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Selective production of valuable chemicals from biomass by two-step conversion combining pre-oxidation and hydrothermal degradation.

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ABSTRACT

Biomass is getting notable as a new energy resource to replace fossil resources and to restrain CO_2 emission recently. However, it is obvious that the energy use of biomass is unsuitable for its limit of available amounts. Consequently, we investigated the possibility of new refinery scheme of biomass to utilize biomass as an alternative raw material to fossil resources with suggested two-step treatment method. We oxidized cellulose and biomass with H_2O_2 first and put the residue into hydrothermal condition to obtain some specific chemicals. Through the first oxidation of cellulose, 0.26 g/g-cellulose of organic acid was obtained, and 0.35 g/g-cellulose of oxalic acid was obtained under the catalytic condition. Both cedar and cellulose decreased their crystallinity through the first oxidation and increased their reactivity, we could obtain

1

hydroxymethylfurfural(HMF) from cellulose and biomass through the hydrothermal degradation, 0.11 g/g-cellulose and 0.12 g/g-cedar respectively.

Key words

Pre-oxidation, Hydrothermal degradation, HMF, Oxalic acid

1. Introduction

The recent growth of economy is rapid and leading to the increase of the annual world energy consumption. We mostly depend on fossil resources for the energy production, which is leading to the drying up of those resources. The CO_2 emission with burning those resources is considered as the problem as well for promoting the global warming. To solve these problems, biomass is getting notable as a new energy resource to replace fossil resources and to restrain CO_2 emission recently. It takes an important role for creating recycling society for its nature of carbon neutrality and sustainability [1-3]. However, as the source of energy, biomass has huge barriers such as the relatively low energy content, seasonality or discrete geographic availability [4]. As an alternative raw material, on the other hand, biomass would be profitable by being converted into valuable chemicals because chemical production requires far lower volumes of biomass to satisfy demand. For example, in 2007, chemical products took only 3 % of the petroleum consumption in the United States [5]. Consequently, the US Department of Energy identified 12 chemicals which should be made from biomass. These chemicals, which could be used as building block chemicals, potentially enable biomass to be main resource of making chemicals which derive from petroleum for now. The important factor for utilizing biomass as an alternative to fossil resources is the choice of material feedstock and target product. Because biomass consists of several components, we should aim not just one but various kinds of products so that we do not waste any of them [6]. In other words, there is a need of proposition

2

of biorefinery scheme that enables to use "wastes" as "byproducts" or "materials". For example, glycerol used to be recognized as "waste material" for its less value. However, as being the material for propylene glycol, it has established its position as a "low-cost building block material" recently [7]. As with the example, we need to broaden our sights for utilizing biomass and to obtain various kinds of products such as fuels, power, materials and chemicals from biomass not wasting any components through conversion [5]. Although there are some opinions that use of biomass as renewable fuel in agro-industrial field would be profitable for saving fossil resources, converting biomass into chemicals is still effective. That is because the residue through the conversion is one of the source of energy, and the products also would be the energy resources through combustion in their final stage of life. In this way, almost same amount of energy as through direct combustion could be extracted from biomass eventually. That means converting biomass into valuable chemicals is profitable in the point of economy and reducing consumption of fossil resources. For converting biomass, many studies using biochemical technology have been done so far [8-10]. For example, we can obtain ethanol or organic acids from biomass by fermentation with high selectivity [11-13]. However, the bioprocess requires high technology of sewage treatment and complicated control of reactor, which leads to a high cost. In addition, it produces sludge which decreases efficiency and causes long reaction time. Considering these disadvantages of biotechnology process, thermal conversion of biomass now should be investigated. Oxidation, among the many reactions on biomass, is disadvantageous for energy recovery since it decreases the low heat of combustion of biomass further. On the contrary, for converting biomass into some valuable chemicals, oxidation would be advantageous since some functional groups containing oxygen in biomass work as active sites. However, in thermochemical process, the problem of low selectivity of final products remains

[14,15]. To overcome this problem, we proposed two-step treatment method. The idea of this method is to change the materials into desired precursor under the mild conditions first. Then the modified precursor is degraded under the hydrothermal condition at higher temperature to valuable chemicals. Although a lot of studies about oxidative pretreatment have been done before, most of them are followed by biotechnologies such as enzymatic saccharification or fermentation [16,17]. There are some studies about thermochemical two-step treatment method, but the target products are low molecular weight chemicals breaking the natural structure of biomass [18,19]. Our objective is to obtain valuable chemicals leaving the advantage of natural structure of biomass, such as carbocyclic ring. In this study, we especially focused on the degradation of cellulose, one of the major components of woody biomass. Cellulose is expected to be converted into valuable chemicals for its clear structure unlike the other components of biomass. However, there are some blocking factors for the degradation of cellulose, such as the rigid structure and crystallinity of cellulose or a physical barrier by surrounding components, lignin and hemicellulose [20]. For the degradation of cellulose in biomass, it would be effective to remove the inhibitors like lignin and to break the rigid structure of cellulose through the pretreatment. H_2O_2 is one of the oxidants, which is known to be capable of removing lignin and lowering the crystallinity of cellulose [21,22]. Thus, in this study, we oxidized biomass with H_2O_2 to obtain desired precursor first. Then we degraded obtained precursor to valuable chemicals solving the problem of low selectivity and examined the validity of the proposed method. In summary, we proposed a new refinery scheme of biomass.

