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Low Temperature Pyrolysis of Woody Biomass under Steam for Selective Production of Coniferyl Aldehyde

Fu WEI*1 Shinji KUDO*2,*3,*4,† Xinyu WANG*1 Shusaku ASANO*2,*3
Jun-ichiro Hayashi*2,*3,*4
†E-mail of corresponding author: shinji_kudo@cm.kyushu-u.ac.jp

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Multi-product strategy is a key to the establishment of economically feasible technologies for the utilization of biomass as feedstock for fuels and chemicals. Studies on this strategy generally consider hemicellulose, cellulose, and lignin as sources of chemical compounds. This work focused on a minor part of lignocellulosic biomass. We found pyrolysis of a woody biomass under steam at low temperatures enabled selective production of coniferyl aldehyde that was rarely reported in literature as a compound in pyrolysis products. Experiments under different pyrolysis conditions revealed that the release of coniferyl aldehyde from biomass needed steam and a temperature of around 220°C. A comparative study with lignin as a reference feedstock suggested that it was derived from lignin-carbohydrate complex. Furthermore, staged pyrolysis produced terpenes as well as coniferyl aldehyde as separate products. The yield of coniferyl aldehyde was very low because it was derived from minor structure in biomass. Meanwhile, the solid residue after pyrolysis largely retained original chemical structure, enabling its further conversion into chemicals.

Key words: *Lignocellulosic biomass, Pyrolysis, Steam, Multi-product, Extractives, Coniferyl aldehyde*

1. Introduction

The world is currently facing a challenge of shifting from reliance on fossil fuels to sustainable resources. Biomass, especially lignocellulosic biomass, is a unique, renewable, and carbon-neutral resource that can be used to produce green fuels and chemicals.[1–3] Lignocellulosic biomass consists mainly of hemicellulose, cellulose, and lignin. Glucose is considered to be a key platform for various chemical compounds in a future biomass-based chemical industry.[4,5] Glucose is available from lignocellulosic biomass by the separation of cellulose from other components, followed by saccharification. Many technologies have been developed for the components separation and saccharification, but lignocellulose-derived glucose is currently too expensive to be competitive with petrochemicals and widely prevalent as feedstock for fuels and chemicals.[6] The manufacturing process is generally designed so as to produce only glucose with other components being combusted for generating a low-grade heat. An effective way for reducing the cost of glucose production is to valorize other components (multi-product strategy), which include not only hemicellulose and lignin, but also minor components such as terpenes.[7]

Pyrolysis is a thermal conversion method for decomposing biomass, which produces solid (char), liquid (biooil), and gaseous products. During heating up, hemicellulose firstly starts to decompose, followed by cellulose and then lignin, although there is overlapping in temperature ranges.[8–10] Focusing on differences or heterogeneity of biomass components in reactivity, we have recently proposed staged pyrolytic conversion as a method for multi-product production from lignocellulosic biomass.[11] When Japanese cedar was pyrolyzed at 250−350°C, anhydrosugars consisting mainly of levoglucosan were selectively obtained. Glucose is readily available from levoglucosan by its hydrolysis under acid catalysis.[12,13] Further pyrolysis of the solid residue after pelletization simultaneously produced lignin-derived phenolic compounds, a mechanically strong

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*1 Department of Applied Science for Electronics and Materials, Graduate student
*2 Department of Applied Science for Electronics and Materials
*3 Institute for Materials Chemistry and Engineering
*4 Transdisciplinary Research and Education Center for Green Chemistry

coke, and combustible gas. The staged pyrolysis, thus, enables valorization of a large portion of lignocellulosic biomass.

In the present work, pyrolysis at temperatures lower than 250°C is investigated as a part of staged pyrolysis. Steam is employed as an agent to support the release of desired compounds during pyrolysis. Heating of biomass under steam, known as steam distillation, is widely used in industry for extracting essential oils consisting mainly of terpenes. Steam also induces thermal degradation and/or hydrolysis of some biomass active components over a wide range of temperatures and treatment times as a chemical-free and water-only media treatment.[14,15] Herein we report that coniferyl aldehyde (CA) is selectively obtained with steam pyrolysis under appropriate conditions. This is a high-value added compound and rarely found in products of biomass pyrolysis. To the best of our knowledge, there has been no report on the pyrolytic synthesis of this compound, excepting organic- or bio-synthesis approach using phenolic compounds as substrates.[16] The yields of CA reported in this work are low, well below 1 wt%, but its production as a part of staged pyrolysis or other biomass conversion processes would have a considerable impact on economic performance of the processes, considering the current price in market.

