

Utilization of wood cell wall components

Yasumitsu Uraki¹ · Keiichi Koda¹

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Abstract This article summarizes current utilizations of wood cell wall components in relation to biorefinery of woody biomass as a separation method of its constituents. Especially, utilization of isolated lignins, involving transformation and molding, are demonstrated with respect to productions of carbon fibers and their further functionalization, such as developments of activated carbon fibers and electrodes for second battery and electric double-layer capacitor.

Keywords Biorefinery · Lignin · Fusibility · Moldability

Significance of utilization of wood cell wall components

Wood cell wall consists of about 45 % of cellulose and 20–30 % of hemicelluloses and lignin. The ratio of hemicelluloses to lignin varies depending on the wood species, softwood or hardwood. In 1975, I. S. Goldstein demonstrated “potential for converting wood into plastics” in Science [1], where 95 % of plastics or synthetic fibers in the USA at that time could be produced from wood components, lignin and cellulose. Especially, lignin was a

promising feedstock for thermosetting resins and aromatic polymers. Thereby, he claimed that woody biomass and its components were alternative feedstock to petroleum for polymer production. As a social background of the paper, the price of petroleum was increased due to its expanded consumption and shortage. In this century, the fear of shortage of fossil resources was slightly relieved because of the development of shale gas and oil. However, environmental impacts of consumption of fossil resources, such as exhausting greenhouse gases and reducing them from the Earth, are still of great concern. Therefore, utilization of woody biomass as a renewable alternative resource to fossil resources provides one of the solutions to such an environmental problem.

Fossil resources have two aspects: one, as a source of energy for fuel and electricity; and the other, as a source of raw material for organic chemicals and plastics. Electricity may be produced from some renewable resources, such as solar, wind and geothermal powers, but liquid fuel, such as bioethanol and biodiesel, and organic chemicals cannot be produced from such renewable resources. These organic materials can be prepared from another renewable resource such as wood and its constituents, instead. From this viewpoint, woody biomass and its components, the most abundant biomass on Earth, can be an alternative organic feedstock to fossil resources.

In this article, we introduce the recent progress in research for utilization of woody biomass components, in particular lignin. Now, lignin is merely used as an energy source for the pulp and paper industry. However, lignin is rarely used as a material source, except for utilization of lignosulfonate as a cement dispersant (including concrete) [2] and as an electrode of the second battery [3]. In the woody biomass utilization, lignin utilization is a key subject, as pointed out by Goldstein [1].

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✉ Yasumitsu Uraki
uraki@for.agr.hokudai.ac.jp

¹ Research Faculty of Agriculture, Hokkaido University, N-9, W-9, Kita-ku, Sapporo 060-8589, Japan

Cellulose utilization

β -(1 \rightarrow 4) glucan, cellulose, has been used widely as a raw material for fabrics and paper since the dawn of time, and also as a first feedstock for man-made plastics (cellulose nitrate) and man-made fiber (rayon). Even now, it is a very important feedstock in the paper-making industry and in the production of cellulose derivatives, such as cellulose esters and ethers. Recently, cellulose derived from low-quality wood and annual herbaceous biomass has also been focused on as a feedstock of glucose for the production of bioethanol and other fermentation compounds. However, since there are piles of published articles on these applications of cellulose, very recent topics are briefly introduced in this section.

In the twenty-first century, nanotechnology has been focused on as an innovative technology. In the cellulose chemistry, cellulose nanofiber (CNF) also draws much attention worldwide as a novel type of reinforced fiber for plastics. As CNF consists of single or several microfibrils, its aspect ratio (length to diameter) is very large and its diameter ranges from 3 to 20 nm. Therefore, CNFs, when dispersed in resin matrix, are invisible because of little scattering of visible light [4, 5], resulting in transparent resin or film. In addition, CNF-reinforced resin has very high mechanical strength due to the high elasticity of cellulose. Therefore, CNFs are considered to be a very unique reinforcing material as compared to conventional glass fibers in glass fiber-reinforced plastics.

