Study on the Pyrolytic Behavior of Wood-Plastic Composites using Py-GC/MS

Jian-Ping Sun,[a, b] Shu-Juan Sui,[a] Zhi-Jun Zhang,[a] Shun Tan,[a] and Qing-Wen Wang [a,*]

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was employed to investigate the primary pyrolysis product distribution of the pyrolysis of wood-plastic composites (WPCs) and the mutual effects of poplar wood (PW) and high-density polyethylene (HDPE). The PW, HDPE, and WPCs were pyrolysed at 475, 550, and 625 °C. The effect of temperature on the WPC pyrolysis products was examined. The comparison of the degradation composition results for HDPE, PW, and WPCs indicated that thermal degradation of WPCs comprised individual poplar wood and HDPE pyrolytic decompositions, and the pyrolytic products of PW and HDPE did not react with each other. The experimental results demonstrate that the pyrolytic product distribution of HDPE changed apparently in the presence of PW during pyrolysis. The PW decomposed at lower temperature during pyrolysis provided radicals, enhancing the scission of polymer chains to obtain more light paraffins. Further, the proposed pathway for the evolution of the main volatile organic products was probed. This study provides insights into the fundamental mechanisms of WPC pyrolysis and a basis for developing more descriptive models of WPC pyrolysis.

*Contact information: a: Key Laboratory of Bio-Based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040 China; b: School of Municipal and Environmental Engineering, Shenyang Jianzhu University, Shenyang 110168, China; * Corresponding author: qwwang@nefu.edu.cn*

INTRODUCTION

Waste plastic has been a main environmental concern as one of the primary municipal solid wastes (MSWs). The total global production of plastics was as great as 245 million tons (MT) in 2006, and 60% of all plastic solid waste goes to landfills (Panda *et al.* 2010). The disposal of waste plastics is an important problem due to the high amount of waste generated and its non-biodegradability. The same applies to lignocellulosic materials, as sawdust and rice husks from the agriculture and wood industries are abundant in China, with an annual production above 900 MT (Xu *et al.* 2009). Wood plastic composites (WPCs) are composites that are primarily composed of a plastic matrix reinforced with biomass-based fibers and other additives (Soury *et al.* 2009). WPC commercial products are increasingly replacing many products, especially in outdoor applications such as fences, park benches, and landscaping materials (Liu *et al.* 2008). WPCs are considered to be an effective way to utilize waste lignocellulosic materials and recycling plastic waste, as well as offering alternative applications for virgin materials. Although WPCs can be reprocessed many times (Beg and Pickering 2008), new waste will be produced eventually, as the mechanical properties of WPCs decrease in quality

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because of the degradation of macromolecules. It is important to develop effective recycling techniques for realizing WPCs waste resource utilization.

Fast pyrolysis is one of the thermochemical processes that can directly convert biomass into a liquid product called "bio-oil". Bio-oil has received much attention in recent years due to the feasibility of it being a crude oil replacement. Polyolefinic polymers can also be readily thermally decomposed to gaseous and liquid hydrocarbons (Sharypov *et al.* 2002). Because WPCs consist of a mixture of biomass and polymeric material, fast pyrolysis provides an alternative way to convert WPCs into valuable products such as chemicals or fuels.

There have been some recent studies concerning the co-pyrolysis of biomass and synthetic polymers. Wood with plastic co-pyrolysed in an auger reactor was reported, and the pyrolysis oil obtained from co-pyrolyses of HDPE with pine wood were upgraded relative to bio-oils produced from pine wood alone, with higher heating values and lower oxygen contents, acid values, water contents, and densities (Bhattacharya *et al.* 2009). Brebu *et al.* (2010) studied the co-pyrolysis of pine cone with synthetic polymers and found that higher amounts of liquid products were obtained compared to theoretical ones due to the synergistic effect in the pyrolysis of the biomass/polymer mixtures. Similarly, it has been suggested by other researchers that polyolefinic polymers could provide hydrogen during thermal co-processing with wood biomass and could lead to an increase in liquid production. They concluded that there was a synergistic effect in the co-pyrolysis of biomass-plastic mixtures in the form of enhanced oil yields (Zhou *et al.* 2006; Rutkowski and Kubacki 2006).

Most of these previous studies were carried out with a focus on yields of liquids under various temperatures and heating rate conditions, or on the properties of the pyrolysis oil produced. However, the interaction between biomass and plastic on the product distribution of pyrolysis oils remains relatively unexplored, especially with respect to the effect of thermal degradation of biomass on the decomposition of plastics. Moreover, understanding the interplay of the reactions between PW and HDPE decomposition products comprising the complex mechanism, and specifically how the products are formed, is critical to subsequent catalytic upgrading of WPCs pyrolysis oil. Py-GC/MS has been shown previously to be a reliable analytical technique for on-line separation and analysis of the volatile components, as well as an important tool for gaining insight into the critical degradation pathways, of WPCs pyrolysis. In addition, Py-GC/MS has been successfully applied to the qualitative and quantitative analysis of WPCs, *e.g.* wood type, the polymer matrix, and the ratio of thermoplastic polymers and wood in WPCs (Fabiyi *et al.* 2008; Schwarzinger *et al.* 2008; Windt *et al.* 2011).