2. Experimental Section

To achieve the hydrothermal degradation effectively, we pretreated cellulose or biomass with H_2O_2. The experiments were performed by using Swagelok (316 stainless steel) batch reactor with an internal volume of 30 cm^3.

2.1. Samples. Crystalline cellulose, amorphous cellulose and biomass were used to examine their oxidative degradation behaviors. To investigate the difference between the kinds of biomass, pulverized cedar (cryptomeria japonica), cypress and beech were chosen. The ultimate analyses of those samples used are listed in **Table 1**.

2.2. Thermal Degradation of Cellulose. Crystalline cellulose and amorphous cellulose were oxidized in a batch reactor under the condition of high pressure and high temperature with H_2O_2. Cellulose concentration was prepared at the range of 0.10 – 0.37 wt% and H_2O_2 was prepared at 0.001 – 1.23 wt%. The reactor vessel was put in an oil bath heated to 80 – 200 ℃ for 5 - 150 min as first treatment. Then, the reactor was cooled in a water bath and the products were filtered by suction after the reactions. Filtrates were diluted with pure water by 50 mL and analyzed using gel permeation chromatography(GPC) and ion chromatography. Oxidized cellulose, which was collected as residue, was put in the hydrothermal condition at higher temperature, from 200 to 260 ℃, as second treatment. The products were filtered by suction, then filtrates were treated as after first treatment and residues were analyzed using a CHNS analyzer. For comparison, first treatment was conducted under the catalytic condition as well. As the catalyst, $FeSO_4(\text{Ⅱ})$ was added by 5 % of cellulose.

2.3. Thermal Degradation of Biomass. 0.5 g of cedar, 30 g of pure water and 0 – 1.5 g of H_2O_2 were mixed in a sealed batch reactor and put in an oil bath heated to 200 ℃ for 60 min as first treatment. The reactor was cooled in a water bath and the products were filtered by suction after

5

the reactions. Filtrates were diluted with pure water by 50 mL and residues were put in the hydrothermal condition at higher temperature, from 200 to 260 ℃, as second treatment. The products were filtered by suction, then filtrates were treated as after first treatment and residues were analyzed using a CHNS analyzer. For comparison, first treatment was conducted under the catalytic condition as well. As the catalyst, $FeSO_4$ was added by 5 % of biomass. To investigate the difference between the kinds of biomass, the whole process was conducted using cypress and beech instead of cedar as well.

2.4. Analyses of Products.   Ultimate analysis of the samples was performed using a CHNS elemental analyzer (BEL Japan, Inc., ECS4010). Crystallinity of samples was measured using X-ray diffraction(XRD) (Rigaku Corporation). The GPC was used to estimate the molecular weight distribution of the product solution after oxidation and hydrothermal degradation. The packed column used is Shodex OHpak SB-802.5 (SHOWA DENKO), and an eluent distilled water was supplied at the flow rate of 1.0 mL/min to the high performance liquid chromatography(HPLC) equipped with an refractive index detector(RID) (Shimadzu, RID-10A). For the organic acid analysis, an aqueous solution containing 951 mg/L of p-toluene sulfonic acid, 4185 mg/L of Bis-Tris, and 29 mg/L of ethylenediamietetraacetic acid was used as the eluent, and it was fed at 0.8 mL/min to the HPLC equipped with a sulfonated polystyrene gel column (Shim-pack SCR-102H) and an electric conductivity detector (Shimadzu, CDD-6A). The yield of each component of organic acids estimated from the above measurements was represented on the basis of dry and ash-free samples.

