Selective Production of Phenolic-rich Bio-oil from Catalytic Fast Pyrolysis of Biomass: Comparison of K_3PO_4, K_2HPO_4, and KH_2PO_4

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Phenolic-rich bio-oil can be selectively produced from catalytic fast pyrolysis of biomass impregnated with K_3PO_4, K_2HPO_4, or KH_2PO_4. In this study, the catalytic effects of the three catalysts on the pyrolytic product distribution were investigated and compared *via* analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments. The results indicated that the three catalysts were all able to inhibit the pyrolytic decomposition of holocellulose to form volatile organic products, while promoting the formation of phenolic compounds from lignin. Hence, phenolic-rich bio-oil could be selectively produced. Among the three catalysts, K_3PO_4 and K_2HPO_4 possessed similar capability to increase the yield of the phenolics, which was better than KH_2PO_4. The phenolic contents among the total pyrolytic products steadily increased as the K_3PO_4 or K_2HPO_4 dosage increased. The maximal peak area of the phenolics reached as high as 68.8% (at 50 wt.% K_3PO_4) or 50.6% (at 50 wt.% K_2HPO_4) of the total peak area. Therefore, based on these results, K_3PO_4 was the best catalyst for the selective production of phenolic-rich bio-oil.

Keywords: Biomass; Phenolic compounds; Catalytic fast pyrolysis; K_3PO_4; K_2HPO_4; KH_2PO_4

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INTRODUCTION

Fast pyrolysis of biomass is a thermal decomposition process, with rapid biomass heating and decomposition followed with quick vapor condensation, to convert solid biomass into liquid bio-oil (Bridgwater 2012; Mohan *et al.* 2006). Chemically, bio-oil is a complex mixture of water and hundreds of organic compounds. There are many valuable chemicals in conventional bio-oils (Demirbas 2006), but most of them are in very low proportions due to the poor pyrolytic selectivity during the conventional fast pyrolysis process. Therefore, to obtain specific bio-oils rich in desired products, it is necessary to selectively control the biomass pyrolysis pathways toward the formation of target products. Currently, various selective pyrolysis techniques have been proposed to produce different value-added chemicals from different biomass components, such as levoglucosenone (Kudo *et al.* 2011; Lu *et al.* 2012; Wang *et al.* 2011) and 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one (Fabbri *et al.* 2007) from cellulose, furfural from holocellulose (Branca *et al.* 2012; Oh *et al.* 2013), and aromatic hydrocarbons from lignin or whole biomass (Carlson *et al.* 2011; Zhang *et al.* 2013).

One of the valuable chemical fractions in bio-oil is the phenolic compounds, which can be used for the synthesis of phenolic resins. Phenolic compounds are mainly derived from lignin (Lou *et al*. 2011); thus, phenolic-rich bio-oil can be produced from fast pyrolysis of lignin or special lignin-rich biomass, such as bark (Ren *et al*. 2013). However, for common biomass materials, the lignin content is much lower than the holocellulose content. Therefore, to selectively produce the phenolic-rich bio-oil, it is essential to enhance the pyrolytic decomposition of lignin to form phenolic compounds while inhibiting the formation of volatile organic compounds from holocellulose. To date, only Bu *et al*. (2012; 2013) have reported a way to selectively produce phenolic-rich bio-oil through microwave-assisted pyrolysis of biomass using activated carbon as the catalyst. With fir wood as the feedstock, the phenolic concentration in the catalytic bio-oil reached as high as 66.9% (relative to the total peak area % detected in the bio-oil by GC/MS) at a catalyst-to-biomass ratio of 3:1. Phenol and 4-methyl phenol were the two most abundant phenolic compounds formed in the catalytic process. Recently, we found another way to selectively produce phenolic-rich bio-oil by catalytic fast pyrolysis of biomass impregnated with K_3PO_4 (Lu *et al*. 2013). With poplar wood as the feedstock, the highest phenolic concentration (peak area % by GC/MS) was over 60% at high K_3PO_4 dosages. Phenol and 2,6-dimethoxyphenol were formed as the two most abundant phenolic compounds.

In this study, K_3PO_4, K_2HPO_4, and KH_2PO_4 were selected as the catalysts for the selective production of phenolic-rich bio-oil. These catalysts were impregnated into poplar wood using the incipient wetness impregnation method, which differed from the K_3PO_4 impregnation method in our previous study (Lu *et al*. 2013). Analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) experiments were conducted to reveal and compare the catalytic effects of the three catalysts on the pyrolytic product distribution.

EXPERIMENTAL

Materials

Poplar wood was used as the feedstock in this study. Prior to experiments, the poplar wood was ground and sieved; particles of 0.2 to 0.3 mm in size were selected and dried prior to pretreatment and further experimentation. The chemical composition of poplar was 49.8% cellulose, 24.4% hemicellulose, 23.3% lignin, 2.2% extractives, and 0.3% inorganic ash. Its elemental composition on a dry basis was 49.58% C, 6.33% H, 0.08% N, 0.09% S, and 43.62% O.

Methods

Pretreatment of poplar wood

The poplar wood was pretreated to impregnate the K_3PO_4, K_2HPO_4, or KH_2PO_4 catalyst using the incipient wetness impregnation method. Aqueous K_3PO_4, K_2HPO_4, or KH_2PO_4 solutions with different concentrations were prepared by dissolving prescribed amounts of K_3PO_4, K_2HPO_4, or KH_2PO_4 into 50 mL of deionized water. Afterwards, each solution was added to 10 g of poplar wood and agitated by ultrasonification for 12 h. The mixture was then dried at 105 °C in air for 4 h and stored in a desiccator prior to experimentation. A total of 18 pretreated poplar wood samples were prepared, six samples for each catalyst. The catalyst dosages (*i.e.*, K_3PO_4, K_2HPO_4, or KH_2PO_4) examined were 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% (on wood).