Preparation of CNFs is classified mainly on two methods: one is the mechanical refining of delignified wood and pulp [5, 6], and the other is TEMPO-oxidation followed by gentle refining [7, 8]. The former method seems to be simpler and easier than the latter, but the diameter of the obtained fibers by mechanical refining is relatively large (15–20 nm). By contrast, TEMPO-oxidation gives thin fibers with a similar diameter to microfibrils (ca. 3 \times 3 nm) of native cellulose. This phenomenon can be explained by the change in osmotic pressure and/or the occurrence of electrostatic repulsion between microfibrils, caused by the introduced carboxylate on the surface of microfibril by TEMPO-oxidation, which renders the following refinery and separation of fibers much easier. Development of CNF preparation method expands its application study in relation to production of composite materials. However, there is an obstacle: CNFs show low compatibility with hydrophobic compounds, synthetic polymers and their monomers. If we are to overcome the problem, it seems necessary that CNF-reinforced plastics should be developed like a conventional composite material, such as carbon fiber-reinforced plastics.

Hemicellulose utilization

Utilization of hemicelluloses, non-cellulosic heteropolysaccharides, as a feedstock for value-added material is another issue to achieve for the full utilization of woody biomass for chemicals. At present, however, most of the hemicelluloses, together with lignin, are removed during the pulping process, only to be burned to recover energy. The use of the current material, xylan, for conversion into furfural or xylitol is an exception [9].

There has recently been a lot of research work on functionalization of hemicelluloses that has been summarized in some excellent review articles [10, 11]. Extensive studies on carboxylic esters of hemicelluloses, for example, from wheat straw [12, 13] and sugarcane bagasse [14, 15], have been published. Development of films of arabinoxylan esters and their blends was also reported [16].

Of hemicelluloses, modification of xylan draws most attention, due to its abundance compared to the other hemicellulose components. Iwata and his research group have made efforts to develop xylan-based synthetic polymers. Xylan extracted from hardwood kraft pulp was acylated and characterized to observe the effect of their carbon chain length of the introduced acyl groups on the properties of the esters, and they successfully fabricated transparent film from those xylan esters [17, 18]. Based on their findings, Iwata and his coworkers developed polylactic acid blends with xylan esters [19, 20]. They further tried to develop xylan-based graft copolymers [21], and xylan butyrate-based triblock polymers [22]. They have also made attempts to fabricate glucomannan-based esters [23, 24].

Song and his coworkers have done extensive research on modified hemicellulose-related compounds. Corn cob holocellulose was oxidized with hydrogen peroxide to develop dry-strength additive for paper making [25]. Carboxymethylated glucomannan was also modified to a paper-strengthening agent [26]. A prebiotic food additive was developed by producing xylooligosaccharides from xylan of triploid *Populus tomentosa* by xylanase treatment [27]. Application of a cereal-derived hemicellulose-rich by-product, namely β -D-glucan (a glucan fraction composed of β -1,4-D- and β -1,3-D-linkages) from oat processing, was also exploited. For example, β -D-glucan can be utilized as a paper-strengthening agent after being derivatized by TEMPO-mediated oxidation [28] and by carboxymethylation [29].

Galactglucomannan is another target to develop hemicellulose-based hydrogels [30], film laminates for oxygen barriers [31], cationized material [32], and multifunctional macroinitiator for single-electron transfer-mediated living radical polymerization [33].

Lignin utilization

The chemical and physical properties of lignin isolated from woods significantly vary depending on wood species, hardwood or softwood, and separation methods of wood cell wall components. Thereby, utilization of isolated lignins should be considered in relation to the separation processes. Chemical pulpings, such as kraft pulping and sulfite pulping, are considered to be representative separation processes of wood components. Sulfite lignin, or liginosulfonate, comprises a hydrophobic lignin backbone (phenylpropane unit) and anionic sulfonate groups. Accordingly, it has amphipathic nature in addition to water solubility [34, 35]. Based on such unique nature, liginosulfonate is widely utilized as a cement (and concrete) dispersant and electrode admixture for lead secondary battery as mentioned above. On the other hand, kraft lignin is insoluble in water, but soluble in aqueous alkaline solution. Accordingly, kraft lignin cannot be utilized in the application fields of liginosulfonate. Thus, even though both lignins are isolated from aqueous phase, the characteristics of the isolated lignins are quite different. In this section, current studies on lignin utilizations are introduced in relation to the chemical nature of various types of isolated lignins.

Fusibility of organosolv lignins

Organosolv pulping, using organic solvents as a cooking solvent, is often called solvolysis pulping. In organosolv pulping, the solvent used reacts with pulping feedstock, resulting in the introduction of the solvent molecule to pulp and lignin. Consequently, such an introduced moiety adds

very unique characteristics to the resultant lignin, such as thermal fusibility and high reactivity. In synthetic polymers, they can be molded into various shapes on the basis of the fusible characteristics. Thereby, fusible property is very important in terms of moldability.