2. Experimental

As-received Japanese cedar from Oita prefecture, Japan, was ground and sieved to sizes of 2.0–4.0 mm for the use as feedstock. Alkali lignin purchased from Sigma-Aldrich was also used as feedstock. The samples were dried before use in pyrolysis experiments.

Steam pyrolysis experiments were performed in a home-made reaction system shown in Fig. 1. The system consisted of a reaction tube, steam and N_2 mixing-supplying system, oven, and liquid product recovery system. The reactor loaded with 8 g of sample was heated to a prescribed temperature (T_p = 130, 160, 190, 220, or 250°C) under 10 mL/min of N_2. After reaching the temperature, water was supplied to the system with a syringe pump for 2 h at a flow rate that made a mass ratio between total supplied water and loaded biomass (water/biomass) be 0, 2, 5, 10, or 15. Steam and compounds volatilized from biomass were recovered as liquid products in the recovery system at 0°C. After stopping the water supply, the oven was left at T_p for 10 min to completely remove the moisture inside reactor, and then cooled to a room temperature.

The pyrolysis experiments were carried out in two modes. The one is a direct pyrolysis mode (DP) mentioned above. Another is a staged pyrolysis mode (SP), where the steam treatment was carried out in sequence at 130, 160, and 220°C. Briefly, after the pyrolysis under steam at 130°C (1st step), the sample was heated to 160°C without cooling, followed by the steam treatment for 2h (2nd step). The treatment was further carried out at 220°C in the same manner (3rd step).

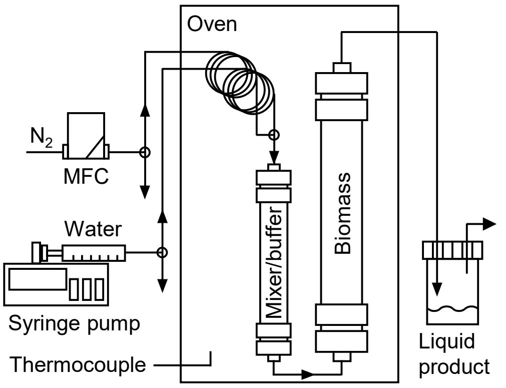

Fig. 1 Experimental apparatus for pyrolysis of biomass under steam.

The pyrolysis experiments were hereafter denoted by DP-T_p or SP-T_p, using the mode of pyrolysis and temperature for steam treatment.

The recovered liquid products contained not only the product from pyrolysis under steam, but also volatiles generated in the course of heating under N_2. In SP, the liquid products were recovered separately at the three steam treatments: initial 130°C steam treatment (SP-130), 160°C steam treatment including heating from 130°C (SP-130-160), and 220°C steam treatment including heating from 160°C (SP-160-220).

The liquid product was mixed with dichloromethane (DCM) for extracting DCM-soluble compounds, and the extracts were recovered by evaporating DCM with a rotary evaporator operated at 30°C for 6 h. The yields of DCM extracts and solid product on a feedstock sample basis were calculated from their mass.

DCM extracts were dissolved in tetrahydrofuran and then subjected to a composition analysis by gas chromatography-mass spectrometry (GC-MS) on a PerkinElmer Clarus SQ8. Details for the analytical method are reported elsewhere.[11,17] Relative percentages of identified compounds were calculated from their peak area in the total ion chromatogram for a semi-quantification of composition of extracts. The concentration of CA was determined using a gas chromatogram-flame ionization detector (GC-FID: Shimadzu, GC-2030). Chemical compositions of cedar and solid residue (char) from pyrolysis were analyzed by two-step acid hydrolysis according to a method reported by the US National Renewable Energy Laboratory (NREL).[18]

3. Results and discussion

CA formation during pyrolysis of lignocellulosic biomass under steam was unexpectedly found during our experiments for investigating residual terpenes in hydrochars. The hydrochars were prepared by hydrothermal treatment of cedar or rice straw at 160°C for 1 h in an autoclave, and then heated under steam at 220°C. Fig. 2 shows GC-MS chromatograms for DCM extracts of liquid products. CA was the major compound in the extracts from cedar. The extracts from rice straw also contained CA and, in addition, sinapyl aldehyde having a similar structure. Aromatic compounds contained in biooil are generally derived from lignin. Aromatic nuclei in softwood lignin (cedar) and herbaceous biomass (rice straw) are guaiacyl type and guaiacyl/syringyl/*p*-hydroxyphenyl type, respectively,[19] which roughly explains detection of sinapyl aldehyde only in the extracts of rice straw. Among aromatic compounds in biooil, *p*-unsubstituted phenols such as phenol, guaiacol, and syringol, are the most abundant, and phenols having propyl chain at para-position like CA are scarcely found.[20] Because the chromatograms of Fig. 2 do not agree with this trend, it was anticipated that CA and sinapyl aldehyde were not derived from lignin. The heating temperature of 220°C was in fact too low to induce substantial occurrence of lignin pyrolysis. Furthermore, the formation of double bond between α and β carbons in lignin was unlikely to occur during the treatments (Fig. 3 (a) shows the typical linkage between monolignol units). A potential source of CA and sinapyl aldehyde was lignin-carbohydrate complex (LCC). As shown in Fig. 3 (b), ferulic acid structure presents in LCC.[21] The hydrothermal treatment supposedly removed hemicellulose, leaving ferulic acid bound to lignin, and the subsequent steam treatment effectively cleaved the linkage to release the ferulic acid portion as CA.