Bio-oil is known to be viscous, acidic, and thermally unstable, and it contains high proportions of oxygenated compounds (Bridgwater 2012). Therefore, bio-oil should be refined before it can be used as a transportation fuel. There are several methods of improving bio-oil quality. One recent upgrading technique is to apply olefination to raw bio-oil under acid-catalyzed conditions. In this approach, the acid-catalyzed addition reactions of carboxylic acids, phenolic compounds, alcohols, and water across the olefins formed less hydrophilic, higher fuel value products such as esters, alkylated phenols, ethers and alcohols. It would be interesting to determine if hydration, esterification, etherification, and phenol alkylation reactions with olefin happened during pyrolysis of WPCs because of a large amount of olefin formed by pyrolysis of HDPE (Zhang *et al.* 2010, 2011, 2013).

In the present study, WPCs, PW, and HDPE were pyrolysed in a micro-scale reactor using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) to investigate the mutual effects of HDPE and PW and to ascertain whether thermochemical process was appropriate for converting WPCs into liquid fuel.

EXPERIMENTAL

Materials

HDPE (5000S resin) from Daqing Petrochemical Co., China, was used in the study as the matrix. Poplar wood from Heilongjiang Province, China, was ground in a high-speed rotary cutting mill, and the derived wood flour was passed through a sieve of 40-mesh size (425 μm) and retained on a 70-mesh (212 μm) sieve.

Composites Samples Preparation

Wood flour was dried at 105 °C for 24 h to remove moisture. HDPE was mixed with the wood particles (1:1 wt/wt ratio) in a high-speed mixer for 15 min at 75 °C. The mixtures were melted and extruded by a twin-screw extruder to form WF/HDPE composite particles. The processing parameters for the twin-screw extrusion systems are presented in Table 1. The WPCs material used in the study was poplar-wood/high-density-polyethylene (HDPE) composites (Ou *et al.* 2010).

Prior to experiments, the PW, HDPE, and WPCs were dried at 110 °C for 12 h and ground in a high-speed rotary cutting mill. Particles with a diameter of less than 125 μm were selected for experiments.

Table 1. Feeding Speed, Rotary Speed of Screw, and Temperature of Heating Zone during the Extrusion Process

Heating zone	Temperature in different zone (°C)								Feed speed (kg h-1)	Rotary speed (rpm)
	1	2	3	4	5	6	7	Die		
Twin screw	160	170	180	180	175	170	165	160	6	40

Methods

Py-GC/MS analysis was carried out with an integrated system composed of a CDS5200HP-R pyrolyser (Chemical Data Systems), an Agilent 6890 gas chromatograph equipped with a capillary column DB-17MS capillary column (30 m × 0.25 m i.d., 0.25 μm film thickness), and an Agilent 5973 mass spectrometer. The samples were filled in a quartz tube and heated by an inductively heated platinum filament coil at set temperature and held for 15 s, with a heating rate of 20 °C /ms. The PW, HDPE, and WPCs were pyrolysed at 475, 550, and 625 °C. The GC was operated at a constant helium column flow of 1.0 mL/min and a 1:70 split ratio. The oven program started at 40 °C for 2 min and was heated to 250 °C at a constant 5 °C /min with a final hold time of 5 min. The mass spectrometer employed was operated in full scan mode between 40 and 450 atomic mass units (amu) at 1 scan per s and set to an ionisation energy of 70 eV. Identification of the evolved species was achieved on the basis of their mass spectra using a NIST MS library by comparing their elution times with those of a commercial standard. Py-GC/MS experiments for the thermal degradation of WPCs were conducted at least in duplicate, which confirmed the optimum reproducibility of the reported procedure.

RESULTS AND DISCUSSION

Figure 1 presents the pyrogram of PW, HDPE, and WPCs at 475, 550, and 625 °C. As is seen from Fig. 1, the yield and distribution of pyrolysis products from PW at 625 °C were similar to those found at 550 °C, which implies that PW can be sufficiently pyrolysed at 550 °C (Schwarzinger *et al.* 2008). Likewise, the distribution of hydrocarbons from pyrolysis of HDPE at 625 °C was also similar to that found at 550 °C. The identified pyrolysis products and abundances based on GC area% of WPCs are presented in Table 2. The HDPE pyrogram reveals the presence of homologous triplets formed by alkanes, alkenes, and alkadienes with increasing carbon atoms. From Fig. 1(b) and Table 2, it can be seen that few hydrocarbons were produced for HDPE and WPC pyrolysis at 475 °C, with the obtained products coming mainly from PW. Additional residue formation was observed in the quartz tube for HDPE and WPCs at 475 °C after pyrolysis, which indicates that HDPE cannot be sufficiently pyrolysed at a relatively low temperature. It can also be observed in Fig. 1 and Table 2 that an increase in reaction temperature promoted the yield of hydrocarbons for WPCs, from 3.22% (at 475 °C) to 25.35% (at 550 °C) and 64.80% (at 625 °C), probably because the increase in reaction temperature favored the cracking of polyolefin. Compared with the degradation composition of HDPE and PW, almost all identified products originated from WPCs thermal decomposition were observed in the individual pyrolyses of PW or HDPE. This indicates that the thermal cracking of WPCs includes HDPE and poplar wood pyrolysis (Bhattacharya *et al.* 2009), and the addition reactions (e.g., olefin hydration, phenol alkylation, etherification, *etc*.) did not occur during pyrolysis, probably due to the absence of acid-catalyzed conditions. However, there was an obvious effect of thermal degradation of PW on the decomposition of HDPE.

