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Research article

Pyrolysate formation from four different phenyl propanols and classification of the initial reaction pathways

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Abstract

Four phenyl propanols with different ring pendant groups; cinnamyl alcohol, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol were subjected to analytical pyrolysis (pyrolysis-GC/MS) to evaluate the effects of hydroxyl and methoxyl groups on the pyrolysis mechanism and pyrolysate distribution. In the case of cinnamyl alcohol, which does not have phenolic hydroxyl group, over 40% of the starting material was recovered as an unreacted compound, indicating that the phenolic hydroxyl group accelerates pyrolysis reaction to produce gas, char, and pyrolysates. However, side chain reactions, such as formation of cinnamaldehyde and phenyl ethenyl, were produced in high yield as major products. The pyrolysis of *p*-coumaryl alcohol yielded many products that suffered from loss of the side-chain C_1 or C_2 carbons. Sinapyl alcohol and coniferyl alcohol exhibited similar pyrolysis behavior, with similar compounds detected as the major products. The basic reaction pathways are initiated by the homolytic cleavage of C–O and H–O bonds followed by C-C bond cleavage. Therefore, many of the pyrolysates were produced via reactions involving hydrogen and hydroxyl radicals. These initial reactions were classified into four principal categories: 1) donation of hydrogen radical, 2) abstraction of hydrogen radical, 3) donation of hydroxyl radical and 4) abstraction of hydroxyl radical. Isomerisation and methyl radical donation also occurred during the pyrolysis of phenyl propanols.

Keywords: Pyrolysis, bio-oil, phenyl propanols, reaction pathway, reaction category

1. Introduction

Bio-oil produced from the fast pyrolysis of biomass is a potential substitute fuel for oil and diesel in many static applications, such as boilers, furnaces, engines and turbines, which are used for electricity generation and chemical production [1]. Many types of biomass have been examined for bio-oil production, and pilot plants have been established worldwide [2, 3]. Several studies on pyrolysis conversion using crops, such as wheat straw [4], rice husk [5], tobacco residue [6], orange waste[7], giant cane [8], softwood barks [9], bamboo [10] and microalgae [11], have been reported. These plants comprise cellulose, hemicellulose and lignin. Therefore, bio-oil contains a mixture of pyrolysates from these components.

Lignin is the second most abundant natural biopolymer found in lignocellulosic plants. It is a heterogeneous and complex polymer synthesised mainly from three *p*-hydroxycinnamyl alcohols differing in their degrees of methoxylation, namely, *p*-coumaryl, coniferyl and sinapyl alcohols. Each of these monolignols gives rise to a different type of lignin unit, which are referred to as *p*-hydroxyphenyl, guaiacyl and syringyl units, respectively, and together generate a variety of structures and linkages within the polymer [12, 13, 14]. Distribution of phenols in the pyrolysate of lignin significantly affects the physical and chemical properties of bio-oil. Notably, the formation of different phenols and consequent phenol distribution are determined by the pyrolysis conditions and original lignin structure. Therefore, a better understanding of the chemical reactions that occur during the fast pyrolysis of lignin could provide useful information to help control the pyrolysis process for suitable bio-oil production.

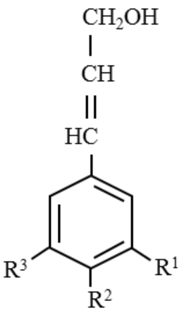
Analytical studies of pyrolysates from isolated lignin have been performed using Py-GC/MS, HPLC, NMR and FT/IR. Lou et al. prepared enzymatic/mild acidolysis lignin (EMAL) from bamboo, which they pyrolysed by using an analytical flash pyrolyser and GC/MS [15, 16]. Huang et al. prepared corncob acid hydrolysis residue (CAHL) from lignin and analysed the obtained char by using TG/FTIR, Py-GC/MS and SEM [17]. They also detected phenolic compounds that they suggested were mainly generated from the cracking of aryl glycerol-β-ether (β-O-4) linkages in CAHL. In addition, phenol and benzene were identified at temperatures up to 780 °C. Huang et al. proposed that these compounds were formed via multiple pathways, which involved further cleavage and degradation of macromolecular compounds at high temperature. Ye et al. prepared enzymatic hydrolysis residues using cornstalks as a lignin model and pyrolysed the lignin in a stainless steel autoclave reactor with different reaction (residence) times (30–180 min) [18]. The product distributions were analysed using GC/MS, and it was found that increasing the residence time increased the yields of 4-ethylphenol, 4-ethylguaiacol and syringol, while decreasing the yields of 2,3-dihydrobenzofuran and vinylguaiacol.

Moreover, lignin model compounds, such as lignin monomers and dimers, have been pyrolysed in order to investigate the mechanism of phenol formation. Akazawa et al. proposed and classified a basic pyrolysis reaction pathway [19, 20]. Harman-Ware et al. attempted to estimate the S/G ratio f the biomass from which sinapyl alcohol and coniferyl alcohol were pyrolysed, and several pyrolysates were identified using model compounds [21]. Huang et al. applied density functional theory using β-O-4 type lignin dimer model, and syringol as lignin model compound, and proposed three possible pyrolytic pathways; the homolytic cleavage of C_β-O bond, the homolytic cleavage C_α-C_β bond and the concerted reactions [17].