Because hemicellulose is removed during pyrolysis at the lowest temperature among three major components, it was believed that the selective formation of CA would occur even from a raw cedar in the pyrolysis using steam at low temperatures. Therefore, pyrolysis of cedar using steam is investigated under different conditions.

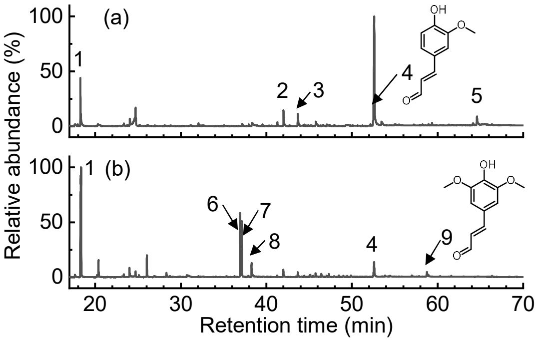

Fig. 2 GC-MS chromatograms of DCM extracts from pyrolysis of (a) cedar and (b) rice straw hydrochars. Major compounds: 1) furfural, 2) vanillin, 3) 4-propyl-guaiacol, 4) CA, 5) a type of diterpene, 6) coumaran, 7) 4-vinyl-guaiacol, 8) 5-hydroxymethylfurfural and 9) sinapyl aldehyde.

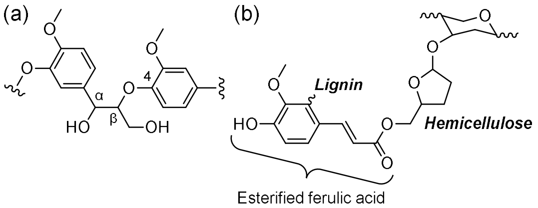

Fig. 3 (a) Typical linkage between monolignols (β-O-4 linkage) and (b) a potential source of CA in lignocellulosic biomass: LCC.

Fig. 4 shows the yields of DCM extracts. DP of lignin under steam produced little extracts. This was reasonable because employed alkali lignin is produced under harsh conditions during a type of kraft process, which removed volatile small molecules. The yield of extracts from cedar in DP increased with T_p and water/biomass ratio. Compounds in the extracts could be derived largely from three different pathways: (a) steam distillation of water-insoluble or slightly soluble compounds such as terpenes, (b) pyrolysis of hemicellulose, cellulose, and lignin, and (c) steam-induced pyrolysis. Steam distillation occurs even at a low temperature like 130°C,[22] but the content of terpenes in biomass is generally low as shown by the extracts yield of 0.1 wt% in DP. The pathway (b) is affected significantly by T_p. Although pyrolysis is not remarkable at the range of temperature examined in this study, a substantial portion of extracts is considered to be derived from this pathway at high T_p. The presence of pathway (c) is demonstrated by the increase in yield with water/biomass ratio. Different from DP, the yield of extracts in SP-160-220 was hardly affected by water/biomass ratio. In other words, a low water/biomass ratio of 2 sufficed for releasing compounds from cedar treated by SP-130 and 130-160.

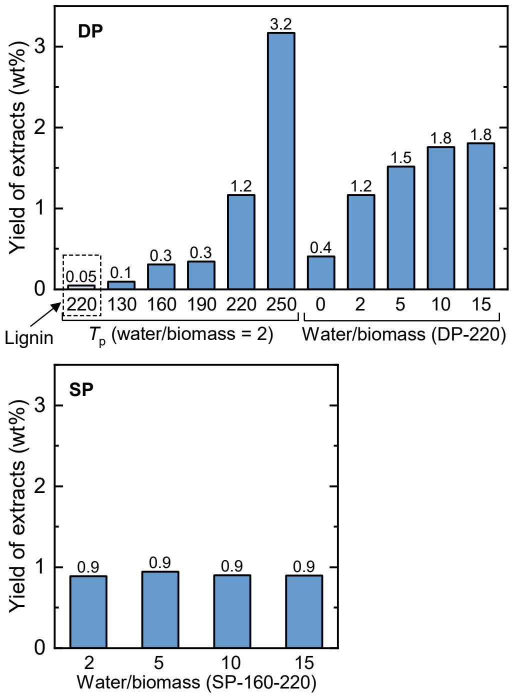

Fig. 4 Yield of DCM extracts.