Figure 2 illustrates the distribution of the paraffins and olefins from pyrolysis of HDPE and WPCs at different temperatures. The abundance of the hydrocarbon products is listed and compared in Fig. 2 in terms of area (%), which is related to the total ion intensity. It can be observed from this figure that for hydrocarbon products obtained from HDPE alone, normal paraffins predominate (C17-C24). The hydrocarbons produced by thermal cracking of HDPE contained approximately 14.56% C5-C9, 20% C10-C16, and 46.22% C17-C24; the ratio of them was 0.31:0.43:1. In the case of WPCs pyrolysis, 25.35% hydrocarbons were obtained at 550 °C; these hydrocarbons included 7.92% C5-C9, 7.55% C10-C16, and 11% C17-C23 with the ratio of 0.72:0.69:1. At 625 °C, the produced hydrocarbons accounted for 64.80%, of which 15.92% were C5-C9, 22.51% were C10-C16, and 26.36% were C17-C22; the ratio of these three was 0.60:0.85:1. Compared with HDPE alone, WPCs obtained more light paraffins (C5-C9, C10-C15). This demonstrates how the product distribution of HDPE changed significantly in the presence of PW during pyrolysis.

It has been suggested by Jakab that biomass has lower thermal stability compared to plastics, which could affect their radical degradation mechanism by promoting the degradation of synthetic macromolecules (Jakab *et al.* 2000; Jakab *et al.* 2001). Marin *et al.* (2002) studied the copyrolysis of wood biomass-polyolefins in a rotating autoclave. Their results showed that the biomass reacts, and during the pyrolysis at 400 °C, the formed solid evolves to act as a radical donor; when assisted by radicals from biomass, the polymer chain scission leads to the production of light liquids. Thus, it is reasonable to explain the effects of PW on the thermal degradation of HDPE as follows: due to the lower temperature of biomass component decomposition compared with polyolefins, free

radicals are formed from biomass pyrolysis and participate in reactions of plastic decomposition, yielding more light paraffins.

As can be seen from Table 2, fast pyrolysis at 550 °C initiated decomposition of the WPCs to produce a complex mixture of compounds that can be further categorized into anhydrosugars, aldehydes, ketones, carboxylic acids, furans, and aliphatic hydrocarbons.
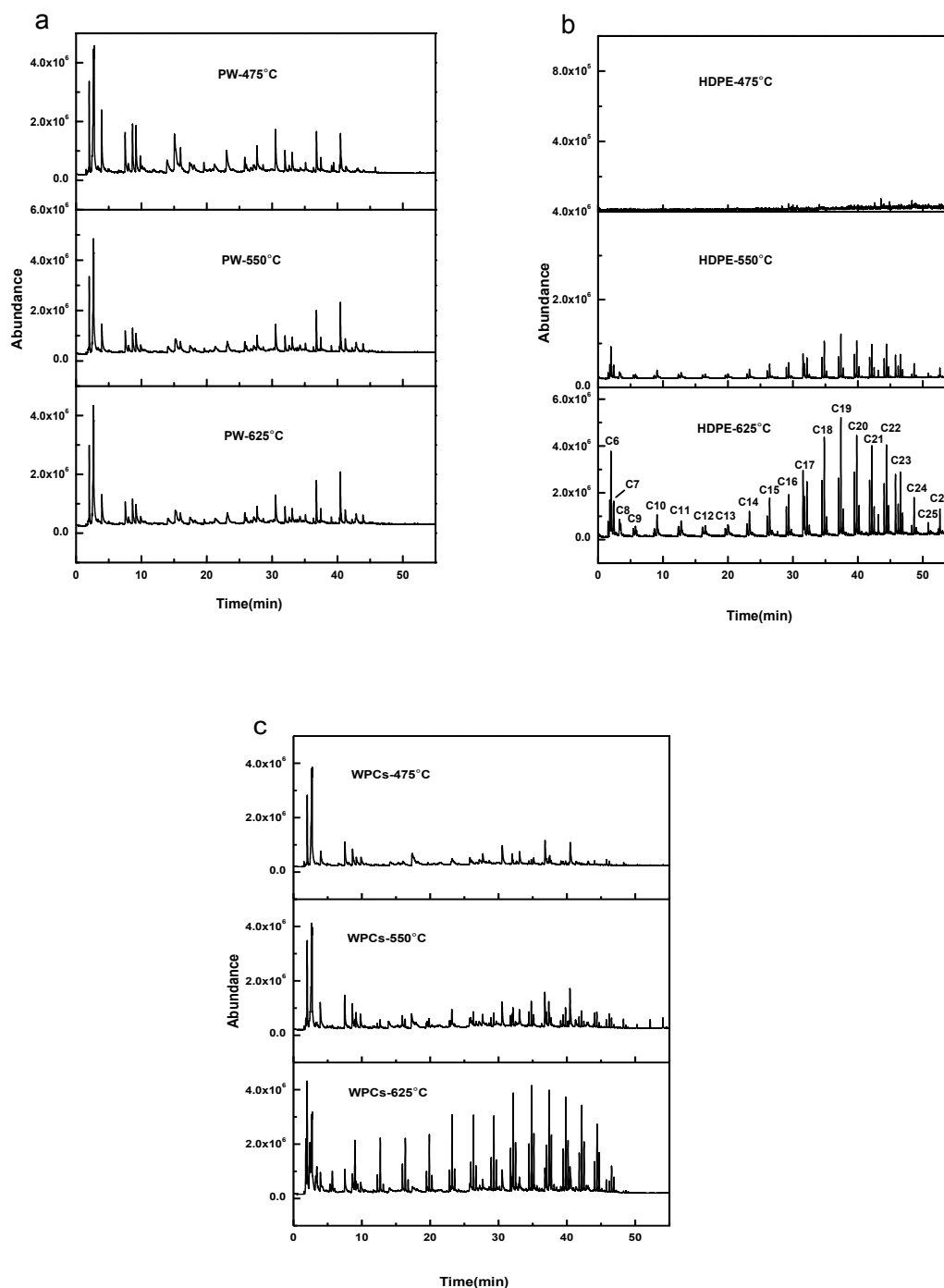