Hage et al. developed the Curie-point LC/MS analysis method for the detection of oligomeric and polar compounds present in bio-oil prepared from lignin dimer models [22]. Kuroda et al. reported that the major pyrolysis product from a β-5 structure model (dehydrodiconiferyl alcohol) and its methylated compound (dehydrodiisoeugenol) was 4-methylguaiacol, as determined using Py-GC/MS [23]. They concluded that 4-methylguaiacol was produced from the aryl ether of the ring-opened dimer formed via hydrogenation of the C_{α}–C_{β} bond of the dimer model. Furthermore, they evaluated the effects of the coniferyl alcohol end group of lignin on pyrolysate distribution and concluded that such groups contribute significantly to the pyrolysates of the bulk dehydrogenation polymer and contribute slightly to those of cedar wood and its milled wood lignin [24]. Kawamoto et al. evaluated the relative reactivity of depolymerisation and condensation/carbonisation (primary pyrolysis) reactions based on the formation of the major pyrolysis products by using four lignin dimer models (α-O-4, β-O-4, biphenyl and β-1) [25]. They concluded that the order of reactivity for depolymerisation was α-O-4, β-O-4 > β-1 > biphenyl and that both phenolic and non-phenolic forms of these compounds influenced the reactivity. They also studied the influence of side-chain hydroxyl groups at the C_{α} and C_{γ} positions on the pyrolytic β-ether cleavage of aryl ether-type dimer models and proposed that cleavage of the β-ether bond proceeds via a quinone methide intermediate, with intermolecular hydrogen bond formation between the C_{α} and C_{γ}-hydroxyl groups as the first step [26]. Klein et al. studied lignin pyrolysis using phenethyl phenyl ether as a lignin model for β-aryl ethers and detected phenol and vinylphenol as major products [27]. The bond dissociation enthalpies for the homolytic cleavage of β-aryl ethers have also been reported based on computational studies using a β-O-4 dimer model [28]. Robert et al. pyrolysed lignin dimer models, namely, arylglycerol-β-guaiacyl ether derivatives, and classified the pyrolysis reactions as follows: 1) cleavage of β-ether bond presumably via an oxirane intermediate, 2) α, β-dehydration, 3) cleavage of C_{β}–C_{γ} bond presumably via oxetane, 4) formation of α-O-α condensed structure and 5) cleavage of C_{α}–C_{β} bond [29]. Kim et al. studied the pyrolysis mechanisms of α-O-4 dimer models using electron paramagnetic resonance, and these studies indicated that a methoxyl group on the aromatic ring accelerates the oligomerisation reaction to form high molecular weight compounds [30]. The first object of the present study was the detection and identification of the abundant pyrolysis products from four phenylpropanoids and elucidation of the formation pathways of the pyrolysis products. The second goal was classification of the initial reactions of the formation pathways into four principal categories.

2. Materials and Method

Cinnamyl alcohol [**M1**], coniferyl alcohol [**M3**] and sinapyl alcohol [**M4**] (all E-isomers) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) as guaranteed grades. *p*-Coumaryl alcohol [**M2**] was



(**M1**); R^1=H, R^2=H, R^3=H: (*E*)-Cinnamyl alcohol
(**M2**); R^1=H, R^2=OH, R^3=H: (*E*)-Coumaryl alcohol
(**M3**); R^1=OCH_3, R^2=OH, R^3=H: (*E*)-Coniferyl alcohol
(**M4**); R^1=OCH_3, R^2=OH, R^3=OCH_3: (*E*)-Sinapyl alcohol

Figure1. Phenyl propanols used in this study

synthesised via reduction of trans-*p*-coumaric acid using lithium aluminium hydride (Itoh et al., 2008). The chemical structures of the model compounds are illustrated in Figure 1. These samples were pyrolysed with a Frontier Lab PY-2020iD pyrolyser. Each dried sample cup was inserted into the pyrolyser chamber, which was previously purged with helium. After pre-heating the pyrolyser furnace (400 °C–600 °C), each sample was placed in the middle of the furnace for 0.2 min and then moved to the top of the furnace. The pyrolysates produced at these temperatures were separated and analysed using a GC/MS system coupled directly to the pyrolyser. The GC/MS conditions are described below. An Agilent GC/MS system consisting of an Agilent 6890 gas chromatograph and Agilent 5975 inert mass selective detector was used to separate and obtain the mass spectra of the compounds in each sample. The samples were injected in split mode (100:1 ratio). The carrier gas was helium with a flow rate of 0.93 mL/min. The oven was initially maintained at 40 °C for 5 min, increased to 250 °C at a rate of 4 °C/min and maintained at this temperature for 60 min. Rtx-Wax fused-silica capillary columns (RESTEK, 60 m × 0.25 mm i.d., 0.25 μm film thickness) were used to separate the pyrolysis products. These columns were directly connected to the electron impact ion source of the mass spectrometer. The ion source was operated at 70 eV, and the injection port was set at 250 °C. The separated peaks were identified using the NIST05 MS Library.

3. Results and Discussion

3.1 Identification and distribution of pyrolysis products from phenyl propanols

Percent area, rather than absolute area, was utilised as the dependent variable in order to eliminate any inconsistencies due to variations in the sample sizes and product carryover. It was confirmed that the area contribution for a given peak was statistically similar between experiments. As is common for Py-GC/MS, identification of the majority of pyrolysis products was achieved by comparing their mass data with a widely used MS database. However, some of the pyrolysis products were not registered in this MS database. Therefore, the compounds were identified using mass fragmentation, GC retention times and the MS database.

The total ion chromatograms (TIC) obtained for Py-GC/MS of *(E)*-cinnamyl alcohol (**M1)**, *(E)*-*p*-coumaryl alcohol (**M2)**, *(E)*-coniferyl alcohol (**M3)** and *(E)*-sinapyl alcohol (**M4)** at 600 °C are shown in Figures 2–5. Area percentages of abundant pyrolysates from each lignin models are shown in Table 1.

