attached.

3.2.3 Neutral Pulping Chemistry

As currently practiced in North America, the goal of neutral-sulfite cooking is not the removal of lignin, but instead the ''softening'' of the lignin before mechanical refining.[28] With the near-neutral pH, the rate of hemicellulose and ether hydrolysis is slow, as indicated by a typical yield of 70–80%.[29] Sulfonation does continue at this pH and is likely the origin of the desired changes in lignin properties.

3.2.4 Acidic Pulping Chemistry

Under acidic conditions, the aryl ethers of lignin may be cleaved by ionic acidolysis and hemolytic cleavage.[30] The carbocations formed during the first step of acidolysis likely participate in condensation reactions that often result when lignin is exposed to acidic conditions. When the acid is sulfurous acid, as in acid-sulfite pulping, the β-O-4 cleavage reaction is suppressed, and the dominant reaction is sulfonation at the α-position[31] (Figure 3.1). This conclusion is also supported by the analysis of commercial lignosulfonates, which shows that the degree of polymerization is high, 20–300 C_9 units, and approximately 50% of the monomer units are sulfonated.[32]

3.3 Paper Industry Attempts to Get More Than Energy out of Lignin

3.3.1 Lignin Sulfonate

As discussed above, kraft pulping dominates North American chemical pulp production, but early in the last century calcium-bisulfite pulping was much more common. Spent sulfite liquors contain sulfonated lignin and sugars. In an effort to recover value from this waste stream, the sugars were often fermented to ethanol and the lignosulfonates were precipitated using lime.[33] The washed lignosulfonates were aggressively marketed as extenders and binders. While the early market penetration was slow, there is now a solid global market of approximately 1.1 million metric tons per year. With the March 2001 closure of Georgia-Pacific's Bellingham, Washington mill, the United States became a net importer of lignosulfonate, which has become a common concrete additive, among other uses.

3.3.2 Vanillin Production

Vanillin production from lignin is a complex story. Starting in the early 1900s Guy Howard[34] and others developed ways of isolating vanillin from oxidized lignosulfonate. In 1936, commercial production of vanillin from lignin as a coproduct of pulping operations was started in Rothschild, Wisconsin[35,36] and two facilities in Canada soon started producing vanillin, as well. A facility at Thorold, Ontario, reached a maximum production of 3.4 million kg per year,[37] which was 60% of the global demand at that time. Now, operations in North America have ceased due to waste handling problems, limited demand for sulfite pulp, and less expensive petroleum-based routes to vanillin.[38]

The isolation of vanillin from lignin involves a series of unit operations that winnow the wide range of chemical products formed from lignin oxidative depolymerization down to the desired product. The elegant solution was to use a carbonyl sulfite addition step, which is a unique reaction for benzaldehydes.[37] The sulfite addition makes the desired compound soluble in water, while many of the similar substituted phenols remain insoluble in water. This switching of extraction properties during the process results in dramatic improvements in separation (Figure 3.2).

The sequence of unit operations can be summarized as follows:

1. oxidize softwood lignosulfonate under alkaline conditions;
2. make a vanillin/bisulfite complex by adding sulfurous acid;
3. use organic solvent to remove any small molecules not sulfonated;
4. dissociate the complex by neutralization and recover sulfur dioxide;
5. use organic solvent to extract the vanillin, which is no longer charged;
6. evaporate the solvent;
7. recrystallize the vanillin.

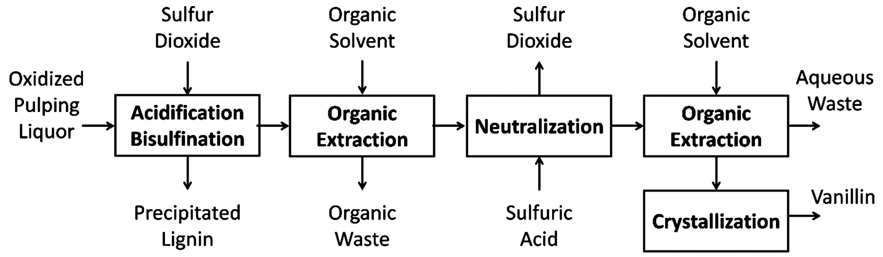

Figure 3.2 Commercial process for purifying vanillin from pulping liquors.

A Norwegian company, Borregaard, continues to operate a lignin-to-vanillin plant in Sarpsborg, Norway.[39] The details of their process design are not publicly available but likely include innovations like membranes and ionic adsorption columns to significantly reduce the process waste streams that led to the demise of the North American operations.

3.3.3 Kraft Lignin Recovery

Ever since soda pulping was first practiced, it has been known that acidification of black liquor results in lignin precipitation. As mentioned above, this change in solubility is caused by protonation of phenols in dissolved lignin fragments. Kraft lignin has long been a material of commerce, but on a small scale. For example, Westvaco Corporation (now Ingevity) has produced and sold kraft lignin in a variety of forms and under several tradenames, including Indulin A and C. With loss of lignosulfonate production capacity in North America, opportunities for other lignin products is emerging. Renewed efforts have brought two other processes from laboratory and pilot trials to commercial-scale operations. ''LignoBoost,'' inspired by Westvaco's work and further developed by Innventia and Chalmers University, is now installed and operating by Domtar in Plymouth, North Carolina and a second facility has been installed by Stora Enso in Kotka, Finland.[40] This process uses carbon dioxide to lower the pH of the black liquor, causing the lignin to precipitate. The solid lignin is removed with a filter and the filtrate is returned to the pulp mill. After an acid washing step, the lignin is filtered again and dried.