Fig. 1. Py-GC/MS chromatogram of PW (a), HDPE (b), and WPCs (c) at 475 °C, 550 °C, and 625 °C.
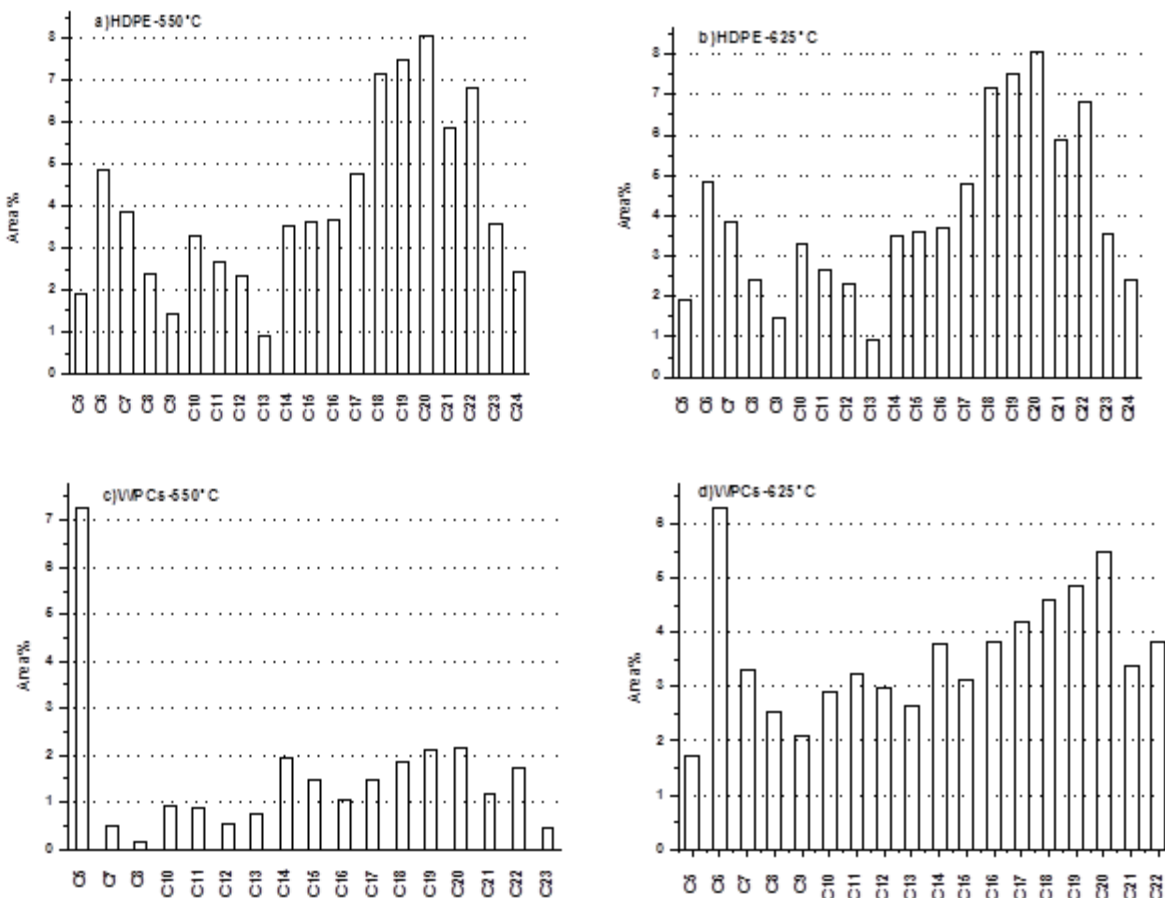
Fig. 2. Py-GC/MS data on distribution of the hydrocarbons (paraffins-olefins): (a) HDPE-550 °C; (b) HDPE-625 °C; (c) WPC-550 °C; and (d) WPC-625 °C