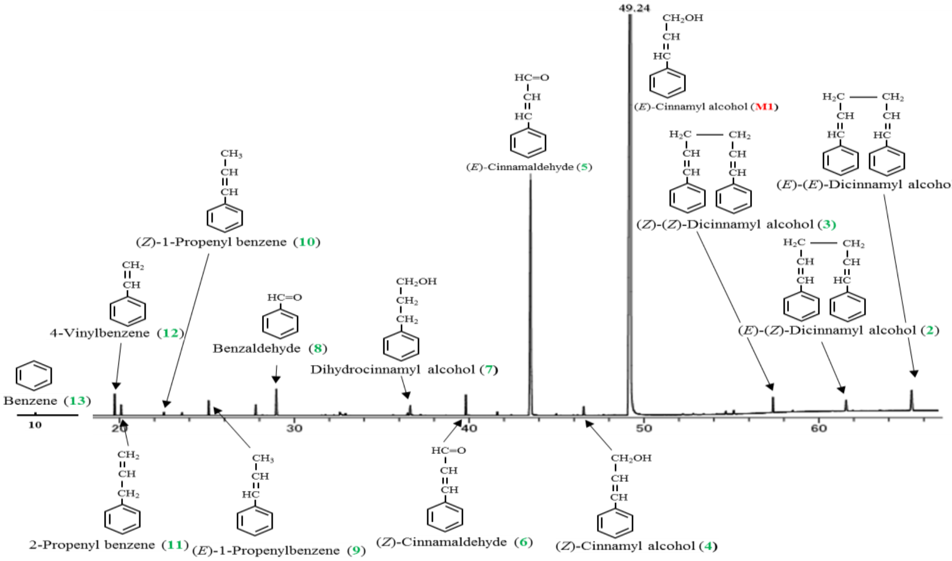


Figure 2. Total ion chromatogram for Py-GC/MS of cinnamyl alcohol at 600 ° C

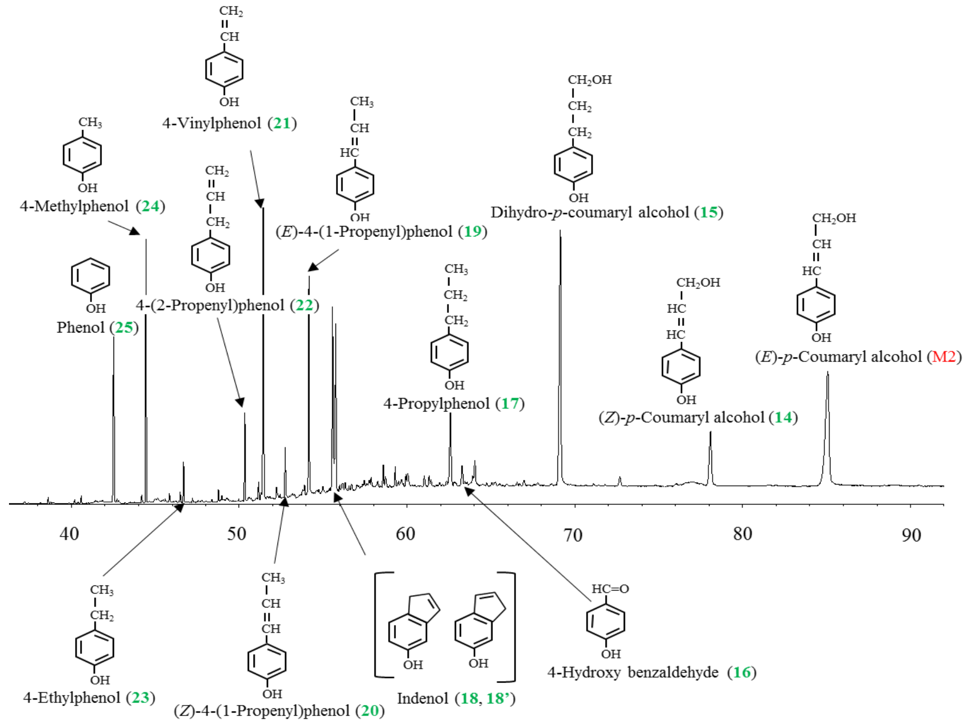


Figure 3. Total ion chromatogram for Py-GC/MS of *p*-coumaryl alcohol at 600 ° C

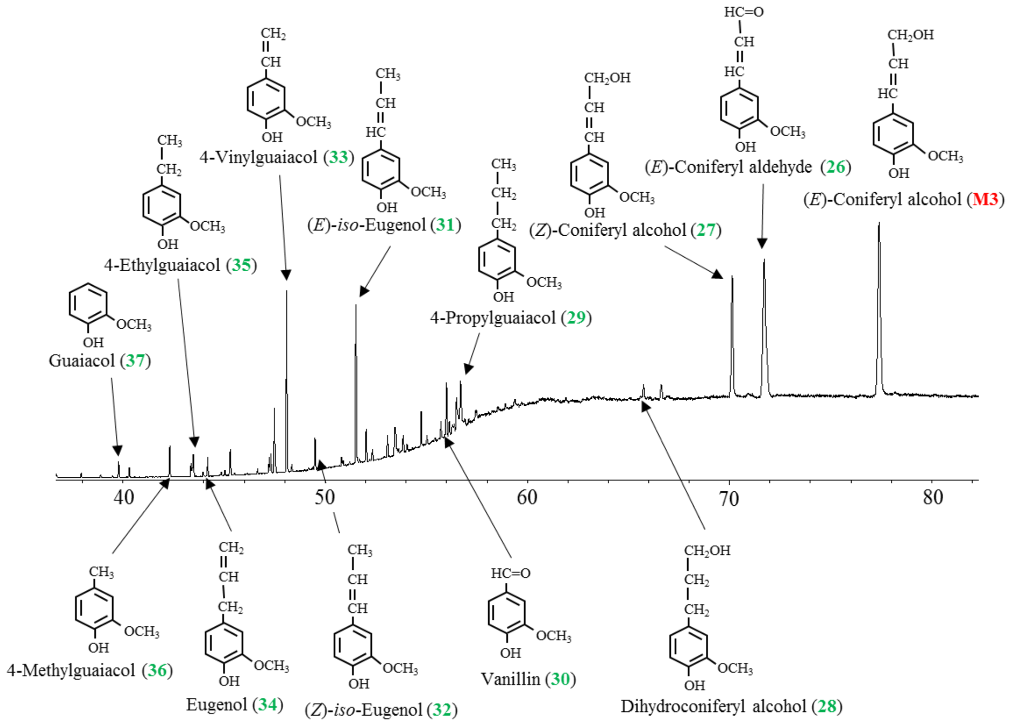


Fig.4. Total ion chromatogram for Py-GC/MS of coniferyl alcohol at 600 ° C

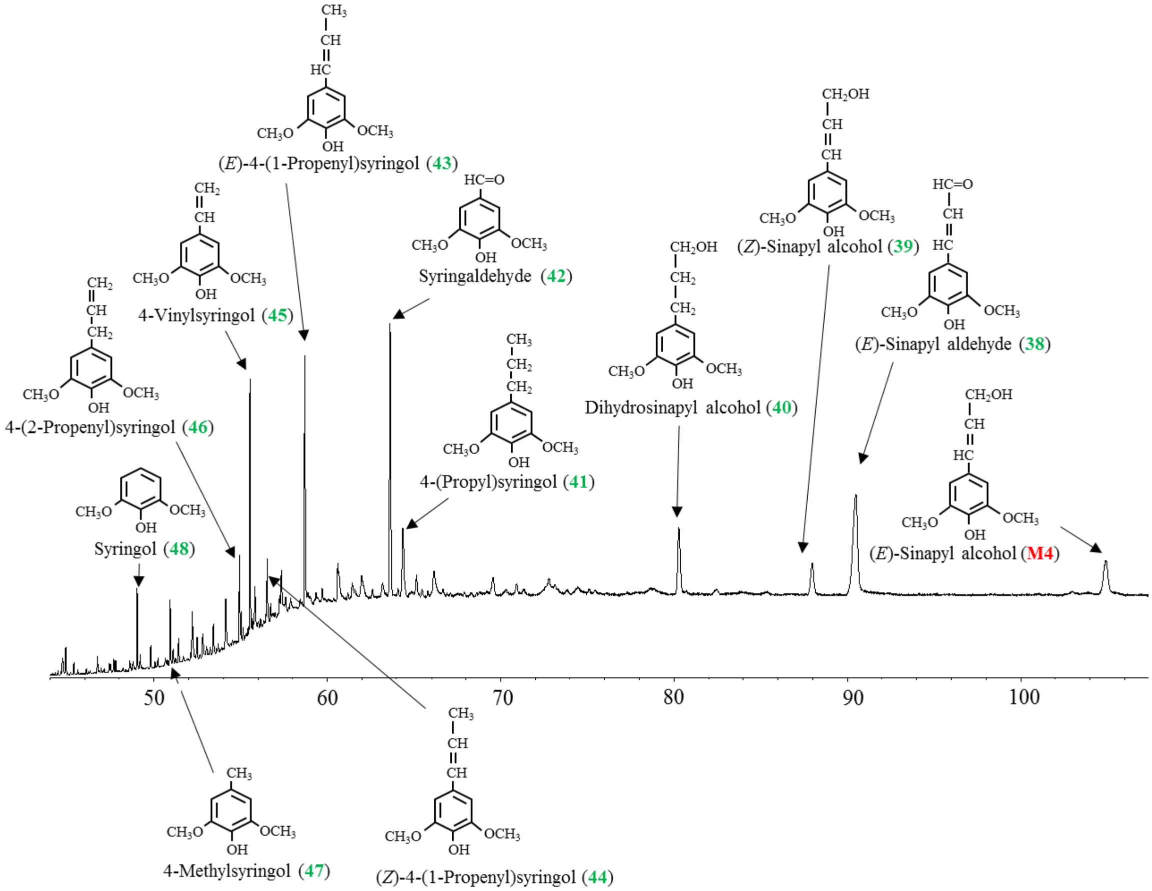


Figure 5. Total ion chromatogram for Py-GC/MS of sinapyl alcohol at 600 ° C

In the case of cinnamyl alcohol (**M1)** pyrolysis, 13 pyrolysis products and unreacted (**M1)** were identified. Unreacted (**M1)** was recovered in high yield (41.28%), reflecting its thermal stability, and the only major pyrolysis product was *(E)*-cinnamaldehyde (**5)** (36.94%). As a result of the formation of (**5**), a significant amount of hydrogen radicals should be formed and released as hydrogen. Three dimers were detected as C_γ-C_γ linkage structures of two phenyl propenyls.