Atmospheric acetic acid pulping was carried out with 90–95 % aqueous acetic acid containing 0.1–0.32 % mineral acid, such as HCl and H₂SO₄. Since the pulping condition was similar to an acetylation condition, the separated components, pulp and lignin, was partially acetylated. As a result, the resultant lignin derived from its hardwood pulping (hardwood acetic acid lignin; HAL) showed fusibility [36], although susceptibility of the resultant pulp toward cellulolytic enzyme, cellulase, was very low. The fusibility of HAL was found to be attributed to the existence of the acetyl group and the polydispersity of its molecular mass. The acetylation of the hydroxyl group in lignin inhibited the formation of the hydrogen bond, giving rise to thermal mobility so that the acetyl group can act as an internal plasticizer. Low-molecular-mass fraction of HAL had higher thermal mobility than its high-molecular-mass fraction and, therefore, acted as an external plasticizer. This synergy effect contributed to the fusibility of HAL. Afterward, thermal fusibility was found in most organosolv lignins, such as alcell lignin [37] and cresol lignin [38]. To these organosolv lignins, solvent molecules were also introduced; the molecules were found to bind at the C α and C γ positions under acidic conditions in organosolv pulpings. Hydroxy groups C α and C γ positions were first protonated and then subjected to nucleophilic substitution reaction accompanied by elimination of water, as shown in Fig. 1.

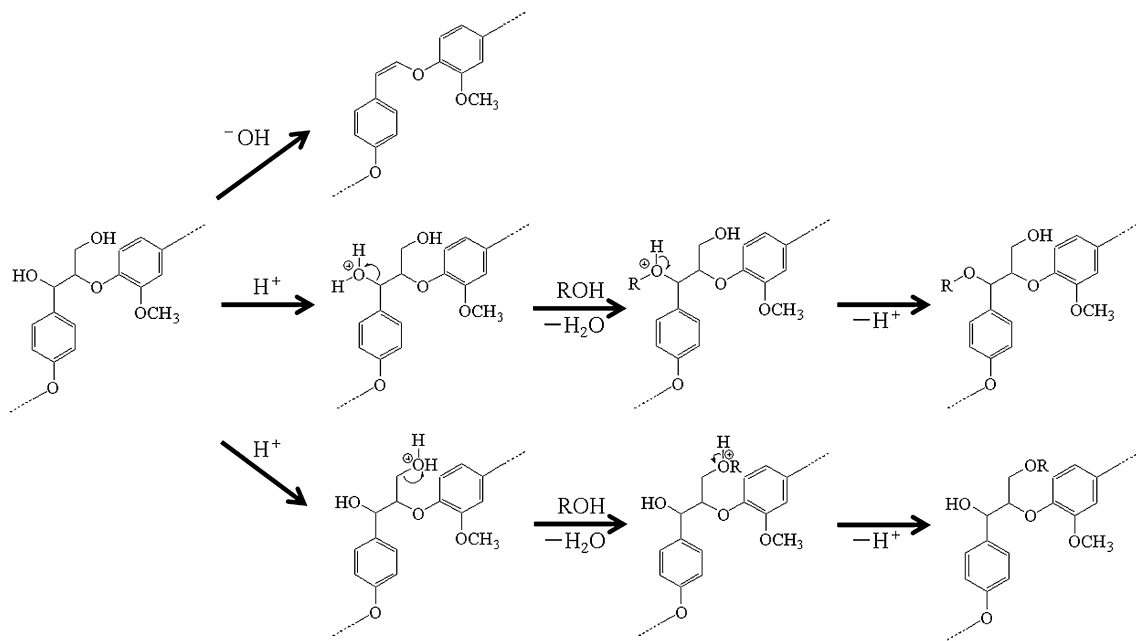
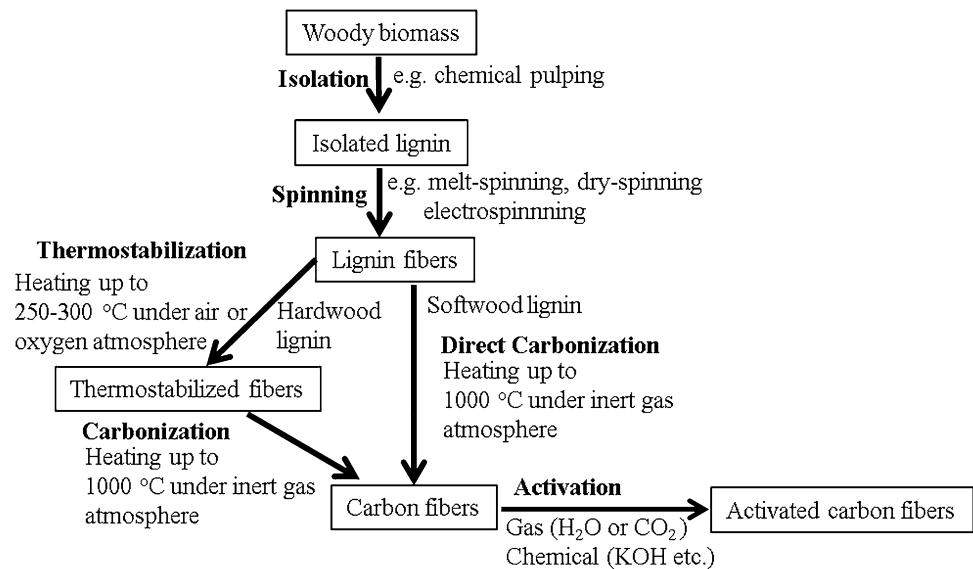