Table 2. Identification, Yield of Pyrolysis Products at 475, 550, and 625 °C

Groups	Compound	Formula	Area percent (%)		
			475 °C	550 °C	625 °C
Anhydrosugars			6.01	4.40	-
	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	$C_6H_8O_4$	0.48	0.33	-
	2,3-Anhydro-d-mannosan	$C_6H_8O_4$	0.76	0.47	-
	levoglucosan	$C_6H_{10}O_5$	4.77	3.60	-
Aldehydes			9.09	3.19	5.77
	Acetaldehyde, hydroxy-	$C_2H_4O_2$	5.20	1.10	5.16
	2-Butenal, 2-methyl-	C_5H_8O	0.89	0.11	-
	Butanedial	$C_4H_6O_2$	3.00	1.98	0.61
Ketones			14.02	11.17	4.10
	Acetone	C_3H_6O	6.01	5.20	2.71
	2-Propanone, 1-hydroxy-	$C_3H_6O_2$	4.55	3.76	1.16
	2-Cyclopenten-1-one	C_5H_6O	0.30	-	0.13
	2-Cyclopenten-1-one, 2-hydroxy-	$C_5H_6O_2$	2.11	1.58	0.10

Groups	Compound	Formula	Area percent(%)		
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	1.05	0.63	-
Furans			3.80	4.09	0.85
	Furan	C_4H_4O	0.40	-	-
	Furan, 2-methyl-	C_5H_6O	0.16	-	-
	Furfural	$C_5H_4O_2$	2.06	1.63	0.85
	2(5H)-Furanone	$C_4H_4O_2$	0.89	1.13	-
	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$C_6H_6O_3$	0.29	1.33	-
Acids			17.28	15.22	3.69
	Acetic acid	$C_2H_4O_2$	17.28	13.83	3.69
	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	-	0.61	-
Phenols			24.87	25.62	5.77
	Phenol	C_6H_6O	4.58	2.10	-
	phenol,3-methyl-	C_7H_8O	-	0.05	-
	Guaiacol	$C_7H_8O_2$	1.23	1.15	0.31
	2,3-Dihydroxybenzaldehyde	$C_7H_6O_3$	-	0.14	-
	p-Methylguaiacol	$C_8H_{10}O_2$	1.05	0.85	0.22
	1,2-Benzenediol	$C_6H_6O_2$	-	0.46	-
	1,2-Benzenediol, 3-methoxy-	$C_7H_8O_3$	-	1.28	-
	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	1.66	1.33	0.53
	Hydroquinone	$C_6H_6O_2$	-	0.31	-
	Eugenol	$C_{10}H_{12}O_2$	0.42	0.98	0.20
	Syringol	$C_8H_{10}O_3$	4.51	2.06	1.51
	3-allyl-6-methoxyphenol	$C_{10}H_{12}O_2$	-	0.21	-
	1,2,3-Benzenetriol	$C_6H_6O_3$	-	1.03	-
	Isoeugenol	$C_{10}H_{12}O_2$	1.52	1.34	0.56
	Vanillin	$C_8H_8O_3$	0.68	1.12	0.32
	Benzoic acid, 4-hydroxy-3-methoxy-	$C_8H_8O_4$	1.97	1.47	-
	phenol,2-methoxy-4-propyl	$C_{10}H_{14}O_2$	0.50	0.54	-
	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_9H_{10}O_3$	0.90	0.39	-
	Benzoic acid, 4-hydroxy	$C_7H_6O_3$		-	
	3-Hydroxy-4-methoxycinnamic acid	$C_{10}H_{10}O_4$	1.36	2.35	-
	Methoxyeugenol	$C_{11}H_{14}O_3$	2.57	0.66	0.22
	Syringaldehyde	$C_9H_{10}O_4$	0.51	2.38	1.67
	4-Hydroxy-2-methoxycinnamaldehyde	$C_{10}H_{10}O_3$	0.51	1.57	0.13
	Acetosyringone	$C_{10}H_{12}O_4$	0.73	1.03	-
	3,5-Dimethoxy-4-hydroxycinnamaldehyde	$C_{11}H_{12}O_4$	0.17	0.66	0.10
Hydrocarbons			3.22	0.16	-
	1-Pentene	C_5H_{10}	-	25.35	64.80
	pentane	C_5H_{12}	-	0.83	1.73
	1-Hexene	C_6H_{12}	-	6.42	-
	Heptane	C_7H_{16}	-	-	6.28
	1-Heptene	C_7H_{14}	-	0.51	-
	Octane	C_8H_{18}	-	-	3.31
	1-Octene	C_8H_{16}	-	0.17	0.89