In the case of *(E)-p*-coumaryl alcohol (**M2)**, 13 pyrolysis products and unreacted (**M2**) were identified. The recovery yield of (**M2**) was low indicating it was unstable under pyrolysis conditions. As major products, phenol (**25**), 4-methylphenol (**24**), 4-vinylphenol (**21**), *(E)*-4-(1-propenyl) phenol (**19**) and dihydro-*p*-coumaryl alcohol (**15**) were detected. This result suggests that hydrogen radical donation, hydroxyl radical abstraction and elimination of the side chain occurred in the (**M2**) structure. Two isomers of indenol also detected as the result of intermolecular coupling.

In the case of *(E)*-coniferyl alcohol (**M3**), 12 pyrolysis products and unreacted (**M3**) were identified and (**M3**) was recovered in low yield (17.77%), indicating its neutral stability during pyrolysis. (*E*)-Coniferyl aldehyde (**26**), *(Z)*-coniferyl alcohol (**27**), iso-eugenol (**31**) and 4-vinylguaiacol (**33**) were detected as major pyrolysis products. Formation pathway of iso-eugenol is initialised by hydroxyl radical abstraction from the C_γ-side chain following hydrogen radical donation.

In the case of sinapyl alcohol (**M4**), unreacted (**M4**) was recovered in 3.81%, indicating high reactivity as same as (**M2**). Syringaldehyde (**42**), 4-(1-Propenyl) syringol (**43**) and 4-vinylsyringol (**45**) were detected as major pyrolysis products. These pyrolysis products were produced via hydroxyl radical donation, hydroxyl radical abstraction, hydrogen radical abstraction and hydrogen radical donation.

Table 1 Major product yields (% of peak area) from M1-M4

Side chain structure	M1	M2	M3	M4
(*E*)–CH=CH-CH$_2$OH	41.28	12.55	17.77	3.81
(*E*)–CH=CH-CHO	36.94	N.D.	16.20	11.89
(*Z*)–CH=CH-CH$_2$OH	3.04	2.47	8.53	2.48
–CH$_2$-CH$_2$-CH$_2$OH	N.D.	7.86	0.85	4.02
–CH$_2$-CH$_2$-CH$_3$	N.D.	N.D.	2.99	3.30
–CHO	2.83	0.34	2.13	8.38
(*E*)–CH=CH-CH$_3$	3.46	2.02	5.35	5.60
(*Z*)-CH=CH-CH$_3$	N.D.	N.D.	0.96	1.61
–CH=CH$_2$	7.38	7.05	5.97	4.86
–CH$_2$-CH=CH$_2$	0.82	0.89	2.26	1.65
–CH$_2$-CH$_3$	N.D.	1.47	0.58	1.36
–CH$_3$	N.D.	6.55	0.94	1.16
–H	0.16	4.23	0.51	1.50

3.2 Categorisation of pyrolytic radical reactions for phenyl propanols

The pyrolysis pathway initiated by hydrogen abstraction is shown in Figure 6. These reaction pathways occur in (**M1)**, (**M3)** and (**M4)** at the C$_\gamma$-side chain to produce the corresponding aldehydes (**5, 26, 38)** in high yield. Harman-Ware et al. reported that coniferyl aldehyde is the major product from coniferyl alcohol pyrolysis [21]. After the reaction, only cinnamaldehyde [**5**] is subjected to further isomerisation reaction to produce its *(Z)*-form (**6)**. This isomerisation is known to occur at elevated temperature for thermal treatment of olefin compounds [31].

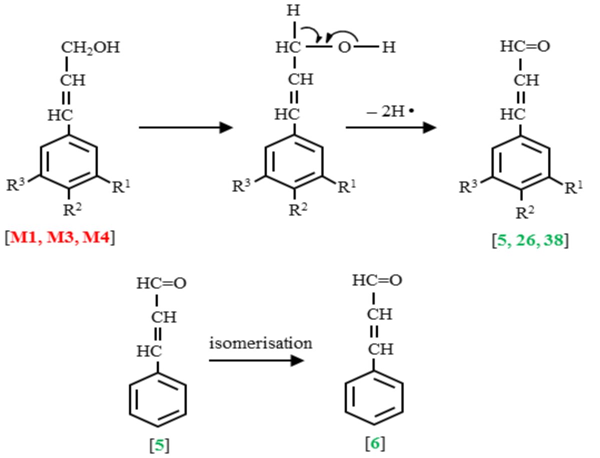


Figure 6. Hydrogen radical abstraction from γ-hydroxymethyl group to form aldehyde and isomerization

In Figure 7, the reaction pathway via hydrogen radical abstraction followed by C_γ displacement is illustrated. Hydrogen radical abstraction from the C_γ-hydroxyl group induced cleavage of C_β–C_γ to produce the corresponding vinylphenol derivatives. This process occurred for all phenyl propanols as one of major reaction pathway and yielded products **(12)**, **(21)**, **(33)** and **(45)**. Formation of vinylbenzene **(12)** from cinnamyl alcohol in high yield indicated that the role of phenolic hydroxyl group for the formation of vinylphenol structure should be small. Vinylphenols are known as typical pyrolysates from wood and lignin. For example, vinylphenol was produced as a major product in a yield of >20% in the fast pyrolysis of moso bamboo [10], in which the *p*-coumaryl alcohol structure was present in the lignin polymer. These vinylphenol derivatives have potential use as resources for production of bio-polymers, such as a poly-vinylphenol.