Figs. 5 and 6 show the composition of extracts. Among GC-MS chromatograms of Fig. 5, CA was found only in SP-160-220 and DP-250. The absence of CA in the extracts from lignin supported our hypothesis that it was not derived from lignin. The result also indicated that steam and a temperature around 220°C were necessary for cleaving the linkage holding CA precursor. As shown in Fig. 6, extracts from DP-130 and 160 consisted mainly of terpenes because the temperature was too low for major components in biomass to be pyrolyzed. Pyrolysis of hemicellulose in biomass generally becomes pronounced from around 180°C, where pyrolysis of lignin also starts, although the reaction rate is much slower than that of hemicellulose.⁹⁾ Because the release of terpenes was almost completed below 160°C, its portion in the extracts decreased with T_p, and, instead, the contribution of phenols and furans increased. Furans were derived from hemicellulose. Phenols included CA and lignin-derived phenols. A large terpenes content in the extracts of DP-220 at water/biomass = 0 showed that steam had an important role in the formation of phenols and furans. These results are supposed to be related to the permeability of steam, causing enhanced desorption, distillation, and transport of the produced volatiles. In addition, steam acts not only as a carrier, but also as a reactant to stabilize radicals generated from thermal decomposition of biomass components and inhibit polycondensation to form less char.²²⁾ The extracts from SP-160-220 had much smaller terpenes content, compared to the extracts from DP, because most of terpenes were removed from cedar in previous steam treatments (SP-130-160 and 130) as shown in GC-MS chromatograms (Fig. 5). As a result, the chromatogram of extracts from SP-160-220 showed distinct peaks of CA and furans. Thus, SP enables separate production of extracts rich in terpenes and CA.

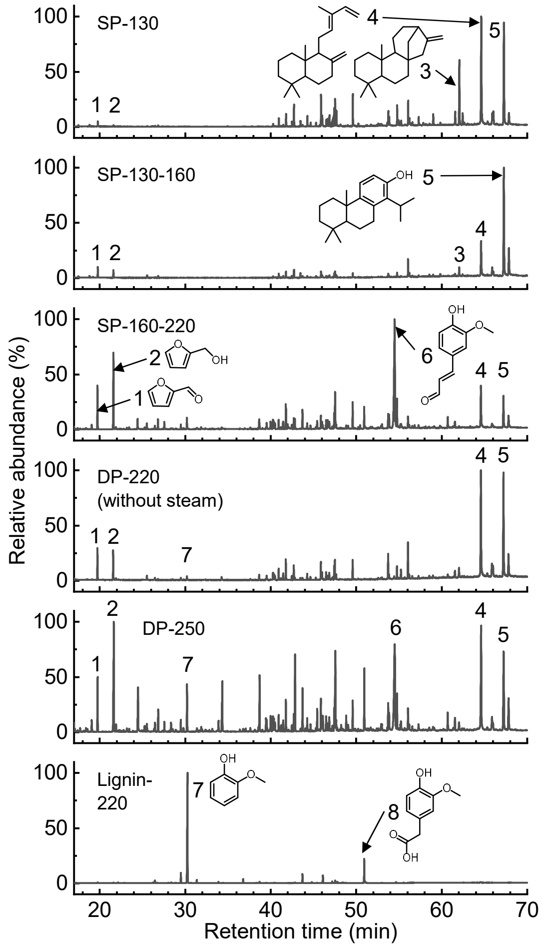

Fig. 5 GC-MS chromatograms of DCM extracts obtained from selected pyrolysis conditions. Water/biomass ratio = 2. Major compounds: 1) furfural, 2) 2-furanmethanol, 3) phyllocladene, 4) biformen, 5) totarol, 6) CA, 7) guaiacol and 8) homovanillic acid.

Fig. 7 quantitatively shows the yield of CA in each pyrolysis. The trend generally agreed with that observed in the yield of overall extracts (Fig. 4), showing the importance of T_p and steam. An exception was that the yield of CA increased with water/biomass ratio whereas the yield of overall extracts was unchanged. As a result, the content of CA, i.e., selectivity to CA, increased with water/biomass ratio up to 26.5 wt%. The result indicated higher steam concentration was effective for suppressing secondary reactions of CA to be degraded into other products. According to Table A1, guaiacylacetone could be one of the derivatives from CA since its proportion in extracts decreased with water/biomass ratio, although the trend was not remarkable. The highest CA yield was 0.28 wt%, achieved by DP-250. However, due to the inclusion of terpenes and enhanced pyrolysis by the high temperature of 250°C, CA content in extracts was only 8.8 wt%. In this regard, SP-160-220 at water/biomass ≥ 10 was considered to be a better condition for selectively producing CA. Overall, the result confirmed that the formation of CA during pyrolysis needed steam and a temperature of around 220°C, and that lignin was not the source of CA.