3. Results and Discussion

3.1. Non-Catalytic Oxidation of Cellulose. Cellulose was oxidized with H_2O_2 and some organic acids were obtained as solution. The whole amounts of carbon converted into the gas fraction were calculated as CO_2. Oxidation of amorphous cellulose was conducted at first. At the temperature of 200 ℃, formic, acetic, succinic and glycolic acid were obtained, while oxidation was not enough under the temperature below 150 ℃ leaving H_2O_2 unreacted. **Figure 1** shows the result of oxidation, the yields of organic acids and the carbon conversion into CO_2 at 200 ℃ with 0.41 wt% of H_2O_2. This result shows CO_2 emission appeared in the early stage of reaction and increased slightly as the reaction time got longer. In contrast, organic acids were not generated in the early stage, while their yields started increasing over 40 min. 26 wt% of cellulose turned out to be organic acid eventually. It indicates that organic acids were mainly produced over 40 min, contrary to this, CO_2 was mainly produced with time. Concerning the chemical structures, succinic acid and glycolic acid tend to come out first, however, they seem to be degraded to formic acid and acetic acid in the early stage of the reaction because of the attack by unreacted H_2O_2. At the later stage, being oxidized well, cellulose got reacted easily. In addition, since H_2O_2 had already reacted at this stage, glycolic and succinic acid were able to exist which led to the higher yields of them. To confirm this, we conducted the experiments to see the behaviors of glycolic and succinic acid against the concentration of H_2O_2. This experiment revealed that the yields of glycolic and succinic acid against H_2O_2 concentration increase gradually first then decrease on parabolic curve as the concentration gets higher. Consequently, controlling H_2O_2 concentration and reaction time figured out to be crucial to improve the yields of organic acids, which indicates the possibility of converting cellulose into organic acids effectively.

3.2. Catalytic Oxidation of Amorphous Cellulose. Through the catalytic reaction, amorphous cellulose mainly turned into oxalic acid. Reaction temperature needs not to be as high as non-

catalytic reaction since Fe ion produces hydroxyl radical efficiently. **Figure 2** shows the changes in the yield of oxalic acid through the catalytic oxidation. According to the results, the concentration of H_2O_2 has bigger effect than reaction temperature on the yield. The yield reached to top, 34.7 wt%, through 80 ℃, 90 min reaction with 0.55 wt% of H_2O_2. Carbon conversion into residue reached 75 – 88 %, while it reached only 15 – 30 % through non-catalytic reaction, which means oxalic acid was obtained with high selectivity. Furthermore, the elemental composition of residue changed in oxygen content through the non-catalytic reaction, while it had no change through the catalytic reaction (**Table 2**). This fact means that the fast consumption of H_2O_2 by the effect of Fe leads to the oxidation mainly on the surface of cellulose and to the immediate degradation. In homogeneous catalytic reaction, recovery of the Fe for recycling is usually a big hurdle, but more than 90 % of Fe recovered as a form of $Fe(COO)_2$ in this reaction, which indicates that separation is not a hurdle problem in this case.

3.3. Estimation of Degradation Mechanism. 20 % of cellulose turned into soluble component producing some amounts of CO_2 without producing organic acid through 200 ℃, 5 min of reaction with the catalyst and 0.03 wt% of H_2O_2. This means degradation began in the early stage of the reaction. For this beginning step of the degradation, the combination of hydrolysis and following elimination of β-keto-ester seem to occur; oxidation of cellulose C-2 and C-3 by hydroxyl radical leads to the elimination of α-hydrogen and to the cleavage of glycosidic bond. H_2O_2 starts to be consumed for producing organic acids after some degradation steps. RID curve showed no glucose peak in every catalytic oxidation, which indicates carbonyl groups were oxidized before cellulose was degraded to monosaccharide. C-3 changes to ketone group by keto-enol tautomerism, C-1 turns into hydroxyl group, and C-6 gets oxidized to carboxyl group simultaneously. C-2 and C-3 get attacked easily for their positive charge and cleaved into

8

carboxyl groups. Subsequently, cleavage of C-4 and C-5 or ether bond occurs. Malic acid produced by the ether bond cleavage gets oxidized moreover and turns into acetic acid + glycolic acid or oxalic acid. The whole estimated degradation path is shown in **Figure 3**.Since the yield of malic acid was very slight under any conditions, C-4 and C-5 cleavage seems to be dominant compared to the ether bond cleavage. Oxalic-1-(2-Oxo-2-Hydroxyethyl) produced by the cleavage of C-4 and C-5 possibly exists while reaction time is short or temperature is low, however, it easily gets degraded by the attack of hydroxyl radical. At 200℃ degradation, acetic acid and oxalic-1-(2-Oxo-2-Hydroxyethyl) were produced from cellulose mainly, then oxalic-1-(2-Oxo-2-Hydroxyethyl) got degraded further to oxalic acid and glycolic acid though the cleavage of ester bond. Acetic acid is known to be degraded to formic acid and oxalic acid [23], while glycolic acid is known to be degraded to oxalic acid [24]. Some amounts of acetic acid and glycolic acid turn into those degraded products. Besides, cellulose produced succinic acid and oxalic acid through the cleavage of ether bond. Oxalic acid turns into CO_2 at high temperature [25,26], and that is confirmed in **Figure 2** as well. These degradation behaviors are summarized as following; through the thermal degradation at 200℃, cellulose produced mainly acetic acid, formic acid, oxalic acid and small amounts of glycolic acid and succinic acid, besides, oxalic acid turned into CO_2 at the temperature. Considering the result shown in **Figure 1**, the yield follows the estimated degradation behaviors, which confirms that the estimation would be correct.