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Groups	Compound	Formula	Area percent(%)		
	Nonane	C_9H_{20}	-	-	1.63
	1-Nonene	C_9H_{18}	-	-	0.52
	1,8-Nonadiene	C_9H_{16}	-	-	1.33
	1-Decene	$C_{10}H_{20}$	-	-	0.24
	1,9-Decadiene	$C_{10}H_{18}$	-	0.91	2.52
	Undecane	$C_{11}H_{24}$	-	-	0.40
	1-Undecene	$C_{11}H_{22}$	-	0.34	0.74
	1,10-Undecadiene	$C_{11}H_{20}$	-	0.56	2.16
	Dodecane	$C_{12}H_{26}$	-	-	0.34
	1-Dodecene	$C_{12}H_{24}$	-	-	1.05
	1,11-Dodecadiene	$C_{12}H_{22}$	-	0.54	1.57
	Tridecane	$C_{13}H_{28}$	-	-	0.37
	1-Tridecene	$C_{13}H_{26}$	-	-	0.57
	1,12-Tridecadiene	$C_{13}H_{24}$	-	0.50	1.64
	Tetradecane	$C_{14}H_{30}$	-	-	0.44
	1-Tetradecene	$C_{14}H_{28}$	-	0.33	0.61
	1,13-Tetradecadiene	$C_{14}H_{26}$	-	1.61	2.56
	Pentadecane	$C_{15}H_{32}$	-	-	0.60
	1-Pentadecene	$C_{15}H_{30}$	-	0.55	0.84
	Hexadecane	$C_{16}H_{34}$	-	0.93	2.27
	1-Hexadecene	$C_{16}H_{32}$	-	0.43	0.91
	1,15-Hexadecadiene	$C_{16}H_{30}$	-	0.60	2.13
	Heptadecane	$C_{17}H_{36}$	-	-	0.78
	1-Heptadecene	$C_{17}H_{34}$	0.38	0.52	1.17
	Octadecane	$C_{18}H_{38}$	0.23	0.94	3.04
	1-Octadecene	$C_{18}H_{36}$	0.36	0.72	1.20
	Nonadecane	$C_{19}H_{40}$	0.63	1.16	3.39
	1-Nonadecene	$C_{19}H_{38}$	0.56	-	1.30
	Eicosane	$C_{20}H_{42}$	0.33	1.24	3.56
	1-Eicosene	$C_{20}H_{40}$	-	0.80	1.25
	1,19-Eicosadiene	$C_{20}H_{38}$	0.17	1.06	2.88
	Heneicosane	$C_{21}H_{44}$	-	0.30	1.38
	1-Heneicosene	$C_{21}H_{42}$	-	0.46	0.96
	Docosane	$C_{22}H_{46}$	0.56	0.71	2.43
	1-Docosene	$C_{22}H_{44}$	-	0.79	0.88
	1,21-Docosadiene	$C_{22}H_{42}$	-	0.72	1.96
	1-Tricosene	$C_{23}H_{46}$	-	0.23	0.97

Pyrolysis Product Distribution

Anhydrosugars

Comparatively, the content of levoglucosan (LG; 1,6-anhydro-*β*-D-glucopyranose) was dominant among all the saccharides in the products. It is widely accepted that primary pyrolysis of cellulose follows two competing pathways: depolymerization to anhydrosugars, and pyranose ring-breaking to light oxygenated species. For cellulose depolymerization, levoglucosan is formed by the cleavage of the 1,4-glycosidic linkage in the cellulose polymer, followed by intramolecular rearrangement of the monomer units (Li *et al.* 2001). Shafizadeh (1982) suggested that the glycosidic bond is displaced by a C2 or C4 hydroxyl group, leading to the formation of 1,2- and 1,4-anhydro glucopyranose, which quickly rearranges to form levoglucosan, while Ponder *et al.* (1992) proposed that the polysaccharides undergo heterolytic glycosidic bond cleavage, producing a glucosyl cation, which ultimately forms 1,6-anhydride. Subsequent heterolytic cleavage of another glycosidic bond liberates a LG molecule. LG could undergo

dehydration and isomerisation reactions to form other anhydro-monosaccharides, such as 1,4:3,6-dianhydro-alpha-d-glucopyranose (DGP) and 2,3-anhydro-d-mannosan (AM) (Lin *et al.* 2009).

As one of the main condensable products from hemicellulose pyrolysis, anhydro-xylopyranose was not detected in the products, which implied that the 1,4-intramolecular-glycosidic bond on the xylopyranose is less stable than the 1,6-acetal bond on the gluco-pyranose (levoglucose), and anhydroxylopyranose acted as an intermediate product to instantly produce low molecular weight products through cracking reactions (Shen *et al.* 2010).