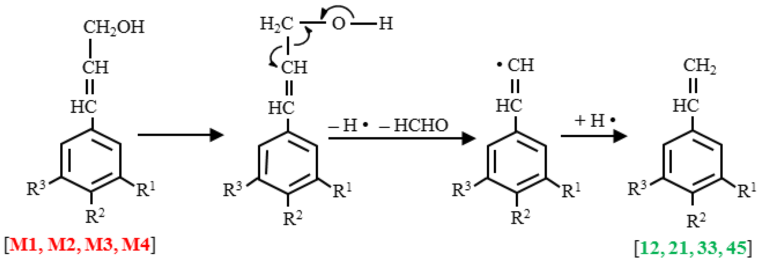


Figure 7. Hydrogen radical abstraction from γ-hydroxyl group followed by C_γ displacement

The reaction pathways for hydrogen radical abstraction followed by C_α–C_β cleavage via a quinone methide are shown in Figure 8. These reactions are categorised as secondary pyrolysis reactions, from which the products are to be used as starting compounds requiring free phenolic hydroxyl groups and saturated C_α–C_β bonds on the side chains. Compounds that meet these requirements are products (**15**), (**17**), (**22**) and (**23**) from *p*-coumaryl alcohol; (**28**), (**29**), (**34**) and (**35**) from coniferyl alcohol and (**41**) and (**46**) from sinapyl alcohol. Some of these products are converted to methylphenol derivatives (**24**), (**36**) and (**47**) via quinone methide intermediates.

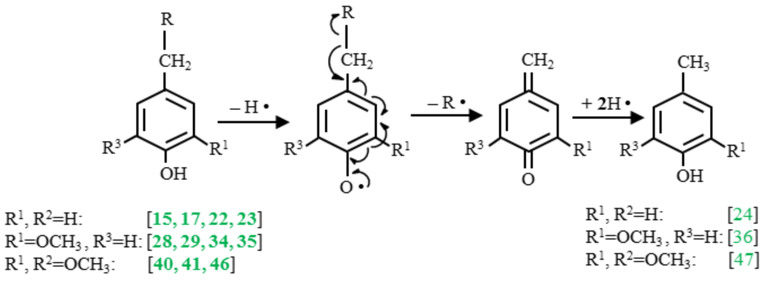


Figure 8. Hydrogen radical abstraction to form quinone methide radical and methyl radical donation

Hydroxyl radical abstraction pathways are shown in Figure 9. Hydroxyl radical abstraction from the C_γ position produces C_γ-radical intermediates **(A)**, then a part of **(A)** is converted to C_α-radical intermediates **(B)** through electron transfer. Hydrogen radical donations to intermediates **(A)** produce 4-(1-propenyl) phenol derivatives **(9)**, **(19)**, **(31)** and **(43)**. In the same manner as for **(A)**, hydrogen radical donation after electron transition to intermediates **(B)** produce 4-(2-propenyl)phenol derivatives

(11), (**22)**, (**34)** and (**46)**. In the case of (**M2)**-(**M4)**, this reaction pathway is one of the major routes for pyrolysis at 600 °C; therefore, compounds with 4-(1-propenyl) side chains were major pyrolysis products. In the pyrolysis of (**M1)**, products (**9)** and (**11)** were produced in low yield suggesting requirement of the phenolic hydroxyl group, and another pathway via quinone methide intermediate must be considered.

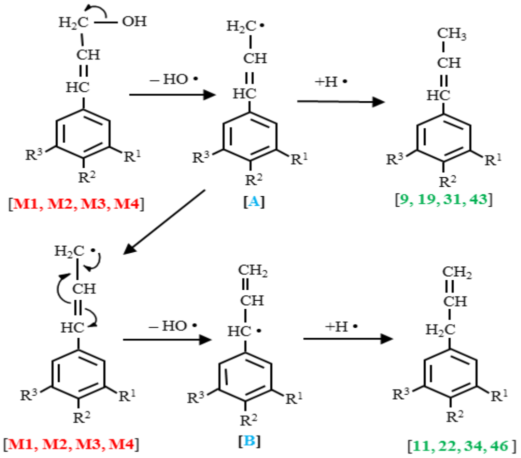


Figure 9. Hydrogen radical abstraction followed by C_{α}–C_{β} cleavage via quinone methide

Alternatively, hydroxyl radical donation into intermediates (**B**) could occur to form phenols (**13, 25, 37, 48)** and benzaldehydes (**8, 16, 30, 42)** via two pyrolysis pathway as shown in Figure 10. The former pathway is abstraction of hydrogen radical from C_{α}-hydroxyl group resulted in C_{α}-C_{β} cleavage. The latter pathway is also abstraction of hydrogen radical from C_{α}-hydroxyl group resulted in C_{α}-C_1 cleavage. These reaction pathways are minor routes and the yield of corresponding products were low.