3.4. Hydrothermal Degradation of Oxidized Cellulose. In this section, oxidized crystalline cellulose was used as sample and Fe-oxidized cellulose means oxidized crystalline cellulose under the catalytic condition. **Figure 4 (a)** shows the cristallinity of the samples used in second treatment, the samples here are the residue of first treatment. The condition of first treatment is

200℃, 60min, 0.5 wt% of H_2O_2. According to the results, crystallinity decreased by 35 % through the oxidation process and 15 % through the catalytic oxidation process. The mild deterioration of crystallinity about Fe-oxidized cellulose is because only surface of cellulose was oxidized rapidly. Both pretreated cellulose increased their reactivity and turned into soluble components more than untreated cellulose through 240 ℃ hydrothermal degradation (the second treatment). Non-catalytic oxidation was more effective for the subsequent hydrothermal degradation. 50 % of oxidized cellulose was converted into water-soluble components producing 10.7 wt% of cellobiose, 10.0 wt% of furfural and 9.0 wt% of HMF (all yields are on the basis of raw material). Although cellulose gets degraded to HMF via glucose, glucose was not obtained in this case, which indicates cellulose was degraded to HMF instantly. Fe-oxidized cellulose was converted into water-soluble components by 40 % through the hydrothermal degradation, producing 5.4 wt% of cellobiose and 2.6 wt% of HMF. Fe catalyst is advantageous to obtain oxalic acid selectively, however, to obtain HMF, it figured out to be disadvantageous. For comparison, we degraded crystalline cellulose under the same condition. To obtain the similar amounts of HMF as pretreated cellulose (8 wt%), the reaction temperature was required to be 280 ℃, which revealed oxidation with H_2O_2 is effective treatment.

3.5. Hydrothermal Degradation of Oxidized Biomass. For the first treatment, pulverized cedar was heated at 200 ℃ for 60 min with 0.51 wt% of H_2O_2 under the catalytic and non-catalytic condition. After the non-catalytic reaction, 48 % of cedar was collected as residue whose the elemental composition and IR curve were very close to cellulose, thus the residue was identified as cellulose. In the produced soluble fraction, HMF, formic acid, acetic acid and succinic acid were detected. Lignin is known to be degraded to organic acid with H_2O_2 [27,28]. Gluco-mannan, which is the component of hemicellulose, is known to produce HMF through hydrolysis. Thus, it

is assumed that organic acids derived from lignin and HMF derived from hemicellulose. For cedar sample, the yield of residue and crystallinity after the first treatment were higher with Fe catalyst than without it as cellulose's case. In hydrothermal degradation process, only non-catalytic oxidized cedar was used as sample since it was estimated to produce larger amount of HMF than Fe-oxidized cedar concerning the result of cellulose's case. Through the reaction, about 70 % of oxidized cedar was solubilized at the temperature of 240 ℃, producing 12.1 wt% of HMF. The product distribution is shown in **Figure 5**, with the result of hydrothermal degradation of raw material for comparison, showing that 240 ℃ seems to be the most proper temperature with close amounts of valuable chemicals produced at 260 ℃. The result showed similar tendency to cellulose's case, which confirms the residue of the first treatment is cellulose.

Figure 6 shows the yield of HMF including the result of hydrothermal treatment at 280 ℃ with the untreated pulverized cedar for comparison, showing the yield increased by approximately three times through the pretreatment. Thus, it was clarified that lignin and hemicellulose were removed from cedar and the structure of cellulose was changed simultaneously through the oxidation, then higher yield of HMF was recovered through the hydrothermal degradation. To examine the degradation behavior of other kinds of biomass, pulverized cypress and beech were oxidized and degraded under the hydrothermal condition as well. The product distribution is shown as **Figure 7**, which describes carbon conversion of samples on the basis of raw materials. For comparison, samples without first oxidation were degraded under the hydrothermal condition. The reaction condition of the results shown in this figure is 240℃, 120 min and the sample names have "O." is oxidized samples. As the result, HMF and furfural were produced through the degradation of cedar but not from the other two kinds of biomass. On the contrary, glucose was obtained from only cypress and beech but not from cedar. Although cedar and cypress are