Analytical Py-GC/MS Experiments

Analytical Py-GC/MS experiments were conducted using the CDS Pyroprobe 5200HP pyrolyzer (Chemical Data Systems; Oxford, PA) connected with a Perkin Elmer GC/MS (Clarus 560; Waltham, MA). Experimental samples (0.30 mg of untreated or a prescribed quantity of pretreated poplar wood) were placed into a quartz pyrolysis tube. Quartz wool was placed at both ends of the tube to prevent the escape of solid wood particles during the fast pyrolysis process. The quantity of the pretreated poplar wood was precisely weighed to be 0.32 mg, 0.33 mg, 0.38 mg, 0.43 mg, 0.50 mg, and 0.60 mg for the samples impregnated with 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, and 50 wt.% catalyst, respectively. Therefore, the polar wood quantity during pyrolysis, excluding the catalyst, remained constant at 0.30 mg for each experimental sample. An analytical balance with a readability of 0.01 mg was used for weighing. A detailed description of the sample preparation procedure has been reported in our previous study (Lu *et al*. 2013).

Pyrolysis was carried out at temperatures from 300 to 700 °C, with the heating rate of 20 °C/s and heating time of 20 s. The pyrolysis vapors were directly analyzed by GC/MS. The GC injector temperature was kept at 300 °C. Chromatographic separation was achieved using an Elite-35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; PerkinElmer; Waltham, MA). Helium (99.999%) was used as the carrier gas with a constant flow rate of 1 mL/min at a 1:80 split ratio. The GC oven was heated from 40 °C (3 min) to 180 °C with a heating rate of 6 °C/min, and then to 280 °C (4 min) with a heating rate of 10 °C/min. The temperature of the GC/MS interface was held at 280 °C, and the mass spectrometer was operated in EI mode at 70 eV. The chromatographic peaks were identified according to the NIST library, Wiley library, and data from previous studies (Dong *et al.* 2012).

For each poplar wood sample, the experiments were replicated three times to confirm the reproducibility of the reported results. The peak area and peak area % values of each pyrolytic product were determined, and the average and standard deviation values were calculated. It is known that the analytical Py-GC/MS technique could not provide direct quantitative analysis of the compounds due to the complexity of the pyrolytic products and the lack of commercially available reference standards. However, the chromatographic peak area of a compound is considered to vary linearly with its quantity, and the peak area % is considered to vary linearly with its concentration. Therefore, for each product, its yield changes can be determined by comparing its average peak area values obtained under different reaction conditions, and the changes to its content among the detected products can be determined by comparing its peak area % values relative to the sum of all the peak area in a chromatogram (Lu *et al.* 2011a). It is noted that biomass fast pyrolysis vapors are composed of permanent gases, water, volatile organic compounds, and non-volatile large molecular compounds. The latter three fractions will be condensed as liquid bio-oil, while the GC/MS is only able to determine the volatile organic compounds.

RESULTS AND DISCUSSION

The non-catalytic analytical fast pyrolysis of poplar wood has been reported in our previous study, with detailed product distribution and formation characteristics (Dong *et al.* 2012). Figure 1a shows the typical ion chromatogram at the pyrolysis temperature of 500 °C. The major pyrolytic products included hydroxyacetaldehyde (HAA), acetic acid (AA), 1-hydroxy-2-propanone (HA), furfural (FF), and levoglucosan (LG), all of which were primarily derived from holocellulose; additionally, various phenolic compounds (*e.g.*, phenol, 2-methoxyphenol, and 2,6-dimethoxyphenol) were detected that were primarily derived from lignin.

The pyrolytic product distribution was significantly altered after the poplar wood was impregnated with the K_3PO_4, K_2HPO_4, or KH_2PO_4 catalyst; typical ion chromatograms are given in Figs. 1b-1d. K_3PO_4 was found to be a promising catalyst for the selective production of phenolic compounds. The major holocellulose-derived products, such as HAA and LG, were significantly decreased or completely eliminated, leaving the HA as the only major holocellulose-derived product when utilizing the K_3PO_4 catalyst. Meanwhile, some lignin-derived phenolic products were remarkably increased and became the dominant catalytic products; these products included phenol, 2-methoxyphenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxyphenol. The results agreed well with our previous study in spite of the different K_3PO_4 impregnation methods (Lu *et al*. 2013). The K_2HPO_4 exhibited similar catalytic effects as K_3PO_4 on the selective production of phenolic compounds; however, KH_2PO_4 was less effective than the other two catalysts. The detailed catalytic effects of the three catalysts and their differences will be presented and discussed in the following sections.