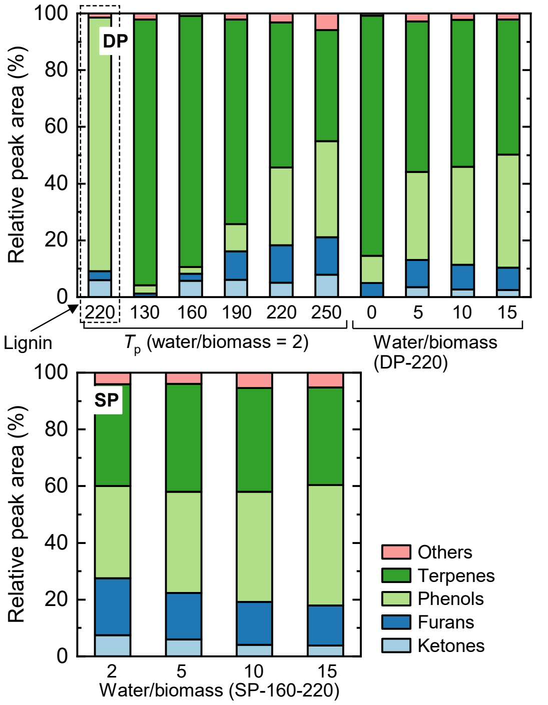

Fig. 6 Composition of DCM extracts (relative peak area of compounds identified in GC-MS analysis). See Appendix for compounds contained in each category.

The yield and chemical composition of residual char are presented in Fig. 8. Glucan is derived mainly from cellulose. Xylan, galactan, arabinan, and mannan are derived from hemicellulose. Because a characteristic structure of hemicellulose in softwood is *O*-acetylgalactoglucomannan,[21)] a part of glucan should be derived from hemicellulose. Others include ash, extractives, and acetyl groups. The yield decreased with T_p. It was little influenced by water/biomass ratio because the proportion of structure, which was decomposed only by supply of steam, in cedar was negligibly small as shown in the yield of extracts (Fig. 4). It was noteworthy that the majority of hemicellulose-related sugars survived the pyrolysis under steam in any conditions even at 250°C. This was contrary to our expectation that CA was generated from LCC after the removal of hemicellulose. The result rather showed a possibility that steam had an ability to cleave the linkages of ferulic acid structure in LCC with both hemicellulose and lignin, leaving the three main components in cedar with little alteration of their chemical structure. Such a trend is favorable for the multi-product strategy, where terpenes and CA production with SP under steam adds value to processes valorizing the main components.

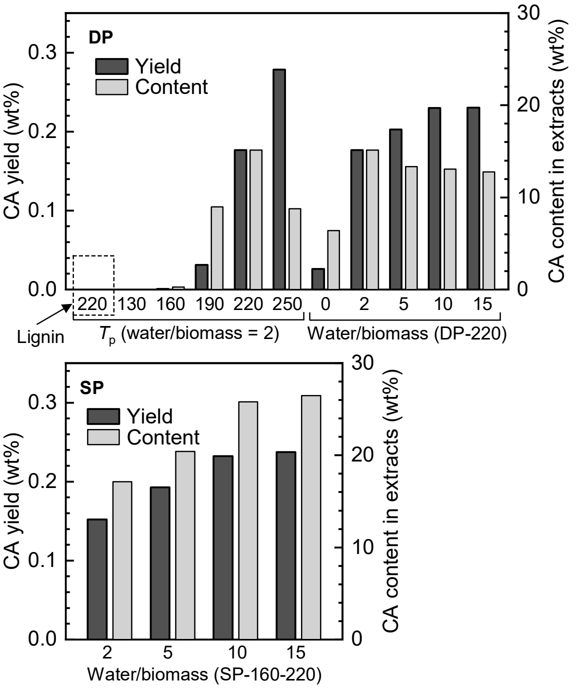

Fig. 7 Yield of CA and its content in DCM extracts.

4. Summary and Conclusion

This study showed a value-added aromatic compound, CA, was selectively available from low temperature pyrolysis of cedar under steam. Different from a common source of aromatic compounds generated during pyrolysis, CA was considered to be derived from ferulic acid structure in LCC. SP under steam produced terpenes as a main product below 160°C and CA at 160–220°C as a main compound in extractives. The yield and content of CA were up to 0.23 wt% and 26.5 wt%, respectively, in SP. The treatment hardly altered the chemical structure of a main portion of cedar. Therefore, pyrolysis under steam is expected to be used as a pretreatment step for extracting terpenes and CA to add value to the process of main conversion of lignocellulose.