Fig. 1 The proposed chemical reactions of lignin during isolation processes, organosolv pulping and alkaline pulping from wood

Fig. 2 Production scheme of carbon fibers and activated carbon fibers from isolated lignins



The bound solvent moieties acted as the internal plasticizer [39]. In addition, such fusible lignins were isolated from hardwood.

Softwood acetic acid lignin (SAL), however, did not show fusibility. The reason was attributed to the structure of the lignin, which was richer in condensed structure, such as β -5 and 5-5 linkages, than HAL. Such carbon-carbon bonds would suppress rotational motion of aromatic rings in lignin, leading to low thermal mobility. SAL was able to be converted to fusible material by elimination of high-molecular-mass fraction or by re-cooking SAL with aqueous acetic acid to encourage the cleavage of residual aryl-ether bond [40]. Polyethylene glycol (PEG)-lignin from cedar is an exceptionally fusible softwood lignin [41]. It had a low glass transition temperature and a thermal-flow temperature. This fusibility was also derived from PEG moiety, the content of which accounted for more than 40 % of the lignin.

Based on the relationship between lignin fusibility and thermal motion of the aromatic ring, infusible lignin from steam explosion of hardwood was successfully able to be converted to fusible lignin by phenolation [42]. Similarly, the fusibility of cresol lignin and lignophenol [43] should also be brought about by the introduced aromatic moiety in the pulping or separation process of wood components.

Thermal molding of lignins

Fusible polymers are easily transformed into fiber, film, and other moldings by thermal processing. Also, fusible lignins can be transformed into fibers by melt spinning [44, 45]. However, the resultant fibers are very weak and cannot be utilized like synthetic fibers or man-made fibers. To overcome the problem and to add functionality, the lignin

fibers are further converted to carbon fibers (CFs). The typical process is shown in Fig. 2.

In this CF production process, thermostabilization, which converts fusible lignin fibers into infusible ones, is a necessary but very tedious and time-consuming step. Without such a conversion step, fusible lignin fibers melt and lose their fibrous morphology in the following carbonization step. In general, this conversion is carried out by heating the fibers slowly up to 250–300 °C under an air or an oxygen atmosphere, where oxygen molecule incorporated in lignin acts as a cross-linker. Thermostabilization of HAL fibers was completed by heating them up to 250 °C at a heating rate of 0.5 °C/min and keeping this temperature for 1 h (total time >8 h). Thus, saving time needed for this thermostabilization step is a key subject to produce CFs from isolated lignins.

In the case of PEG-lignin fibers, very slow heating rate was required for thermostabilization, namely, at less than 0.1 °C/min (almost 2 days). As-spun fibers from a mixture of PEG-lignin and hexamethylene tetramine as a curing agent for phenol-formaldehyde resin were successfully thermostabilized at a heating rate of 2 °C/min (ca. 2 h). On the other hand, SAL fibers could be directly subjected to the following carbonization without thermostabilization [46]. Although infusible SAL could be converted to fusible material by re-cooking as mentioned above, the resulting SAL could barely be spun, and its spinnability was much lower than that of HAL. The low thermal mobility of SAL helped to skip a thermostabilization step.