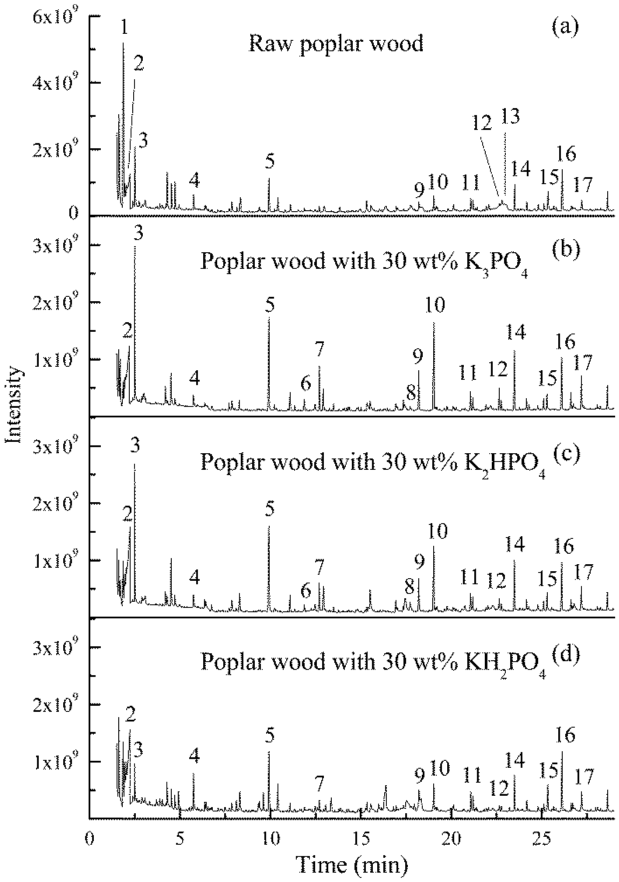

Fig. 1. Typical MS ion chromatograms from fast pyrolysis of raw and pretreated poplar wood: (1) hydroxyacetaldehyde (HAA); (2) acetic acid (AA); (3) 1-hydroxy-2-propanone (HA); (4) furfural (FF); (5) phenol; (6) 2-methylphenol; (7) 2-methoxyphenol; (8) 4-methyl-1,2-benzendiol (9) 2-methoxy-4-vinylphenol; (10) 2,6-dimethoxyphenol; (11) 1,2,4-trimethoxybenzene; (12) 1,2,3-trimethoxy-5-methylbenzene (13) levoglucosan (LG); (14) 3',5'-dimethoxyacetophenone; (15) 3,5-dimethoxy-4-hydroxybenzaldehyde; (16) 4-allyl-2,6-dimethoxyphenol; and (17) 1-(2,4,6-trihydroxyphenyl)-2-pentanone

Effects of Catalyst Impregnation Dosages on the Overall Product Distribution

The pyrolysis vapors emitted from the analytical Py-GC/MS experiments were unable to be collected and quantitatively analyzed. Hence, the distribution (yields and concentrations) of the pyrolytic products could not be quantitatively determined. However, the changes of product yields and concentrations can be estimated by comparing the peak area and peak area % values of the products obtained under different reaction conditions. Figure 2 shows the total peak area values of the total phenolic products and the other products (mainly holocellulose-derived products). Moreover, the pyrolytic products were classified into eight groups, and their peak area % values are presented in Table 1. The eight groups were phenolics, anhydrosugars (*e.g.*, LG), linear aldehydes (*e.g.*, HAA), linear ketones (*e.g.*, HA), linear acids (*e.g.*, AA), furans, cyclopentanones, and others (*e.g.*, hydrocarbons and linear fatty acids). The peak area % sum of the eight groups was less than 100% due to some unidentified chromatographic peaks.

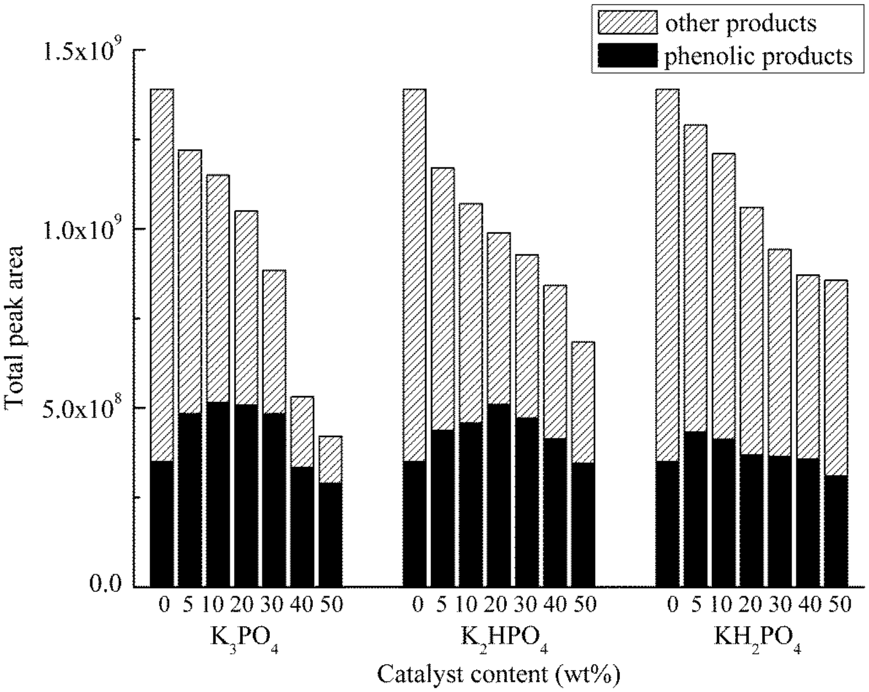

Fig. 2. Total chromatographic peak area values of the phenolic products and the other products for different catalyst dosages employed during pyrolysis performed at 500 °C

According to Figure 2, the peak area values of the total phenolic products, which were proportional to the total phenolic yields, initially increased and then decreased as the catalyst dosage increased. The maximum peak area values of the total phenolic products were obtained with 10 wt.% K_3PO_4, 20 wt.% K_2HPO_4, and 5 wt.% KH_2PO_4, respectively. The three maximum values were 47%, 46%, and 24% higher than the value from the non-catalytic process. The results clearly indicated that the three catalysts were all able to promote the formation of phenolics when properly impregnated into the poplar wood. The K_3PO_4 and K_2HPO_4 catalysts possessed similar capability to increase the yield of phenolics, which was better than the KH_2PO_4 catalyst.