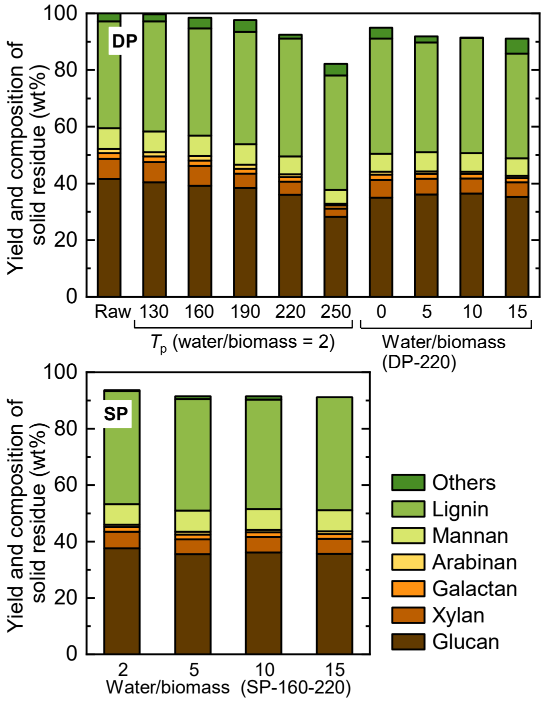

Fig. 8 Yield and composition of solid residue.

Acknowledgments

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Appendix

Table A1 Relative peak area (%) of compounds identified in extracts by GC-MS.

	Lignin	DP, water/biomass = 2					DP, T_p = 220°C				SP, 220°C			
	T_p (°C)	T_p (°C)					Water/biomass				Water/biomass			
Compounds	220	130	160	190	220	250	0	5	10	15	2	5	10	15
Ketones	**5.9**	**0.1**	**5.7**	**6.0**	**5.1**	**7.9**	**0.0**	**3.5**	**2.7**	**2.5**	**7.4**	**5.9**	**4.1**	**3.9**
2,3-butanedione	3.7	0.1	5.7	4.2	1.2	1.5	-	1.9	1.4	1.3	1.0	0.9	1.5	1.4

Table A1 Continued.