The thermostabilized fibers were, in turn, converted to CFs by carbonization, which was conducted by heating up to 1000 °C under an inert gas atmosphere. The mechanical properties of the resultant lignin CFs are listed in Table 1, where polyacrylonitrile (PAN) is a major feedstock for CF.

Table 1 Mechanical properties of lignin-based carbon fibers

| | Diameter (μm) | Tensile strength (MPa) | MOE ^c (GPa) | Elongation (%) | References |
|------------------------------|----------------------------|------------------------|------------------------|-----------------|------------|
| Hardwood kraft lignin | 46.0 \pm 8.0 | 422 \pm 80 | 40.0 \pm 11.0 | 1.12 \pm 0.22 | [52] |
| Alcell lignin | 31.0 \pm 3.0 | 388 \pm 123 | 40.0 \pm 14.0 | 1.00 \pm 0.23 | [52] |
| Exploded lignin ^a | 7.6 \pm 2.7 | 660 \pm 230 | 40.7 \pm 6.3 | 1.63 \pm 0.29 | [44] |
| Hardwood acetic acid lignin | 14.0 \pm 1.0 | 355 \pm 53 | 39.1 \pm 13.3 | 0.98 \pm 0.25 | [45] |
| Softwood acetic acid lignin | 35.3 \pm 6.3 | 108 \pm 65 | – | – | [46] |
| Softwood PEG–lignin | 8.2 \pm 1.0 | 695 \pm 124 | 47.3 \pm 11.5 | 1.51 \pm 0.25 | [41] |
| Acetylated softwood | 6–8 | 1040 \pm 100 | 52 \pm 2 | 2 \pm 0.2 | [55] |
| Kraft lignin | | | | | |
| HWKL-PEO ^b | 44.0 \pm 4.0 | 392 \pm 89 | 44.0 \pm 12.0 | 0.91 \pm 0.16 | [37] |
| Polyacrylonitrile | 5–10 | 3500–6300 | 200–500 | 0.8–2.2 | – |

^a Exploded lignin was converted into spinning raw material by hydrogenolysis followed by thermal condensation

^b Blend of hardwood kraft lignin and polyethylene oxide

^c Modulus of elasticity

The lignin-based CFs are much weaker than the PAN-based counterparts. The reason would be attributed to the existence of non-graphitized carbon derived from lignin and cellulose. Therefore, the lignin CFs are utilized only in a limited area [47]. To expand the application, lignin should be converted to a graphitable carbon-rich compound like mesophase pitch [48].

To use such weak CFs from lignin, further functionalization was attempted. Production of activated carbon fibers (ACFs) was one of the representative examples. The ACFs with large surface area are a promising electrode material for second battery and electric double-layer capacitor, which is described later, in addition to the environmental purification agent [49–51].

CF from kraft lignin

We considered about 20 years ago that softwood and hardwood kraft lignins (SKL and HKL, respectively) would not show fusibility, because no thermally active compound was introduced to lignin in the kraft pulping process. However, melt spinning of HKL was developed by Kadla and his coworkers in 2002 [52]. Although there still is no report on melt spinning of SKL alone, its spinning was achieved by the addition of low-molecular-mass fraction of hardwood kraft lignin in 2013 [53]. The SKL-based fibers could be thermostabilized at a heating rate of 3 °C/min. In addition, this research group successfully spun fibers from SKL alone, which was a low-molecular-mass fraction of SKL prepared by ultrafiltration, and the thermostabilization of the resulting fibers was achieved at a heating rate of 15 °C/min [54]. Last year, CF with a tensile strength of more than 1 GPa, was first prepared from partially acetylated SKL through dry spinning [55]. Thus, most of the isolated lignins can be a feedstock for CF.

Fusibility of polymeric lignin model compounds

Here, we prompt a question: if lignin does not have condensed structure or lignin is comprised exclusively of β -O-4 linkage, which is the major linkage in lignin, then does such lignin show thermal fusibility? To clarify this point, our research group investigated the fusibility of polymeric lignin models, namely C6–C2 [56] and C6–C3 models [57] (Fig. 3).