The other pyrolysis products were primarily derived from holocellulose; their total peak area values decreased monotonically as the catalyst dosage increased. This observation clearly suggested that all three catalysts could inhibit the pyrolysis of holocellulose to form volatile organic products. The K_3PO_4 and K_2HPO_4 catalysts performed much better than the KH_2PO_4 catalyst at all dosage levels; K_3PO_4 performed better than K_2HPO_4 at dosages as high as 40 wt.% to 50 wt.%.

Table 1. Peak Area % Values of the Eight Product Groups at Different Catalyst Dosages Employed during Pyrolysis Performed at 500 °C

Catalyst		Catalyst Dosage						
		0%	5%	10%	20%	30%	40%	50%
Phenolics	K_3PO_4	25.1	39.7	44.6	48.8	54.7	63.0	68.8
	K_2HPO_4		37.7	42.5	51.5	51.0	49.3	50.6
	KH_2PO_4		33.0	34.0	35.1	39.3	41.0	36.5
Anhydrosugars	K_3PO_4	10.2	2.2	1.0	0	0	0	0
	K_2HPO_4		1.9	1.3	0.6	0	0	0
	KH_2PO_4		5.2	5.3	5.2	4.5	3.9	5.3
Linear aldehydes	K_3PO_4	17.0	10.7	7.5	2.8	1.7	2.1	2.1
	K_2HPO_4		11.4	9.6	2.0	2.4	1.7	1.3
	KH_2PO_4		13.1	12.7	5.2	4.0	2.4	2.6
Linear ketones	K_3PO_4	8.5	11.8	12.6	13.4	13.8	16.5	14.1
	K_2HPO_4		10.6	10.2	10.4	10.7	11.1	10.8
	KH_2PO_4		7.2	6.1	5.2	5.0	5.1	5.1
Linear acids	K_3PO_4	13.5	13.2	14.0	16.6	13.3	5.1	2.6
	K_2HPO_4		14.3	15.1	16.2	17.5	20.3	20.8
	KH_2PO_4		14.2	15.1	17.6	17.6	18.7	19.2
Furans	K_3PO_4	6.2	4.5	3.7	3.3	2.6	2.8	2.5
	K_2HPO_4		5.1	4.2	3.7	3.5	3.8	3.9
	KH_2PO_4		7.1	7.9	10.2	10.1	10.6	12.7
Cyclopentanones	K_3PO_4	3.6	4.3	3.9	4.0	3.8	4.7	4.6
	K_2HPO_4		4.5	4.2	4.1	3.5	3.6	3.7
	KH_2PO_4		4.6	4.1	4.8	4.2	4.0	4.4
Others	K_3PO_4	6.1	4.4	3.9	3.2	3.1	2.5	3.4
	K_2HPO_4		5.3	4.2	3.9	4.2	3.2	2.3
	KH_2PO_4		5.7	6.3	6.9	7.2	7.2	7.2

According to Table 1, as the K_3PO_4 dosage increased, the peak area values of the phenolics group, which was proportional to the total phenolics contents, steadily increased, reaching as high as 68.8% at 50 wt.% K_3PO_4. At the same time, the peak area % values of the anhydrosugars, linear aldehydes, linear acids, and furans steadily decreased as the K_3PO_4 dosage increased. Similar trends were observed for the K_2HPO_4 catalysis, except for the linear acids group. The peak area values of the linear acids group significantly decreased at high K_3PO_4 dosages (40 wt.% and 50 wt.%), but increased at high K_2HPO_4 dosages. The highest phenolics peak area % value (50.6%) was obtained when 50 wt.% K_2HPO_4 was used. As the KH_2PO_4 dosage increased, the peak area values of the anhydrosugars, linear ketones, and furans all changed differently from those of K_3PO_4 and K_2HPO_4. The highest phenolics peak area % value (41%) was observed when 40 wt.% KH_2PO_4 was used.

