

Selective Production of Aromatic Aldehydes from Heavy Fraction of Bio-oil via Catalytic Oxidation

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High value-added aromatic aldehydes (e.g. vanillin and syringaldehyde) were produced from heavy fraction of bio-oil (HFBO) via catalytic oxidation. The concept is based on the use of metalloporphyrin as catalyst and hydrogen peroxide (H_2O_2) as oxidant under alkaline condition. The biomimetic catalyst cobalt(II)-sulfonated tetraphenylporphyrin (Co(TPPS₄)) was prepared and characterized. It exhibited relative high activity in the catalytic oxidation of HFBO. 4.57 wt % vanillin and 1.58 wt % syringaldehyde were obtained from catalytic oxidation of HFBO, compared to 2.6 wt % vanillin and 0.86 wt % syringaldehyde without Co(TPPS₄). Moreover, a possible mechanism of HFBO oxidation using Co(TPPS₄)/ H_2O_2 was proposed by the research of model compounds. The results showed that this is a promising and environmentally friendly method for production of aromatic aldehydes from HFBO under Co(TPPS₄)/ H_2O_2 system.

Key Words : Heavy fraction of bio-oil, Aromatic aldehydes, Catalytic oxidation, Metalloporphyrins

Introduction

With the declining of crude oil resources, the development of bio-oil from biomass fast pyrolysis has attracted much attention. Usually, the bio-oil has high oxygen content, which results in low heating value and low stability over time.¹ Upgrading is desirable to remove the oxygen in bio-oil and this way makes the upgraded bio-oil resemble crude oil. Recently, a lot of work has been reported on bio-oil upgrading, including hydrogenation,² catalytic pyrolysis,³ emulsion,⁴ catalytic esterification,⁵ and molecular distillation.⁶ These catalytic processes for bio-oil upgrading face the problem that heavy fraction of bio-oil (HFBO, e.g. polymerization of aromatic compounds) is deposited on the catalyst, which blocks the catalytic bed and makes catalyst deactivation. Consequently, the research concerning the catalytic transformation of bio-oil is limited to the study of model compounds of the bio-oil or to the aqueous fraction (which has a lower amount of aromatic compounds).⁷

Bio-oil can be separated into three parts, including low-boiling fraction (low-boiling organic acids, alcohols, ketones, etc.), crude saccharide (mainly levoglucosan), and heavy fraction (guaiacol, 2-methoxy-4-methylphenol, etc.).⁸ According to the special properties of these separated three parts, respectively, the further upgrading will be more reasonable and effective. For example, low-boiling fraction can be used to form gasoline like products by hydrodeoxygenation,^{1,9} decarboxylation or decarbonylation.¹⁰ Levoglucosan can be obtained by separation and purification of crude saccharide, and it is a kind of expensive chemical product. Moreover, the levoglucosan has great potential for the production of bio-ethanol.¹¹ There are a lot of aromatic compounds in the HFBO,¹² and these aromatic compounds may block the

catalytic bed and make catalyst deactivation, but these aromatic compounds may be a source for the production of high value-added aromatic aldehydes (e.g. vanillin (4-hydroxy-3-methoxybenzaldehyde) and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde)). Aromatic aldehydes could be useful as chemical precursor for pharmaceutical and agrochemical industries.¹³ For example, vanillin has been greatly used as food flavor agent, perfumery additive, antifoaming agent, as well as antioxidant additive.¹⁴⁻¹⁶

Metalloporphyrins are well-known to be engaged in selective oxidation of hydrocarbons (e.g. alkene oxidation to form epoxides, alkanes to form aldehydes or alcohols).¹⁷⁻¹⁹ As selective oxidation catalysts, metalloporphyrins were also found to be capable of performing the oxidation of lignin and lignin model compounds.²⁰⁻²³ It is well known that HFBO was mainly produced from fast pyrolysis of lignin.⁷ Thus, metalloporphyrins have potential application in HFBO for aromatic aldehydes production. In this study, HFBO was obtained from bio-oil by separation, and we proposed the conversion of HFBO to produce valuable aromatic aldehydes by an environmentally friendly method, metalloporphyrins/hydrogen peroxide (H_2O_2) system catalytic oxidation.