coniferous trees and have quite similar components ratio (49-58% of cellulose, 8-24% of hemicellulose, 23-32% of lignin), there are big differences in products between each other. Through the pretreatment, cedar showed the similar tendency to cellulose such as the increase of the yield of HMF and furfural. However, the others, cypress and beech, increased only the yield of organic acid. In addition, the crystallinity decrease through the oxidation only occurred for cedar, and the others increased their crystallinity conversely. Concerning these facts, what occurred through the oxidation of cypress and beech is only the solubilization of a fraction of lignin. Through the oxidation of cedar, on the contrary, H_2O_2 attacked cellulose in cedar and broke its rigid structure, which led to the change in crystallinity and yield as oxidation of cellulose. It seems that cellulose in cypress and beech is strongly protected by the other components and hardly gets attacked by the treatments compared to cedar. HMF and furfural were produced from only cedar for the degradability of its cellulose. Because no HMF was produced through the degradation of cellulose, and because cellulose in cypress and beech hardly gets attacked, glucose produced from cypress and beech probably derived from hemicellulose. As the conclusion of this section, one obvious thing is that proposed two-step treatment method worked effectively in any case. In addition, considering the cellulose's case discussed in previous section, it seems that the reaction temperature should be much higher to obtain close amount of valuable chemicals from raw materials. These facts indicate us two main advantages of first step oxidation for the recovery of valuable chemicals. The first advantage is that H_2O_2 modified the structure of materials selectively to the desired precursor. The second is that the milder condition for hydrothermal treatment prevented the valuable chemicals from getting degraded further.

12

3.6. Proposition of the New Refinery Scheme. Through the H_2O_2 treatment, biomass is converted into HMF, organic acids and oxidized cellulose. HMF is used for medical supplies and organic acids are used as the materials for some polymers. Oxidized cellulose is degraded further to HMF and cellobiose through the hydrothermal treatment. Cellobiose is converted into amylose, oligosaccharide and glucose. Oxalic acid is obtained through catalytic oxidation of cellulose and it could be used as the material for the environmentally benign polymer. The summarized degradation scheme is shown as **Figure 8**. Cedar was converted into HMF, organic acid, cellobiose and furfural with the yield of 15.0, 18.5, 15.0 and 12.5 respectively in carbon-%. Cellulose was converted into formic acid, acetic acid, glycolic acid, succinic acid, cellobiose, furfural and HMF with the yield of 0.098, 0.113, 0.027, 0.019, 0.106, 0.071 and 0.093 respectively in g/g-cellulose. Under catalytic condition, 0.345 g/g-cellulose of oxalic acid was obtained.

4. Conclusion

A new oxidative degradation method was developed for converting cellulose or specific sort of biomass into valuable chemicals. Oxalic acid was obtained with high selectivity with the yield of 37 wt% through the catalytic reaction at the temperature of 80 ℃ with 0.55 wt% of H_2O_2. The degradation mechanism of cellulose to oxalic acid was estimated. Pretreatment with H_2O_2 enhances the selectivity of HMF from cellulose or biomass. The yield reached 0.12 g/g-material at the maximum. The first step in the proposed method has the advantage of modifying raw materials to desired precursors which are suitable for obtaining valuable chemicals selectively. The method also has the advantage of lowering the temperature of hydrothermal degradation

which prevents valuable chemicals from getting degraded further. Consequently, we suggested

the new refinery scheme of biomass with H_2O_2 treatment.

Table 1. Ultimate Analyses of Sample Used

	C [wt%]	H [wt%]	O [wt%]	H/C [-]
Crystalline Cellulose	42.95	6.20	50.85	0.14
Amorphous Cellulose	43.37	6.12	50.52	0.14
Cedar	46.87	4.84	48.28	0.10
Cypress	49.72	6.34	43.93	0.13
Beech	46.35	6.30	47.36	0.14

Table 2. The Elemental Composition of Residues of First Treatment

	H_2O_2 [wt%]	C [wt%]	H [wt%]	O [wt%]	Fe [wt%]
	0.20	40.67	5.27	54.06	-
Non	0.28	38.40	5.38	56.22	-
Catalytic	0.41	38.25	4.84	56.91	-
	0.43	41.47	5.35	53.18	-
	0.55	40.92	5.35	53.74	-
	0.03	43.54	6.39	50.03	0.04
	0.14	43.24	6.74	50.00	0.02
Catalytic	0.20	43.71	6.72	49.54	0.03
	0.40	44.48	7.01	48.45	0.06
	0.50	43.71	5.85	50.38	0.06
	0.58	43.82	6.91	49.25	0.02

Figure 1. Yield of organic acids and carbon conversion into CO_2 through non-catalytic oxidation

(200 ℃ with 0.41 wt% of H_2O_2).

14

Figure 2. Yield of oxalic acid. Reaction temperature - concentration of H_2O_2 is shown in the figure.

Figure 3. The estimated degradation path.

Figure 4. Change in XRD curve through the oxidation. (a) cellulose sample (b) biomass sample

Figure 5. Carbon conversion on the basis of raw materials (120 min). Three on the left side are for oxidized cedar, one on the right side is for raw cedar.

Figure 6. Yield of HMF on the basis of raw material (120 min).

Figure 7. Carbon conversion on the basis of raw materials (240 ℃, 120 min).

Figure 8. Proposed new refinery scheme of biomass.