	Lignin	DP, water/biomass = 2					DP, T_p = 220°C				SP, 220°C			
	T_p (°C)	T_p (°C)					Water/biomass				Water/biomass			
Compounds	220	130	160	190	220	250	0	5	10	15	2	5	10	15
2,3-pentanedione	-	-	-	0.6	<0.1	0.2	-	0.3	0.1	0.1	0.1	0.6	0.1	0.1
acetol	-	-	-	-	1.4	1.9	-	0.3	0.2	0.2	2.8	1.4	0.8	0.8
acetoin	0.9	-	-	0.6	0.3	0.2	-	0.1	0.1	0.1	0.4	0.3	0.2	0.2
2-oxobutanol	-	-	-	0.2	0.5	0.6	-	0.2	0.1	0.1	0.7	0.5	0.3	0.3
acetol acetate	-	-	-	-	0.1	0.2	-	0.1	0.1	0.1	0.2	0.2	0.2	0.1
2-cyclopentene-1,4-dione	0.4	-	-	0.2	0.1	0.2	-	0.2	0.1	0.1	0.2	0.2	0.2	0.1
2-hydroxy-2-cyclopentenone	0.1	-	-	0.3	1.4	2.7	-	0.4	0.5	0.5	2.0	1.7	0.9	0.9
3,4-dimethylcyclopent-2-enone	0.8	-	-	-	-	0.5	-	-	-	-	-	-	-	-
Furans	**3.2**	**1.1**	**2.5**	**10.1**	**13.2**	**13.2**	**4.9**	**9.6**	**8.6**	**7.9**	**20.1**	**16.4**	**15.1**	**14.1**
furfural	0.4	0.7	1.0	3.8	3.0	2.4	<0.1	3.4	2.2	2.0	4.4	4.0	3.9	3.7
2-furanmethanol	0.1	0.2	0.9	4.4	6.7	7.0	3.5	4.2	4.3	4.0	11.0	8.4	8.1	7.6
acetylfuran	-	-	-	0.1	0.1	0.1	-	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1
5-methylfurfural	-	0.1	0.2	0.9	0.5	0.6	0.7	0.5	0.3	0.3	0.6	0.5	0.5	0.5
butyrolactone	1.6	0.1	0.2	0.2	0.3	0.5	0.4	0.2	0.2	0.2	0.4	0.3	0.3	0.3
2(5H)-furanone	-	0.1	0.2	0.6	1.0	1.4	0.2	0.7	0.7	0.6	1.4	1.3	1.1	0.9
methyl 3-furoate	1.1	-	-	-	0.2	0.2	-	0.1	0.2	0.1	-	0.3	0.2	0.1
4-methyl-2(5H)-furanone	-	-	-	-	<0.1	0.1	-	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1
(5S)-5-(hydroxymethyl)oxolan-2-one	-	-	-	-	0.3	0.1	-	0.1	0.1	0.1	0.4	0.3	0.1	0.1
5-acetyloxolan-2-one	-	-	-	-	0.1	0.1	-	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1
hydroxymethylfurfural	-	-	-	0.2	1.1	0.8	0.1	0.3	0.5	0.5	1.6	1.2	0.8	0.7
Phenols	**89.4**	**3.0**	**2.4**	**9.6**	**27.5**	**33.9**	**9.6**	**31.0**	**34.6**	**39.8**	**32.5**	**35.7**	**38.8**	**42.4**
phenol	4.0	-	-	0.5	0.4	0.8	0.3	0.3	0.2	0.2	0.5	0.4	0.4	0.4
guaiacol	60.7	0.1	0.3	0.4	1.1	2.6	0.5	0.8	0.7	0.6	1.2	1.0	1.1	1.1
p-creosol	0.6	-	-	-	0.2	0.7	-	0.2	0.1	0.1	0.3	0.2	0.2	0.2
4-ethylguaiacol	1.9	0.1	0.1	0.1	-	0.1	-	-	-	-	-	-	-	-
4-vinylguaiacol	0.8	-	-	-	-	3.0	-	-	-	-	-	-	-	-
2-methoxy-3-allylphenol	0.2	-	-	-	-	0.7	-	-	-	-	-	-	-	-
syringol	0.2	-	-	-	-	-	1.3	-	-	-	-	-	-	-
isoeugenol	0.3	<0.1	0.4	-	0.8	3.2	0.3	0.7	0.7	0.6	0.9	0.7	0.8	0.8
vanillin	3.7	0.2	0.4	0.8	1.7	1.9	0.3	1.5	1.7	1.5	1.5	1.4	1.8	1.7
cerulignol	0.1	-	-	0.2	0.6	0.9	<0.1	0.7	0.6	0.5	0.6	0.7	0.7	0.7
4-t-butylcatechol	3.3	-	-	-	-	0.6	-	-	-	-	-	-	0.3	0.3
guaiacylacetone	1.2	2.6	1.2	3.5	5.6	4.7	4.3	6.3	5.9	5.4	5.8	5.8	4.4	4.2
coniferol	-	-	-	-	0.3	0.9	0.1	0.2	0.6	0.5	0.2	0.2	0.3	0.3
homovanillyl alcohol	0.7	-	-	-	-	-	-	-	-	-	-	-	-	-
vanillacetic acid	11.5	-	-	1.2	1.6	2.9	-	1.2	1.6	1.4	1.2	1.6	2.1	2.0
coniferyl aldehyde	-	-	-	2.8	15.2	10.8	2.5	19.2	22.6	28.7	20.3	23.6	26.6	30.9
Terpenoids	**0.0**	**93.7**	**88.4**	**72.1**	**51.2**	**39.1**	**84.7**	**53.0**	**51.7**	**47.6**	**35.9**	**38.0**	**36.6**	**34.4**
maltol	-	-	-	-	0.3	0.6	-	0.1	0.1	0.1	1.4	0.2	0.3	0.3
(-)-bete-elemene	-	-	-	-	0.1	0.7	0.7	0.1	0.1	0.1	0.1	0.1	0.1	0.1
cedr-8-ene	-	-	-	-	0.2	0.2	0.2	0.2	0.2	0.2	0.7	0.2	0.1	0.1
2-isopropenyl-4a,8-dimethyl-1,2,3,4,4a,5,6,7 octahydronaphthalene	-	-	-	0.4	0.8	0.5	0.9	0.8	0.7	0.7	1.1	0.9	0.6	0.5
α-muurolene	-	0.3	0.3	1.0	1.8	1.8	2.1	1.9	1.7	1.6	2.5	2.3	1.9	1.8
δ-cadinene	-	0.8	0.4	0.8	0.8	0.6	-	0.9	0.8	0.8	1.1	1.0	0.8	0.8
isoledene	-	-	-	0.1	0.2	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2
1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene	-	0.2	0.2	0.6	0.5	0.4	0.8	0.6	0.6	0.5	0.7	0.6	0.6	0.6
valencen	-	-			0.1		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
calamenene	-	1.2	0.9	1.5	1.8	1.4	2.3	1.9	1.9	1.7	2.4	2.1	2.2	2.0
isolongifolene, 4,5,9,10-dehydro-	-	0.8	0.9	0.6	0.5	0.3	0.7	0.4	0.5	0.3	0.5	0.5	0.5	0.3
α-calacorene	-	2.1	0.8	1.4	1.0	0.6	1.6	1.1	1.0	0.9	1.4	1.0	0.9	0.8
3,4-dehydroionene	-	0.5	0.2	-	-	-	-	-	-	-	-	-	-	-
elemol	-	1.1	0.4	0.6	0.6	0.6	0.9	0.6	0.6	0.5	0.5	0.5	0.4	0.4
γ-elemene	-	0.4	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.3	0.4
2,5,8-trimethyltetralin	-	-	-	0.1	-	-	0.1	-	0.1	0.1	0.2	0.1	0.1	0.1
naphthalene, 1,2,3,4,6,8a-hexahydro-1-isopropyl-4,7-dimethyl-	-	4.0	1.7	-	2.8	1.8	2.9	2.4	2.4	2.2	2.1	1.9	1.6	1.5
γ-eudesmol	-	0.7	0.3	0.6	0.7	0.7	0.9	0.8	0.7	0.7	0.8	0.8	0.8	0.7
T-muurolol	-	0.8	0.2	-	-	0.4	-	-	-	-	-	-	-	-
torreyol	-	1.3	0.4	1.2	1.2	0.7	0.9	0.9	0.9	0.9	1.2	0.9	0.9	0.9
α-cadinol	-	0.4	0.1	0.3	0.3	0.2	0.4	-	0.3	0.3	0.2	0.3	0.2	0.2
juniper camphor	-	1.5	0.5	0.7	-	0.5	0.5	-	-	-	-	-	-	-
apo-12-lycopenal	-	3.4	0.9	2.2	1.9	1.1	2.5	2.2	1.9	1.8	1.9	2.0	2.1	2.0
isophyllocladen	-	3.5	2.0	2.2	2.4	2.1	4.0	2.6	3.0	2.8	1.8	2.3	2.9	2.7
1-oxaspiro[2.5]octane, 5,5-dimethyl-4-(3-methyl-1,3-butadienyl)-	-	2.1	0.7	1.6	2.0	-	2.5	2.2	2.2	2.0	2.0	2.0	2.4	2.3
atiserene	-	0.8	0.4	-	-	0.7	-	-	-	-	-	-	-	-
1,5-cyclooctadiene, 3,4,7,8-tetrakis(1-methylethylidene)-	-	3.3	3.1	3.5	2.0	1.2	4.5	1.8	1.7	1.6	1.3	1.4	1.2	0.9
cembrene	-	-	-	0.3	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.3	0.2	0.2
ethyl cholate	-	0.9	-	0.7	0.4	-	0.4	0.4	0.4	0.4	0.2	0.3	0.3	0.5
o-methylpodocarpinol	-	1.4	0.4	-	-	1.1	-	-	-	-	-	-	-	-
androstan-17-one, 3-ethyl-3-hydroxy-, (5α)-	-	1.9	1.2	2.2	1.1	0.6	1.0	1.2	1.1	1.0	0.8	0.9	0.8	0.7
phyllocladene	-	9.5	3.9	-	-	0.5	-	-	-	-	-	-	-	-