C6–C2 type of polymeric model compound showed fusibility, but C6–C3 type did not. When the hydroxy group at the C γ position of the C6–C3 type model was modified to ester or carboxylate, the modified model underwent thermal flow. Fourier-transfer infrared spectroscopic (FT–IR) analysis demonstrated that the C γ hydroxy group formed intermolecular hydrogen bond, resulting in low thermal mobility of the C6–C3 type model [58]. From this finding, fusibility and thermal mobility of kraft lignins would probably be caused by the elimination of the C γ hydroxy (methylol) group in the pulping process [59].

Electrospun fibers of lignin and their applications

Electrospinning developed in 1930s [60] is one of traditional spinning methods, but it draws much attention as a fascinating method to produce nanofibers. In this method, there are three types of procedures, wet, dry and melt electrospinnings. Most of the isolated lignins can dissolve in general solvents, such as aqueous alkaline solution and organic solvents. Therefore, those lignins can be easily transformed into nanofiber mat by wet electrospinning and dry electrospinning [61, 62]. Their applications have also been proposed, such as in carbonaceous materials, filter and electrode [63–65]. Therefore, fabrication of lignin-derived fibers has been a hot topic for this decade.

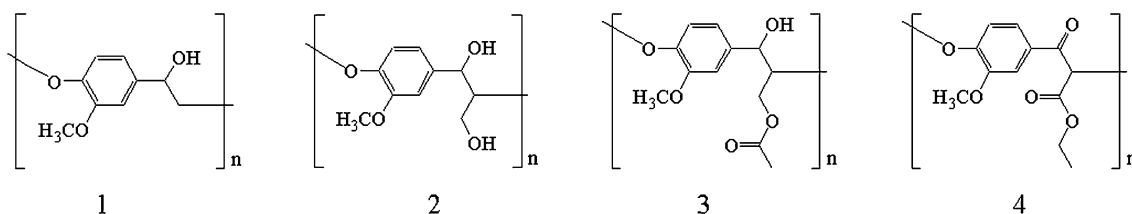


Fig. 3 Chemical structures of polymeric lignin models. 1 C6–C2 type model, 2 C6–C3 type model, 3 acetylated C6–C3 type model, 4 C6–C3 type of carboxylate model

However, wet electrospinning of isolated lignins has not been reported so far.

Lignin resin

The production of phenol–formaldehyde resin from lignin has been a very traditional research subject, and it has still been one of the current research subjects for lignin utilization [66, 67]. Polyurethane resin from lignin has been a well-studied polymer. Since hydroxy groups of general isolated lignins have low reactivity, hydroxypropylation of the lignins with propylene oxide [68] was conducted to convert them into modified lignin preparations for polymerization [69, 70]. There are also some reports on the preparations of lignin-based polyesters [71] and epoxy resins [72]. However, these lignin-based polymers or resins have not been effectively used yet. Only lignin polyurethane has been utilized as an insulate material in domestic houses in Japan [73]. Recently, Kubota et al. developed porous lignin-based polyester from softwood PEG–lignin, which had have opened new application as a separator for electric double-layer capacitor (EDLC) [74].

Future outlook

Nowadays, drilling technologies for shale gas and oil have been developed and established. It looks, then, probable that fossil resources will be supplied stably during this century. Consequently, a steep rise in price of petroleum, which I. S. Goldstein [1] feared, seems not likely to occur in the near future. In this situation, wood components should be converted not only to conventional resins or plastics from a viewpoint of reduced environmental impact, but also to value-added, highly functional materials with respect to reduced production cost. Recently stimuli-responsive and unique functional polymers have been developed from lignin by graft polymerization of atomic transfer radical polymerization (ATRP) [75–77]. This is one of the examples of highly functional material. Based on the fact that isolated lignins have the largest carbon content among wood components, new types of carbonaceous material including carbon fibers have been fabricated

from lignin, especially for electrodes of second battery [78] and EDLC [79, 80]. These products seem to be promising, value-added, lignin-based materials developed in this century.

Furthermore, pulp consumption is decreased these days, while pulp production is excessive worldwide. Some pulp and paper mills in the USA quit pulp production. Bioethanol production from excess cellulose can be a solution to this problem. However, since cellulose can be a feedstock for vinyl polymer [1], the research and development of smart functional polymers from cellulose and pulp as sensor, intelligent materials, and medical goods will/must also be accelerated by their modification with living radical polymerization including atom transfer radical polymerization [81, 82]. Similarly, hemicelluloses will draw attention as a feedstock not only as fuel and aforementioned resins, but also as dietary fibers [83].

To achieve comprehensive utilization of wood components, it is expected to establish effective and efficient biorefinery processes of lignocellulose.

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