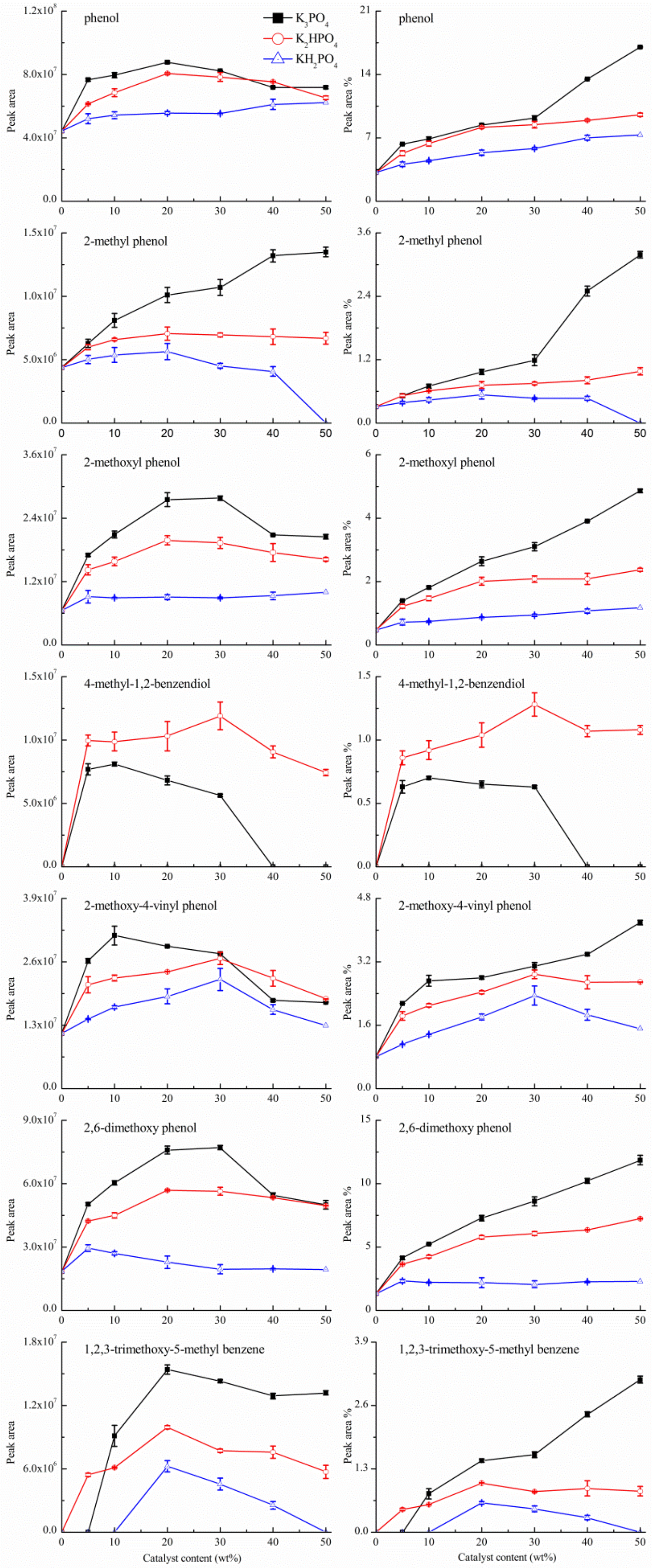

Fig. 3. The effects of the catalyst impregnation dosages on the peak area and peak area % values of major phenolic products of pyrolysis performed at 500 °C

Effects of Catalyst Impregnation Dosages on the Phenolic Products

Various phenolic products were formed during the fast pyrolysis process. They changed differently as the catalyst dosage increased. For most of the phenolic products, their peak area values, which were proportional to their yields, initially increased and then decreased as the catalyst dosage increased. Figure 3 shows the effects of the catalyst impregnation dosages on seven major phenolic products: phenol, 2-methyl phenol, 2-methoxyphenol, 4-methyl-1,2-benzendiol, 2-methoxy-4-vinylphenol, 2,6-dimethoxyphenol, and 1,2,3-trimethoxy-5-methylbenzene.

The peak area % values for most phenols steadily increased as the K_3PO_4 dosage increased, except for 4-methyl-1,2-benzendiol. Similar trends were also observed for the K_2HPO_4 catalysis; however, K_2HPO_4 was less effective than K_3PO_4 in causing an increase the peak area % of these phenolic products, with the exception of 4-methyl-1,2-benzendiol. Phenol, 2,6-dimethoxyphenol, 2-methoxyphenol, and 2-methoxy-4-vinylphenol were formed in relatively high contents. Their highest peak area % values with the K_3PO_4 catalysis were as high as 17.0%, 11.9%, 4.9%, and 4.2%, respectively, compared with 9.5%, 7.2%, 2.4%, and 2.4%, respectively, with the K_2HPO_4 catalysis, and only 3.2%, 1.3%, 0.5%, and 0.5%, respectively, with the control (no catalyst).

Effects of Catalyst Impregnation Dosages on the Other Pyrolysis Products

The other pyrolysis products, including anhydrosugars, furans, linear carbonyls, and linear acids, were primarily derived from holocellulose. Generally, these holocellulose-derived products were significantly inhibited in the presence of the catalysts. Figure 4 shows the effects of the catalyst impregnation dosages on the major holocellulose-derived products, including LG, FF, HAA, HA, and AA.

The anhydrosugar products were primarily derived from the pyrolytic depolymerization of the holocellulose; LG was the predominant product formed during the non-catalytic process (Lu *et al.* 2011b; Shen and Gu 2009). In the presence of catalyst, the LG decreased very rapidly and finally disappeared at 20 wt.% K_3PO_4, 30 wt.% K_2HPO_4, or 40 wt.% KH_2PO_4. This observation indicated that K_3PO_4 was the most effective catalyst to inhibit the LG formation. The results agreed well with previous studies that the formation of LG would be easily inhibited in the presence of various metal salts (Lu *et al*. 2011a; Patwardhan *et al.* 2010). Moreover, the other anhydrosugar products, primarily 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one, 1,5-anhydro-4-deoxy-D-glycerohex-1-en-3-ulose, and 1,4:3,6-dianhydro-α-D-glucopyranose, were also completely inhibited at 20 wt.% K_3PO_4 or 30 wt.% K_2HPO_4. However, these products were still formed when the KH_2PO_4 catalyst was used. With respect to the furan products, most of them were inhibited when K_3PO_4 and K_2HPO_4 were used, whereas some were promoted when KH_2PO_4 was used (*e.g.*, FF in Fig. 4).