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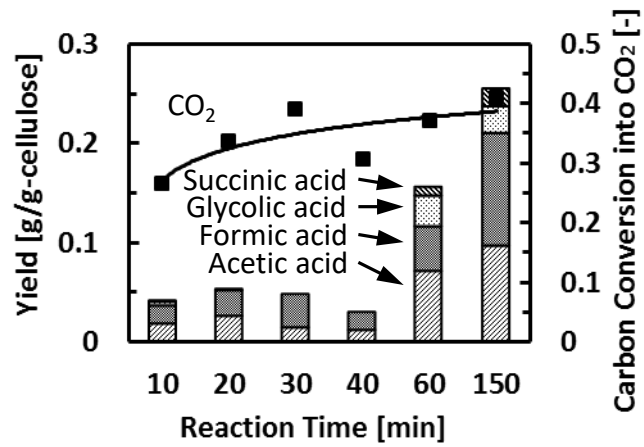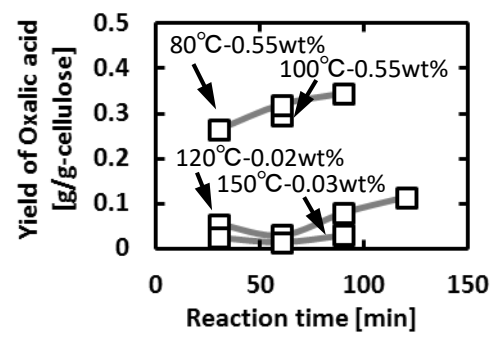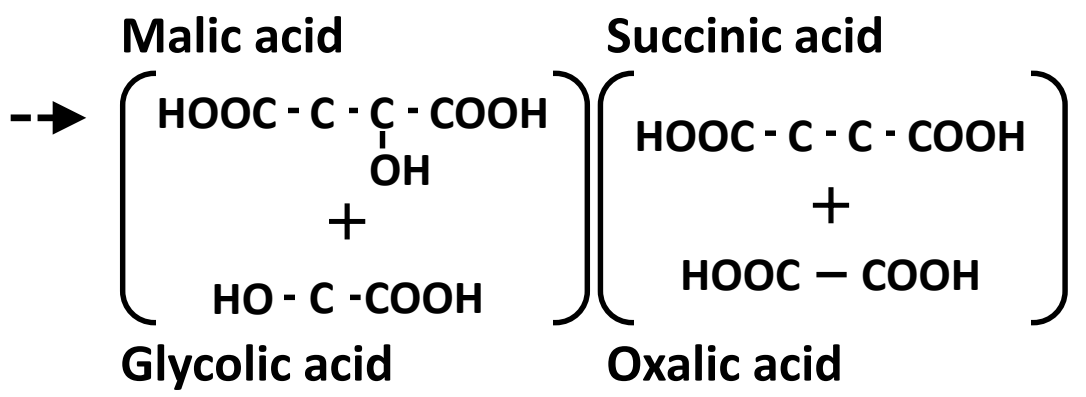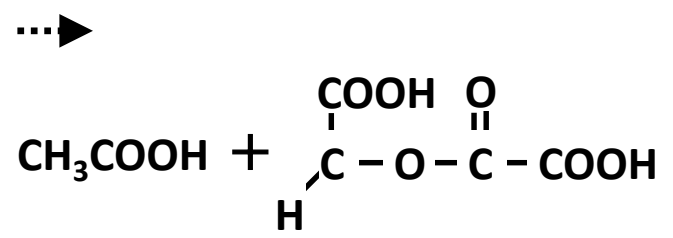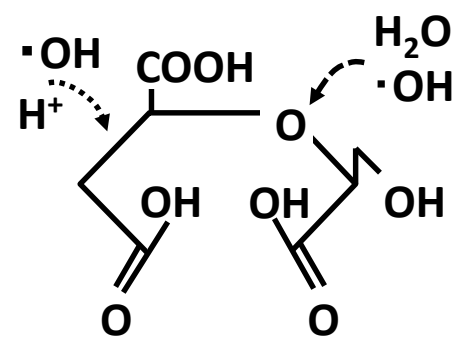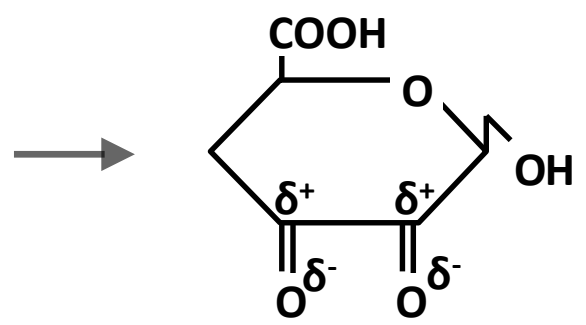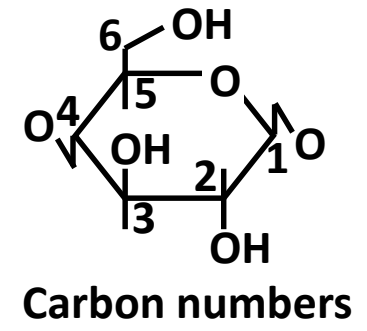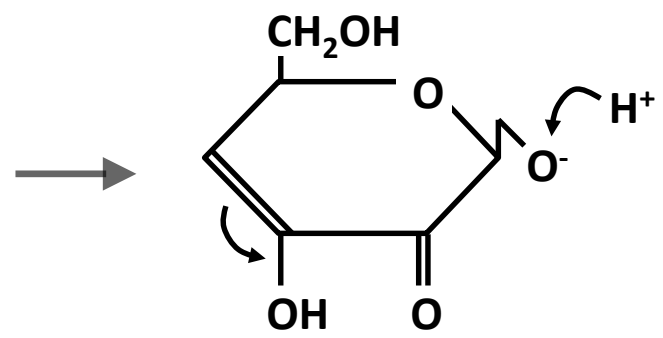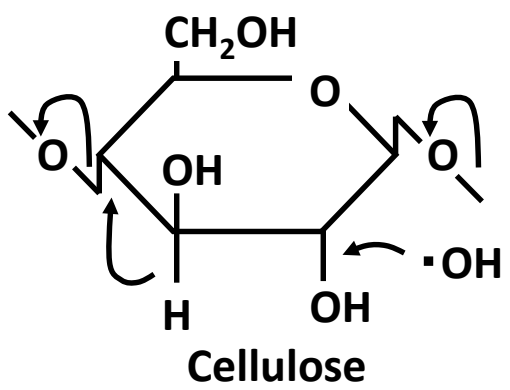