Table A1 Continued.

	Lignin	DP, water/biomass = 2					DP, T_p = 220°C				SP, 220°C			
	T_p (°C)	T_p (°C)					Water/biomass				Water/biomass			
Compounds	220	130	160	190	220	250	0	5	10	15	2	5	10	15
17-oxoandrosta-5,7-dien-3-yl acetate	-	1.8	1.3	-	-	-	-	-	-	-	-	-	-	-
biformen	-	23.5	27.4	21.3	12.2	8.4	26.6	14.6	14.3	13.2	4.3	8.1	7.1	6.7
androsta-5,7-diene, 4,4-dimethyl-	-	4.4	3.2	-	-	1.5	-	-	-	-	-	-	-	-
totarol	-	18.7	29.8	23.4	11.7	6.3	21.7	11.1	10.7	9.8	4.1	4.7	4.9	4.6
14-isopropylpodocarpa-8,11,13-triene-7,13-diol	-	2.2	6.6	4.6	3.1	2.7	4.5	3.3	3.0	2.7	1.6	2.0	2.0	1.9
Others	**1.5**	**2.1**	**0.9**	**2.1**	**3.1**	**5.9**	**0.7**	**2.9**	**2.3**	**2.2**	**4.1**	**4.0**	**5.4**	**5.2**