Based on work reported earlier, the linear carbonyl products were primarily derived from the pyrolytic ring scission of the holocellulose, and the HAA and HA were the most abundant linear aldehyde and ketone products (Lu *et al*. 2011b). All three catalysts significantly inhibited HAA formation; nevertheless, they displayed different effects on HA formation. When K_3PO_4 or K_2HPO_4 were used, the peak area values of HA initially increased at the 5 wt.% catalyst dosage and afterwards decreased at higher catalyst dosages. The peak area % value of HA reached as high as 10.0% or 7.6% at 40 wt.% K_3PO_4 or K_2HPO_4, respectively, *versus* 6.2% for the control (no catalyst). When KH_2PO_4 was used, the peak area and peak area % values of HA gradually decreased as the catalyst dosage increased, with a peak area % value of only 2.0% at 50 wt.% KH_2PO_4.

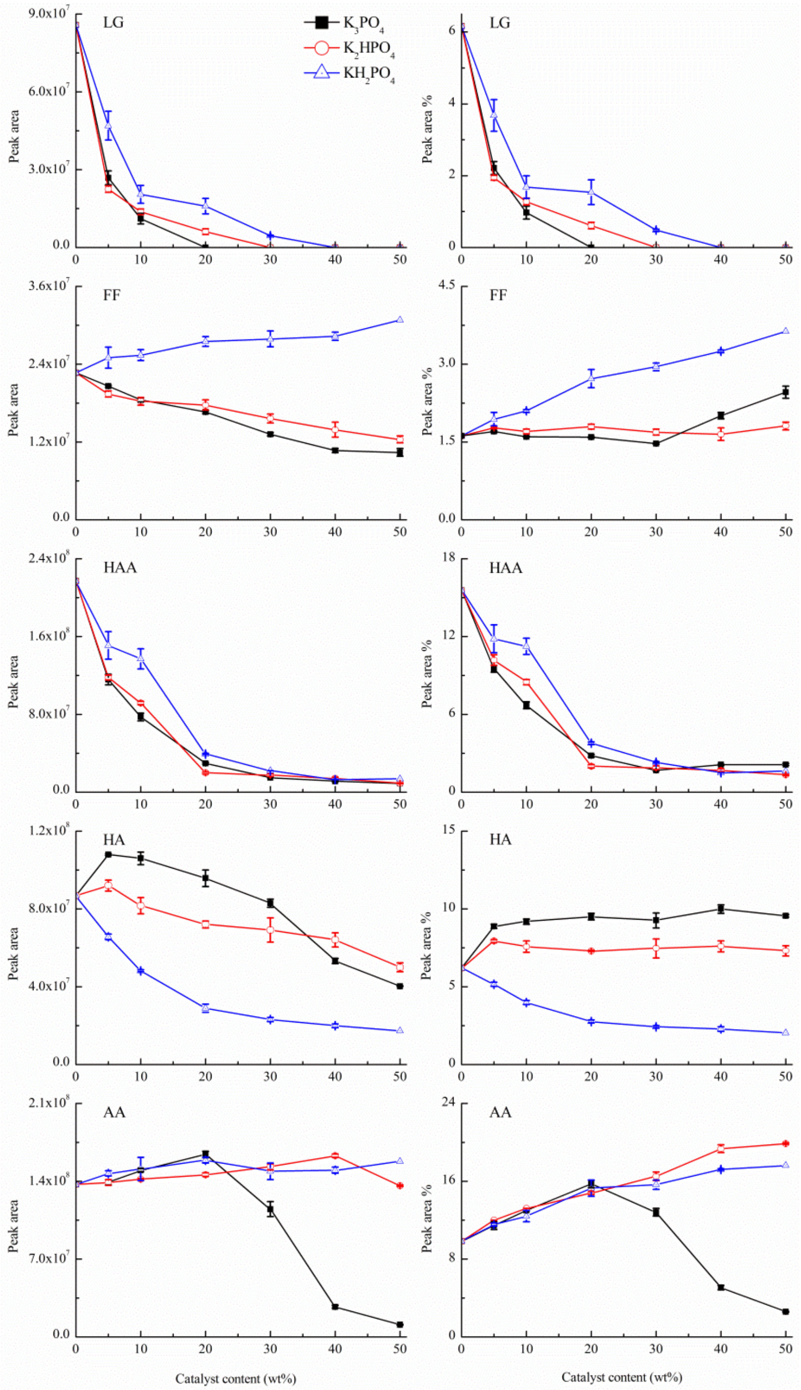

Fig. 4. The effects of the catalyst impregnation dosages on the peak area and peak area % values of major holocellulose-derived products at pyrolysis temperature of 500 °C

AA was the major linear acid product, primarily derived from the deacetylation of the hemicelluloses (Dong *et al*. 2012; Patwardhan *et al.* 2011). The peak area values of AA were not greatly affected when K_2HPO_4 or KH_2PO_4 were used, but decreased greatly when high K_3PO_4 dosages were used. Based on the above results, it is seen that there were two major holocellulose-derived products (HA and AA) at high K_2HPO_4 dosages, while only one major product (HA) at high K_3PO_4 dosages. This was the basic difference in the catalytic effects of K_3PO_4 *versus* K_2HPO_4.