In an attempt to decrease the concentration of reduced sulfur compounds and improve the properties of the resulting lignin, FPinnovations and NORAM have developed ''LignoForce''.[41] This process is similar in concept to LignoBoost in that carbon dioxide is used as an acid to precipitate lignin, but LignoForce has a preoxidation step, which oxidizes some of the reduced sulfur compounds and modifies the lignin properties by introducing new aldehydes and ketones (Figure 3.3). This process has recently been started up by West Fraser in Hinton, Alberta.

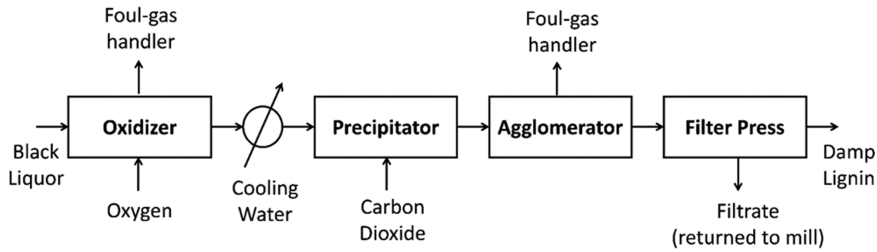

Figure 3.3 LignoForce process.

3.3.4 Black Liquor Gasification

While Tomlinson boilers[12] have served the industry well for 80 years, many are nearing the end of their useful lifetime. Naqvi *et al.*[42] have comprehensively reviewed black liquor gasification technologies. Several projects have moved to pilot-scale over the last 15 years. The production ranged between 20 and 300 tons per day. In addition, a wide range of options have been evaluated for their techno-economic performance. For example, Larson *et al.*[43] modeled the production of ''producer gas'' from black liquor, which could be burned in a gas turbine to produce electricity. The waste heat from this process could be used to produce steam for the pulp mill. They concluded that replacing a Tomlinson boiler with a black liquor gasification combined cycle (BLGCC) cogeneration system could increase the efficiency of converting lignin fuel into electricity while still meeting the steam requirements of the mill.

In another study, Larson *et al.*[44] considered the possibility of producing several synthetic fuels and chemicals from gasified lignin. They concluded that while converting a paper mill into a biorefinery would be a significant capital investment, the returns looked promising.

To date, there have not been any projects that have moved from pilot-scale to wider adoption. The reason for this lack of progress is likely related to (a) capital intensity of the proposed systems, (b) low prices of natural gas and petroleum, (c) recent improvements in evaporator design, which has increased thermal efficiency by allowing mills to fire more concentrated black liquor, and (d) improved Tomlinson boiler controls, which have also increased efficiency.

On a broader scale, the lack of commercialization of gasification illustrates the difficulty of applying new lignin technology in the paper industry. In most cases, paper production will continue to be the major source of revenue. Making paper requires a large amount of energy. While there are efficiency gains to be made, the paper mill still needs a significant fraction of its lignin production to meet its energy demand. Because paper production is tightly coupled to its energy supply, whole mill models are required to effectively predict the impact of taking lignin from the black liquor stream. Any change in one part of the process will have impacts on the other

subsystems of a mill. Mills that have installed gasification, *i.e.*, LignoBoost or LignoForce processes appear to generally have exceeded the capacity of their recovery system and are looking for a way to operate at a pulp production that exceeds the capacity of the boiler.

3.4 Conclusions

Pulp and paper production has followed the rise of large scale printing. Beginning in the 1800s, the pulp industry in North America largely turned to wood for its fiber supply. In the beginning, calcium-sulfite pulping liquors were simply discarded, but as the industry grew, uses for lignosulfonates and sugars were found.

Today, kraft pulping has replaced sulfite pulping. Most kraft mills are fairly efficient and meet much of their energy demands by burning lignin and carbohydrate. There has been a small business using acid precipitation to recover lignin from kraft black liquor, but because mills need energy the commercial value of this recovered lignin needs to be well above the price of other fuels.

Newer technologies, black liquor gasification and organosolv pulping, are being explored as ways to provide lignin-derived feedstocks to the chemical industry. While there are many attractive compounds in lignin, the cost of separating valuable compounds from hundreds, even thousands, of other organic compounds means that they are currently inaccessible on a commercial scale.