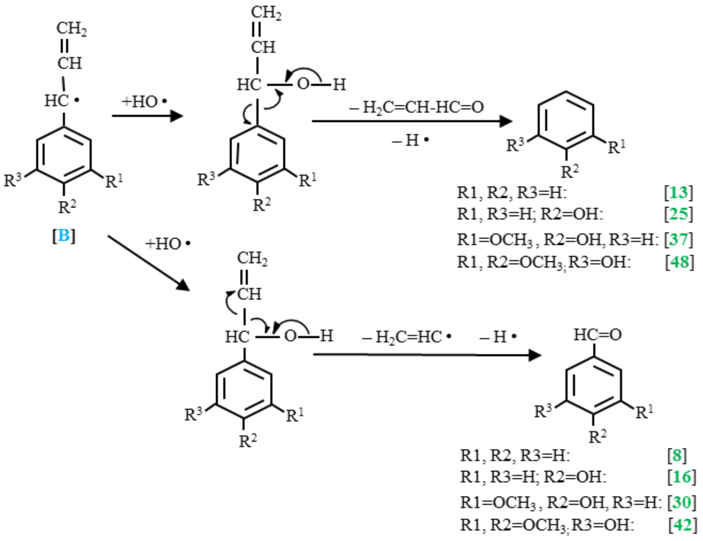


Figure 10. Hydroxyl radical donation and hydrogen radical abstraction followed by homolytic cleavage

Coupling dimerisation of intermediates (**A**) and (**A’**) are observed for only (**M1**) pyrolysis as minor reaction pathways. The proposed pathway is illustrated in Figure 11. A part of the (*E*)-intermediate (**A**) subjected to isomerisation to form (*Z*)-intermediate [A’], and coupling of them produced di-(1-propenyl) benzene; (**A**) - (**A**), (**A**) - (**A’**) and (**A’**) - (**A’**).

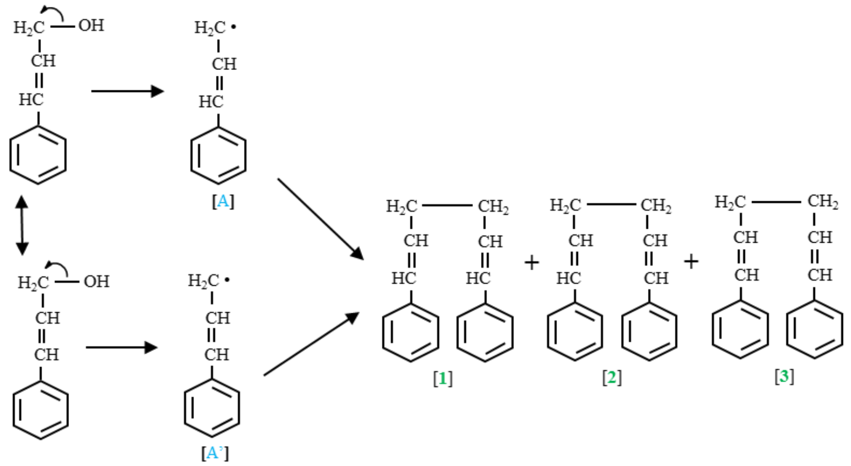


Figure 11. Hydroxyl radical abstraction from γ-hydroxymethyl group to form Cγ-radical and dimerisation

Indenol derivatives were produced from p-coumaryl alcohol via intermolecular radical coupling between side chain C_γ and aromatic C_3 to form two indenol isomers, 1-H-inden-5-ol and 1H-inden-6-ol. Intermolecular radical coupling was also occurred for *p*-coumaryl alcohol (**M2**) pyrolysis, as shown in Figure 12. This reaction initiated by a hydroxyl radical extraction from C_γ and hydrogen radical abstraction from C_2 or C_5 position produced two isomer (**18, 18’)**, 5-hydroxyindene and 6-hydroxyinedene, respectively.

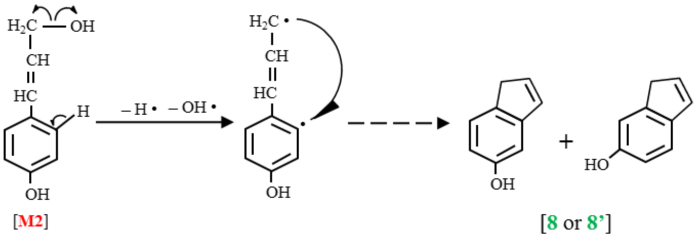


Figure 12. Hydroxyl radical abstraction followed by intermolecular coupling

3-3 Effect of pyrolysis temperature on pyrolysate composition.

The effects of pyrolysis temperature on the pyrolysate compositions from four phenyl propanols were estimated from the TIC peak areas of Py-GC/MS. The recovery yields of the starting materials reflected the reactivity under experimental pyrolytic conditions. The recovery yields of the starting materials, (**M1**) ~ (**M4**) at different pyrolysis temperature are illustrated in Figure 13. A comparison of the starting materials shows that for all experimental temperatures, the higher recovery yield were obtained for (**M1**) and (**M4**), while the lower yield were obtained for (**M2**) and (**M3**).

For phenylpropanols ($Ar-CH_2-CH_2-CH_2OH$) were formed in high yield at 400 °C, and decreased with pyrolysis temperature as shown in Figure 14-A. For cinnamyl alcohol, phenyl propanol (**7)** was undetected in the pyrolysates from 500 and 600 °C pyrolysis. These results indicate that the hydrogen donation occurs at low temperature and the phenylpropanol structure is unstable to the pyrolysis condition over 500 °C. In the case of phenylpropenals (Ar-CH=CH-CHO), pyrolysis of (**M1**) yielded the phenylpropenal (cinnamaldehyde, **5**) in high yield and increased the yield with the pyrolysis temperature, indicating the significant impact of pyrolysis temperature on the hydrogen abstraction from C_γ-OH. The yield of phenylpropenal structures from (**M3**) and (**M4**) were about the same. On the other hand, phenylpropenal (p-coumaryl aldehyde) was not detected from the pyrolysate from (**M2**).These results are illustrated in Figure 14-B.

As shown in Figure 14-C, benzaldehyde structures (Ar-CHO) produced from (**M1**) was one of major pyrolysis product increasing with pyrolysis temperature. For (**M2**) and (**M3**), these products (**16)** and (**30)** are not major and effect of pyrolysis temperature on the product yield is small.