Effects of Catalytic Temperatures on the Product Distribution

Catalytic temperature was another important factor that affected the pyrolytic product distribution. Figure 5 shows the total peak area values of the phenolic products and the other products at pyrolysis temperatures of 300 to 700 °C with 30 wt.% K_3PO_4 or K_2HPO_4. According to Fig. 5, as the catalytic pyrolysis temperature increased, the total phenolics peak area values initially increased and afterward decreased, with the maximal values obtained at 500 °C for both catalysts. Moreover, the peak area % values of the total phenolics from 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C were 50.3%, 53.0%, 54.7%, 50.3%, and 48.7% with 30 wt.% K_3PO_4, and 50.0%, 51.6%, 51.0%, 50.5%, and 49.4% with 30 wt.% K_2HPO_4. The results indicated that the best pyrolysis temperature for high phenolic yields was 500 °C, while the phenolic contents among the pyrolytic products were not greatly affected by the pyrolysis temperatures.

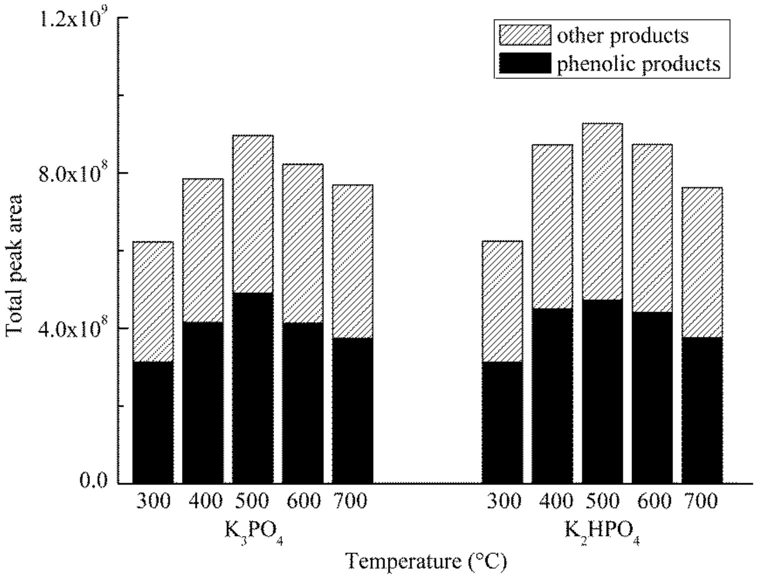

Fig. 5. Total chromatographic peak area values of the phenolic products and the other products at different pyrolysis temperatures of the poplar wood with 30 wt.% K_3PO_4 or K_2HPO_4

Comparison of the Three Catalysts

The catalytic capability of the three catalysts was compared based on the above results. Generally, the phenolic products' yield (based on the peak area results) significantly increased when the proper dosage of K_3PO_4 or K_2HPO_4 was used, but this was not true with KH_2PO_4. The highest phenolics yields from the K_3PO_4 and K_2HPO_4 processes were similar, indicating that the two catalysts possessed similar capability to promote the phenolics formation. Moreover, the relative contents of the phenolics (based on the peak area % results) could be monotonically increased as the K_3PO_4 or K_2HPO_4 dosage increased, with similar results at catalyst dosages lower than 30 wt.%. However, at the catalyst dosages of 40 wt.% and 50 wt.%, the relative content of the phenolics from the K_3PO_4 catalysis was higher than that from the K_2HPO_4 catalysis, because K_3PO_4 was more capable than K_2HPO_4 to inhibit the formation of linear acids at high catalyst dosages. As a result, the peak area % values of the phenolics reached as high as 68.8% at 50 wt.% K_3PO_4, but only 50.6% at 50 wt.% K_2HPO_4. Therefore, K_3PO_4 was judged to be the best catalyst for the selective production of phenolic compounds.

The catalytic performance of KH_2PO_4 differed greatly from those of K_3PO_4 and K_2HPO_4. This can be attributed to the different nature of the three catalysts, as K_3PO_4 and K_2HPO_4 are alkaline catalysts, while KH_2PO_4 is an acid catalyst. Furthermore, K_3PO_4 and K_2HPO_4 exhibited similar catalytic capabilities on most of the pyrolytic products, except for the linear acid products at high catalyst dosages. This might be due to the different alkalinities of K_3PO_4 and K_2HPO_4. The relative strong alkalinity of K_3PO_4 might be able to inhibit the formation of acid products or to convert the acid products after their formation. The detailed mechanisms involved in the catalytic fast pyrolysis process could not be ascertained in this study. Further studies are required to reveal how the three catalysts affected the pyrolytic pathways to form different catalytic products, especially for the phenolic products formed from the cleavage of the phenylpropane lignin units.

Finally, it is noted that although the Py-GC/MS experiment is a powerful tool for the primary catalyst evaluation and selection, it is unable to quantitatively determine the pyrolytic products. Hence, further studies are in progress by using a lab-scale fast pyrolysis set to confirm the above catalytic effects and to collect and analyze the pyrolytic products.

CONCLUSIONS

1. Fast pyrolysis of poplar wood impregnated with K_3PO_4, K_2HPO_4, or KH_2PO_4 inhibited the pyrolytic decomposition of holocellulose to form volatile organic compounds (*e.g.*, HAA, LG), while promoting the decomposition of lignin to form several phenolic compounds (*e.g.*, phenol, 2,6-dimethoxyphenol).
2. The best catalyst for the selective production of the phenolic compounds was K_3PO_4; K_2HPO_4 was also a promising catalyst, while KH_2PO_4 was the least effective catalyst examined.
3. Increasing the dosage of K_3PO_4 or K_2HPO_4 initially increased and afterwards decreased the yield of phenolic products. The maximal phenolics peak area % was 68.8% with 50 wt.% K_3PO_4 or 50.6% with 50 wt.% K_2HPO_4.
4. As the catalytic pyrolysis temperature increased, the phenolic products' yield initially increased and then decreased; the maximal yield was obtained at 500 °C.