References

1. H. Mayhew, *London Labour and the London Poor: Volume 2*, 1851, p. 141.
2. D. Hunter, *Papermaking: The History and Technique of an Ancient Craft*, Alfred A. Knopf, Inc., New York, NY, 1947, Chap. XI.
3. M. Koops, *GB Pat.*, 2,481, 1801.
4. A. Payen, *C. R.*, 1838, **7**, 1052.
5. C. Watt and H. Burgess, *U. S. Pat.*, 11,343, 1864.
6. Supreme Court of the United States, 90 U.S. 23 Wall. 566, 1874.
7. B. Tilghman, *U. S. Pat.*, 70,485, 1867.
8. L. H. Weeks, *History of Paper Manufacturing in the United States*, Lockwood Trade Journal Company, New York, NY, 1916, p. 230.
9. A. Eaton, *U. S. Pat.*, 106,143, 1870.
10. A. Eaton, *U. S. Pat.*, 119,224, 1871.
11. C. Dahl, *U. S. Pat.*, 296,935, 1884.
12. G. Tomlinson, *U. S. Pat.*, 2,070,632, 1937.
13. P. J. Kleppe, *TAPPI J.*, 1970, **53**(1), 35.
14. Food and Agriculture Organization (FAO) of the United Nations, *Pulp and Paper Capacities, Survey 2014–2019*, FAO, Rome, 2015.

15. E. Muurinen, Organosolv Pulping A review and distillation study related to peroxyacid pulping, University of Oulu, Thesis, 2000.
16. T. N. Kleinert and K. Tayenthal, *U. S. Pat.*, 1,856,567, 1932.
17. T. N. Kleinert, *U. S. Pat.*, 3,585,104, 1971.
18. R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2016, **55**, 8164.
19. F. S. Chakar and A. J. Ragauskas, *Ind. Crops Prod.*, 2004, **20**, 131.
20. R. Vanholme, B. Demedts, K. Morreel, J. Ralph and W. Boerjan, *Plant Physiol.*, 2010, **153**, 895.
21. J. Gierer, *Wood Sci. Technol.*, 1985, **19**, 289.
22. C. B. Rolando, B. Monties, C. Lapierre, Methods in lignin chemistry, in *Springer Series in Wood Science*, ed. S. Y. Lin and C. W. Dence, Springer-Verlag, Berlin, 1992, p. 334.
23. L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**(6310), 329.
24. A. K. Sangha, J. M. Parks, R. F. Standaert, A. Ziebell, M. Davis and J. C. Smith, *J. Phys. Chem. B*, 2012, **116**, 4760.
25. P. C. Pinto, D. V. Evtuguin and C. P. Neto, *Ind. Eng. Chem. Res.*, 2005, **44**, 9777.
26. P. Prinsen, J. Rencoret, A. Gutiérrez, T. Liitiä, T. Tamminen, J. L. Colodette, M. A. Berbis, J. Jiménez-Barbero, A. T. Martínez and J. C. del Río, *Ind. Eng. Chem. Res.*, 2013, **52**, 15702.
27. M. Lawoko, G. Henriksson and G. Gellerstedt, *Biomacromolecules*, 2005, **6**, 3467.
28. J. Gullichsen and C.-J. Fogelholm, *Papermaking Science and Technology, Book 6A, Chemical Pulping*, Fapet Oy, Helsinki, Finland, 1999, p. A103.
29. G. Gellerstadt and J. Gierer, *Acta Chem. Scand.*, 1968, **22**, 2510.
30. S. Li, K. Lundquist and U. Westermark, *Nord. Pulp Pap. Res. J.*, 2000, **15**, 292.
31. G. Gellerstadt and J. Gierer, *Sven. Papperstidn.*, 1971, **5**, 117.
32. S. M. Braaten, B. E. Christensen and G. E. Fredheim, *J. Wood Chem. Technol.*, 2003, **23**(2), 197.
33. J. N. Stephenson, *Preparation and Treatment of Wood Pulp*, McGraw-Hill Book Company Inc., New York, NY, 1950, p. 354.
34. G. C. Howard, *U. S. Pat.*, 1,551,882, 1925.
35. L. T. Sandborn, J. R. Salvesen, G. C. Howard, *U. S. Pat.*, 2,057,117, 1936.
36. H. Hibbert, G. H. Tomlinson, *U. S. Pat.*, 2,069,185, 1937.
37. M. B. Hocking, *J. Chem. Ed.*, 1997, **74**(9), 1055.
38. M. Fache, B. Boutevin and S. Caillol, *ACS Sustainable Chem. Eng.*, 2016, **4**, 35.
39. M. M. Bomgardner, *Chem. Eng. News*, 2014, **92**(6), 14.
40. H. Wallmo, A. Littorin, H. Karlsson, K. Lindholm, R. Stern and G. Christiansen, *TAPPI PEERS Conference proceedings*, Jacksonville, FL, 2016.

41. L. Kouisni, A. Gagne, K. Maki, P. Holt-Hindle and M. L. Paleologou, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5152.
42. M. Naqvi, J. Yan and E. Dahlquist, *Bioresour. Technol.*, 2010, **101**, 8001.
43. E. Larson, S. Consonni, R. Katofsky, A Cost-Benefit Assessment of Biomass Gasification Power Generation in the Pulp and Paper Industry. Final Report, Princeton University and Politecnico di Milano, 2003.
44. E. Larson, S. Consonni and R. Katofsky, A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry. Final Report, vol. 1, Princeton University and Politecnico di Milano, 2006.