Consequently, anhydrosugars primarily originated from the decomposition of cellulose. It should also be noted that anhydrosugars (especially LG) are considered to be important intermediates (Lin *et al.* 2009), and their secondary reaction affected the final product composition. Thermal decomposition of LG proceeds through ring-opening of the glucosidic 1,6-acetal bond and rehydration to form the glucopyranose monomer, followed by prompt secondary reactions (Shen and Gu 2009).

Aldehydes and ketones

In view of the results presented in Table 2, hydroxyacetaldehyde (HAA) and butanedial were major components of the group of aldehyde products. It was reported that the ring hemiacetal bond is very active under thermal radiation, and the bond between C2 and C3 is unstable. Thus, the formation of HAA on the C1 and C2 is favored by ring-opening through the cleavage of the above two active bonds, along with the evolution of a four-carbon fragment (Shen *et al.* 2010). Butanedial mainly originated from secondary decomposition of anhydrous sugars, which could be further decomposed through the dehydration or fission reactions (Lv *et al.* 2012).

Hydroxyacetone (HA), acetone, cyclopentanone, and cyclopentenone were the major ketone products. HA is probably produced through the cleavage of the rearranged four-carbon fragments from the direct conversion of the cellulose molecules, where the tetrose fragment is initially dehydrated on C5 and C6 and then broken to HA (Shen *et al.* 2010). The formation of HA also could be attributed to the branched, amorphous structure, and low degree of polymerisation of hemicellulose (Patwardhan *et al.* 2011a).

The formation of acetone is complicated; one transformation pathway for acetone is the decomposition of xylan units, other than the O-acetyl-xylan unit, under high temperature (Shen *et al.* 2010). Meanwhile, cyclopentanone and cyclopentenone mainly originated from the decomposition of sugar units derived from hemicellulose and the recombination of opened bonds (Lv *et al.* 2010).

Furans

As can be seen in Table 2, many furan ring-containing compounds were detected in the pyrolysis products, among which 5-hydroxymethyl furfural (5-HMF), furanose, and furfural were dominant.

Furans are regarded as typical ring-containing products from hemicellulose. It was assumed that hemicellulose exhibit similar competing pyrolysis pathways like cellulose, consisting of depolymerization, dehydration to furan and pyran ring derivatives and furanose and pyranose ring-breakage to furan derivatives (Patwardhan *et al.* 2011a). Sanders *et al.* (2003) proposed that furans are obtained only from substrates containing furanose units.

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The formation of 5-HMF was possibly initiated by the cleavage of the ring gluco-sidic bond on the cellulose unit to form an aldehyde structure on C1, followed by the formation of a double bond between C4 and C5 through chain structure rearrangement. Another double bond between C2 and C3 was formed through the dehydration of the corresponding hydroxyl groups. Then, the acetal reaction of the hydroxyl groups on C2 and C5 was considered to be the essential step to form 5-HFM. Another chemical pathway to produce 5-HMF is the breaking of the pyran ring of LG to the hexose chain structure, followed by dehydration of the hydroxyl groups and sequential acetal reaction on C2 and C5 (Shen *et al.* 2010).

The production of furfural was mainly ascribed to the opening of the xylopyra-nose ring, followed by the formation of a furanose ring and its subsequent dehydration (Patwardhan *et al.* 2011a). Another possible chemical pathway for the formation of furfural is from the secondary reaction of 5-HFM (Shen *et al.* 2010).

It should be stressed that no pyrans were detected in the products. This result was possibly due to the fact that aromatic furan structures are more stable and kinetically favored than pyrans; meanwhile, the pyrolysis of saccharides must involve an inter-mediate that can readily transform into the furanose structure (Patwardhan *et al.* 2009).

Acids

Acetic acid was dominant amid the acidic compounds detected in the products. Acetic acid mainly came from the elimination of O-acetyl groups originally linked to the xylose unit, as well as the ring scission of uronic acid residues after the elimination of the carbonyl and O-methyl groups (Lv *et al.* 2012). Another chemical pathway to produce acetic acid is the cracking and reforming of the aliphatic side chains of the lignin basic units (Lv *et al.* 2010).

There has hardly been any acetic acid found during cellulose pyrolysis, whether in the case of a micro-pyrolyser or a fluidised bed reactor (Patwardhan *et al.* 2011c). This further illustrated that apart from a small amount of acetic acid coming from lignin pyrolysis, hemicellulose definitely has the greatest contribution to the formation of acetic acid due to its structure characteristics.

Phenols

Different from other types of products, phenols mainly originated from the pyrol-ysis of lignin because lignin is constructed of aromatic rings. Lignin is a heterogeneous polymer consisting of phenylpropanes linked through several ether types (*α*-ether, *β*-ether, *etc.*) and condensed (C-C)-types (*β*-aryl, biphenyl, *β*-*β*, *etc.*) of the linkages. Amongst the phenolic compounds, phenol, guaiacol, 2-methoxy-4-vinyl phenol, syringol, eugenol, isoeugenol, vanillin, methoxyeugenol, and syringaldehyde were found to be the major products.