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REFERENCES CITED

Branca, C., Di Blasi, C., and Galgano, A. (2012). "Catalyst screening for the production of furfural from corncob pyrolysis," *Energ. Fuel* 26(3), 1520-1530.

Bridgwater, A. V. (2012). "Review of fast pyrolysis of biomass and product upgrading," *Biomass Bioenerg.* 38, 68-94.

Bu, Q., Lei, H., Ren, S., Wang, L., Zhang, Q., Tang, J., and Ruan, R. (2012). "Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass," *Bioresource Technol.* 108, 274-279.

Bu, Q., Lei, H., Wang, L., Wei, Y., Zhu, L., Liu, Y., Liang, J., and Tang, J. (2013). "Renewable phenols production by catalytic microwave pyrolysis of Douglas fir sawdust pellets with activated carbon catalysts," *Bioresource Technol.* 142, 546-552.

Carlson, T. R., Cheng, Y. T., Jae, J., and Huber, G. W. (2011). "Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust," *Energ. Environ. Sci.* 4(1), 145-161.

Demirbas, M. F. (2006). "Current technologies for biomass conversion into chemicals and fuels," *Energ. Source Part A* 28(13), 1181-1188.

Dong, C. Q., Zhang, Z. F., Lu, Q., and Yang, Y. P. (2012). "Characteristics and mechanism study of analytical fast pyrolysis of poplar wood," *Energ. Convers. Manage.* 57, 49-59.

Fabbri, D., Torri, C., and Mancini, I. (2007). "Pyrolysis of cellulose catalysed by nanopowder metal oxides: Production and characterisation of a chiral hydroxylactone and its role as building block," *Green Chem.* 9(12), 1374-1379.

Kudo, S., Zhou, Z., Norinaga, K., and Hayashi, J. I. (2011). "Efficient levoglucosenone production by catalytic pyrolysis of cellulose mixed with ionic liquid," *Green Chem.* 13(11), 3306-3311.

Lu, Q., Dong, C. Q., Zhang, X. M., Tian, H. Y., Yang, Y. P., and Zhu, X. F. (2011a). "Selective fast pyrolysis of biomass impregnated with $ZnCl_2$ to produce furfural: Analytical Py-GC/MS study," *J. Anal. Appl. Pyrol.* 90(2), 204-212.

Lu, Q., Yang, X. C., Dong, C. Q., Zhang, Z. F., Zhang, X. M., and Zhu, X. F. (2011b). "Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: Analytical Py-GC/MS study," *J. Anal. Appl. Pyrol.* 92(2), 430-438.

Lu, Q., Zhang, X. M., Zhang, Z. B., Zhang, Y., Zhu, X. F., and Dong, C. Q. (2012). "Catalytic fast pyrolysis of cellulose mixed with sulfated titania to produce levoglucosenone: Analytical Py-GC/MS study," *BioResources* 7(3), 2820-2834.

Lu, Q., Zhang, Z. B., Yang, X. C., Dong, C. Q., and Zhu, X. F. (2013). "Catalytic fast pyrolysis of biomass impregnated with K_3PO_4 to produce phenolic compounds: Analytical Py-GC/MS study," *J. Anal. Appl. Pyrol.* 104, 139-145.

Lou, R., Wu, S. B., and Lv, G. J. (2011). "Fast pyrolysis of enzymatic/mild acidolysis lignin from moso bamboo," *BioResources* 5(2), 827-837.

Mohan, D., Pittman, C. U., and Steele, P. H. (2006). "Pyrolysis of wood/biomass for bio-oil: a critical review," *Energ. Fuel* 20(3), 848-889.

Oh, S. J., Jung, S. H., and Kim, J. S. (2013). "Co-production of furfural and acetic acid from corncob using $ZnCl_2$ through fast pyrolysis in a fluidized bed reactor," *Bioresource Technol.* 144, 172-178.

Patwardhan, P. R., Brown, R. C., and Shanks, B. H. (2011). "Product distribution from the fast pyrolysis of hemicellulose," *ChemSusChem* 4(5), 636-643.

Patwardhan, P. R., Satrio, J. A., Brown, R. C., and Shanks, B. H. (2010). "Influence of inorganic salts on the primary pyrolysis products of cellulose," *Bioresource Technol.* 101(12), 4646-4655.

Ren, X., Gou, J., Wang, W., Li, Q., Chang, J., and Li, B. (2013). "Optimization of bark fast pyrolysis for the production of phenol-rich bio-oil," *BioResources* 8(4), 6481-6492.

Shen, D., and Gu, S. (2009). "The mechanism for thermal decomposition of cellulose and its main products," *Bioresource Technol.* 100(24), 6496-6504.

Wang, Z., Lu, Q., Zhu, X. F., and Zhang, Y. (2011). "Catalytic fast pyrolysis of cellulose to prepare levoglucosenone using sulfated zirconia," *ChemSusChem* 4(1), 79-84.

Zhang, H., Xiao, R., Jin, B., Xiao, G., and Chen, R. (2013). "Biomass catalytic pyrolysis to produce olefins and aromatics with a physically mixed catalyst," *Bioresource Technol.* 140, 256-262.

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