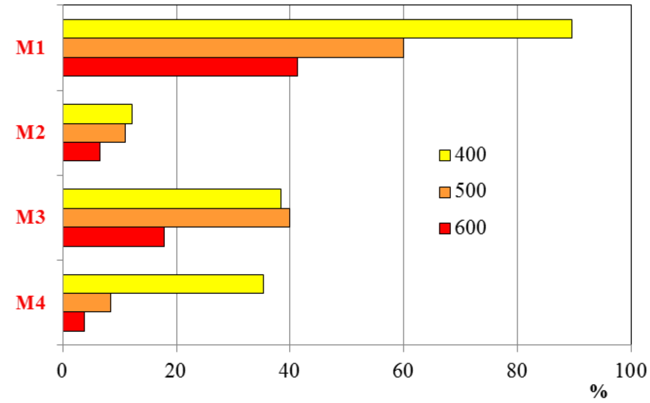


Figure 13. Recovery Yield of starting materials (**M1**)-(**M4**) from pyrolysis at 400-600 ºC

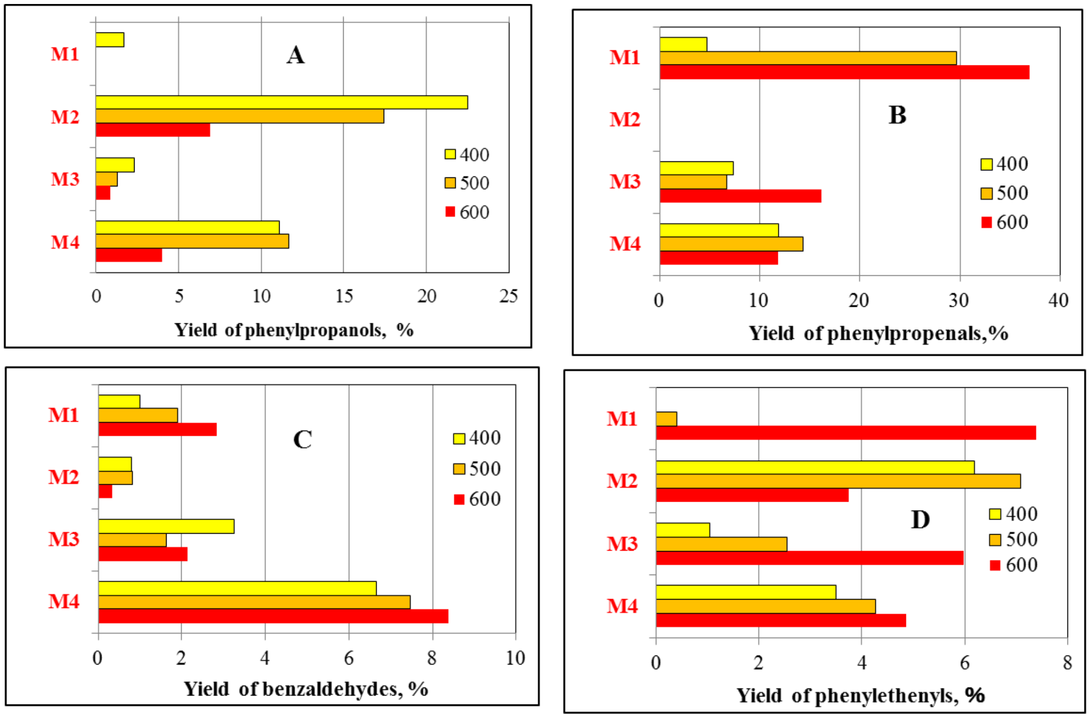


Figure 14. Recovery yield of phenylpropanols, phenylpropenals, benzaldehyde and phenylethenyls from pyrolysis at 400-600 ºC

Products with phenylethenyl structure (Ar-CH=CH_2) are typical product from lignocellulose and is produced from various structure of phenyl propane unit in lignin polymer. As shown in Figure 14-D, these phenylethenyl products are formed from phenyl propanols used in this study and the effect of temperature of the product yield are not significant instead of (**M1**), For (**M1**) pyrolysis, the phenylethenyl product (vinylbenzene, **12**) is not detected in the pyrolysate at 400 °C.

Conclusion

Abundant pyrolysates from four phenyl propanols with different pendant groups on the ring were identified and formation pathways of the pyrolysates were proposed. The results show that the thermal stability of four model compounds was different caused by presence of phenolic hydroxyl and methoxyl groups. Unreacted cinnamyl alcohol was recovered over 40% after pyrolysis, indicating that the lack of a phenolic hydroxyl group increased the thermal stability. Pyrolitic conversion of cinnamyl alcohol to cinnamaldehyde is the preferred reaction pathway. Sinapyl alcohol and coniferyl alcohol exhibited similar pyrolysis behavior, with similar compounds detected as the major products except for recovery yield of starting materials. The pyrolysis of *p*-coumaryl alcohol yielded many products that suffered from loss of the side-chain C_1 or C_2 carbons. The basic reaction pathways involved the oxygen in the C–O and H–O bonds, as well as homolytic cleavage. Therefore, many of the products were produced via reactions involving hydrogen and hydroxyl radicals. These initial reactions were classified into four principal categories: 1) donation of a hydrogen radical, 2) abstraction of hydrogen radical, 3) donation of a hydroxyl radical and 4) abstraction of a hydroxyl radical. Isomerisation and methyl radical donation also occurred during the pyrolysis of the phenyl propanols.

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