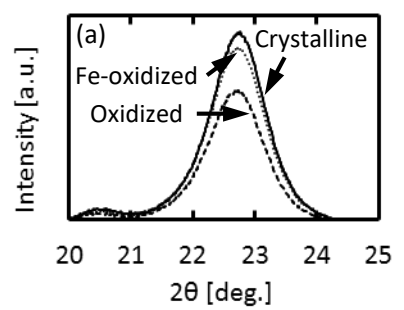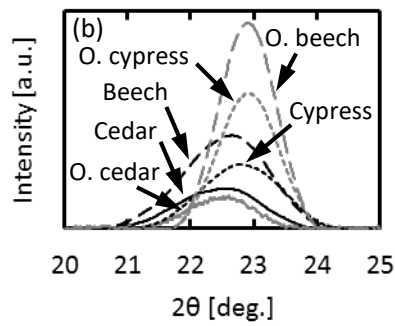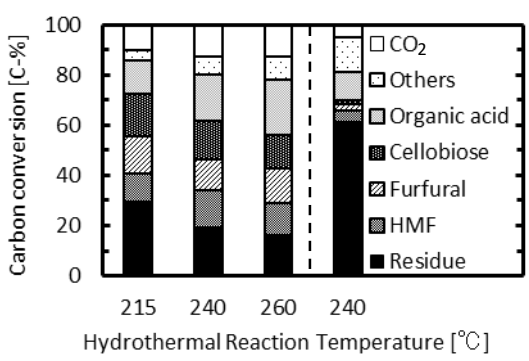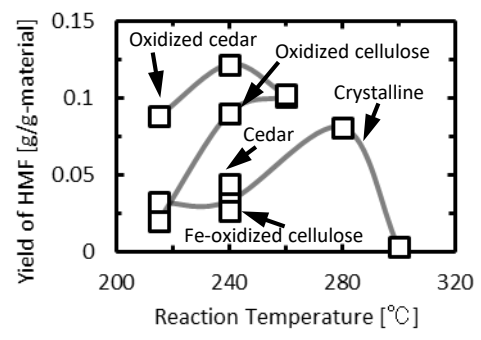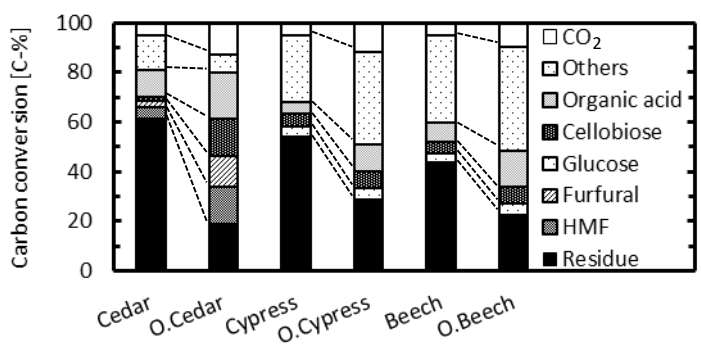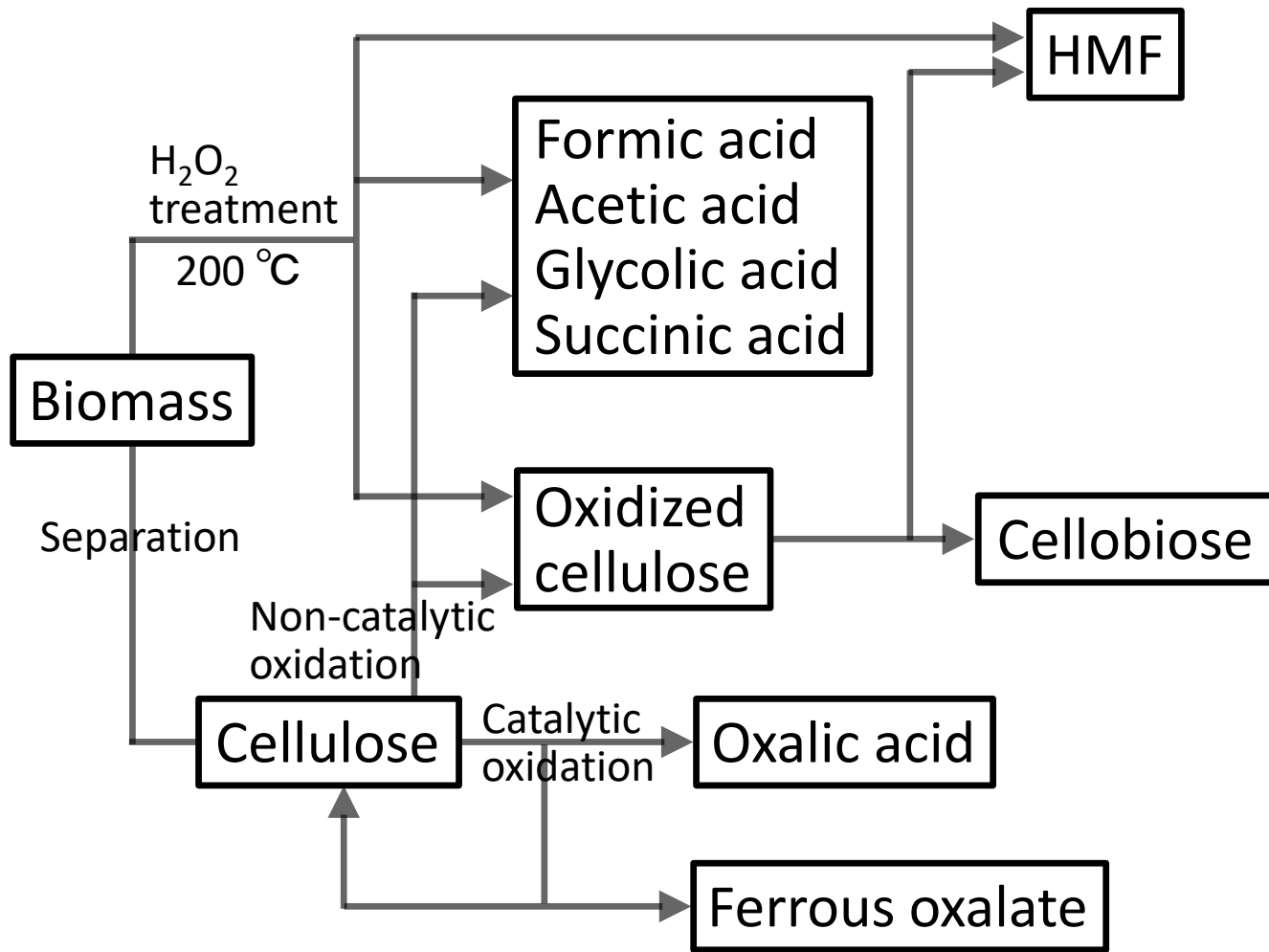
Cellulose

Carbon numbers

Malic acid

Succinic acid

Glycolic acid

Oxalic acid

	C [wt%]	H [wt%]	O [wt%]	H/C [−]
Crystalline Cellulose	42.95	6.20	50.85	0.14
Amorphous Cellulose	43.37	6.12	50.52	0.14
Cedar	46.87	4.84	48.28	0.10

	H_2O_2 [wt%]	C [wt%]	H [wt%]	O [wt%]	Fe [wt%]
Non-catalytic	0.20	40.67	5.27	54.06	–
	0.28	38.40	5.38	56.22	–
	0.41	38.25	4.84	56.91	–
	0.43	41.47	5.35	53.18	–
	0.55	40.92	5.35	53.74	–
Catalytic	0.03	43.54	6.39	50.03	0.04
	0.14	43.24	6.74	50.00	0.02
	0.20	43.71	6.72	49.54	0.03
	0.40	44.48	7.01	48.45	0.06
	0.50	43.71	5.85	50.38	0.06
	0.58	43.82	6.91	49.25	0.02
Cellulose		42.95	6.20	50.85	–