Phenols were formed because of the cleavage and substitution of alkyl groups, ether links, β-O-4 bonds, and C-C linkages in lignin, along with side chains of aromatic subunits; lignin was dissociated through bond breaking of *α-β* and *β-γ* bond dehydro-genation (Lou *et al.* 2010). It was reported that the formation of phenols is mainly attributed to the dehydration of OH groups in the alkyl side chain of the lignin basic units and the breakage of ether linkages contained in the main chains (Wang *et al.* 2009; Liu *et al.* 2008). The pyrolysis reactions of lignin model dimers indicated that phenolic ether types are easily depolymerised as well (Kawamoto *et al.* 2007).

One of the characteristics of the phenol products is that most of them retained their substitution patterns from the lignin polymer, which can be easily identified by the components from p-H, G-, and S-type lignin moieties. Thus, phenol was obtained from the p-hydroxyphenyl (p-H) lignin unit. Eugenol, 2-methoxy-4-vinyl phenol, isoeugenol, and vanillin came from the guaiacyl (G) lignin unit, while syringol, methoxyeugenol, and syringaldehyde were derived from the syringyl (S) lignin unit. Among them, vanillin was generated as a result of the bond cracking of interlinkage Cα-Cβ of lignin phenylpropane as well as the degradation of ferulic acid. The guaiacol was considered to be formed through the Cβ-O and Cα-Cγ cleavage during pyrolysation (Lou *et al*. 2010).

It was found that the decarboxylation and formation of 2-methoxy-4-vinyl phenol were the initial steps in lignin decomposition (Patwardhan *et al.* 2011b), which is in line with the hypothesis that G-model compounds are the first to experience bond cleavage during pyrolysis (Liu *et al.* 2009).

Hydrocarbons

Paraffins and 1-olefins are formed from the thermal decomposition of WPCs. As shown in Table 2, the degradation of the WPCs results in the formation of alkanes from pentane (C5) up to docosane (C22), and alkenes from 1-pentene (C5=) up to tricosene (C23=), as well as some alkadienes. The hydrocarbons originated from the pyrolysis of polyolefins of WPCs. It is well accepted that HDPE degrades *via* a four-step free radical mechanism: radical initiation by random scission reaction of the polymer chain, depropagation, intermolecular, and intramolecular hydrogen transfer followed by β-scission and, finally, radical termination (AlSalem and Lettieri 2010). It was proposed by Levine and Broadbelt (2009) that polymer pyrolysis usually involves three general reaction pathways, *i.e.* unzipping (UZ), backbiting (BB), and random scission (RS). UZ yields monomers from the polymer chain. BB involves specific intramolecular hydrogen transfer reactions followed by mid-chain β-scission to yield a series of specific low molecular weight products (LMWPs), while RS involves intermolecular hydrogen transfer followed by mid-chain β-scission to yield a diverse array of LMWPs. The analysis of HDPE pyrolysis indicated that the RS pathway was found to be controlling, while the BB pathway played a complementary role. Meanwhile, PW, which decomposed at a lower temperature, could start the radical formation by initiating the scission of the synthetic polymer chain.

The products obtained by the thermal degradation of WPCs consisted of poplar wood and HDPE decomposition products. It is well known fast pyrolysis of biomass around 500～550 °C produces high yields of bio-oil. While the degradation of the HDPE by pyrolysis results in the formation of condensable hydrocarbon oil as high as 625 °C. Accordingly, the produced WPCs wastes may be treated with a fast pyrolysis process, which is optimized by suitably designed temperature, residence time, and other processing conditions, to produce liquid fuel.

It is worth noting that although no olefination reaction happened during the pyrolysis of WPCs, the endogenous polymer degradation provided olefins, which lays the groundwork for subsequent catalytic upgrading of pyrolysis oil. Therefore, strongly acidic catalysts should be prepared and used in further studies to promote on-line olefination reactions during the pyrolysis of WPCs to obtain high-quality pyrolysis oil.

CONCLUSIONS

1. The experimental results showed that temperature played an important role in the yield of hydrocarbon products from WPC pyrolysis. When the temperature was increased from 550 °C to 625 °C, the hydrocarbon yields increased from 25.35% to 64.80%.

2. The WPCs pyrolysis did not produce noticeable cross-reaction products between the PW and HDPE, which implied that thermal degradation of WPCs primarily comprise individual PW and HDPE pyrolytic decompositions. However, thermal degradation of PW has an apparent effect on the decomposition of HDPE. The results indicated that free radicals formed by PW decomposition initiated the scission of polyethylene chains and promoted the formation of light paraffins.

3. Concerning the identified pyrolysis compounds from WPCs, anhydrosugars, especially levoglucosans, mainly originated from the depolymerisation of cellulose. Furans, light aldehydes, and ketones were derived from the decomposition of cellulose, hemicellulose, or their derived anhydrosugars; among them, cyclopentanone and cyclopentenone mainly came from hemicellulose. As the predominant product of carboxylic acids, acetic acid was primarily produced from hemicellulose. Phenols were the dominant products of lignin pyrolysis, while hydrocarbons were obtained from the thermal decomposition of HDPE.

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