Experimental

Feedstocks. Bio-oil was supplied by Guangzhou Devotion Thermal Energy Technology Co., Ltd, which is one of the most advanced companies on biomass energy in China. The compositions of bio-oil were as follows: C 53.00%, H 7.01%, N 0.20%, S 0.08%, ash 0.24% and water 20%, respectively. 4-Ethylguaiacol (4-ethyl-2-methoxy-phenol) and ferulic acid (3-Methoxy-4-hydroxycinnamic acid) were purchased from Aladdin. Ethyl acetate was chromatographically pure. The

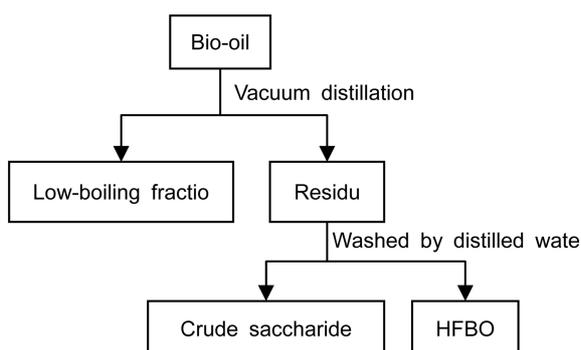


Figure 1. Separation process of HFBO.

other chemical reagents and solvents were analytically pure and used without further treatment.

HFBO Preparation and Analysis. HFBO was obtained according to the following procedures, as shown in Figure 1. Firstly, the low-boiling fraction was distilled out from bio-oil by reduced pressure distillation (T, 60 °C; vacuum degree, 0.03 MPa). Secondly, the residue was washed with distilled water to remove saccharide.¹⁰ Finally, the washed residue was dried to obtain a dark brown powder (HFBO).

The chemical compositions of HFBO were detected by Gas Chromatography-Mass Spectrometer (GC-MS). Identification of the compounds was carried out by comparing the mass spectrum obtained with those contained in the system's database (NIST08). The elemental analysis was determined by an Elementer Vario EL III. Ash was determined according to ASTM D 1102-84. Gel permeation chromatography (GPC) analysis was performed to examine the molecular weight distribution of HFBO by an Agilent 1100 SERIES GPC instrument, using tetrahydrofuran as the eluant at a flow rate of 1 mL/min. Polystyrene standards were used for calibration.

Experimental Setup. In a typical experiment, 0.1 g of HFBO was dissolved in 10 mL of alkaline solution (NaOH, 1 mol/L), along with 0.01 g of cobalt(II)-sulfonated tetraphenylporphyrin (Co(TPPS₄)), 0.5 mL of H₂O₂ solution (30%, v/v) were in pressure bomb (Yantai Chung Ling Chemical Equipment Co., Ltd., China). This bomb consists of a stainless steel body with a PTFE (Polytetrafluoroethylene) sample cup in it. The volume of the PTFE cup is 50 mL. After reaction, the liquid sample was acidified to a pH of 2-3 with a hydrogen chloride solution (15%, v/v). The resulting products were extracted with ethyl acetate (20 mL × 4) at room temperature. Anhydrous magnesium sulfate was also added to the ethyl acetate solution to remove the residual water. After filtration, the ethyl acetate solution was evaporated under reduced pressure at 50 °C and diluted to the known volume. Finally, the qualitative and quantitative analysis of extract products was performed by GC-MS. Standard solution of syringaldehyde in ethyl acetate was used for calibration. The yield of syringaldehyde was determined by the external standard method. The yields of other products were determined by the internal standard method, with a known quantity of syringaldehyde as the internal

standard. The yields of vanillin and syringaldehyde (Y%) are calculated by following equation, W_{product} is the weight of each product and W_{HFBO} is the weight of HFBO.

$$Y\% = \frac{W_{\text{product}}}{W_{\text{HFBO}}} \times 100\%$$

Catalyst Stability. Because of catalyst Co(TPPS₄) dissolving in water phase, the reaction liquid after extraction was filtered to remove residue, and then dried to obtain the catalyst for the next reaction. The catalyst was reused five successive times under the same condition. The reaction liquid after extraction and filtration was detected by UV spectrometer.

Results and Discussion

HFBO Analysis. After separation, the yield of HFBO was about 59 wt % of bio-oil. The compositions of HFBO were as follows: C 62.99%, H 6.49%, N 0.54%, S 0.26% and ash 0.50%, respectively. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) were 557.6 g/mol and 1394 g/mol, respectively, which could confirmed the existence of the oligomer. The GC-MS spectrum reveals that HFBO contained a lot of compounds, and most of which

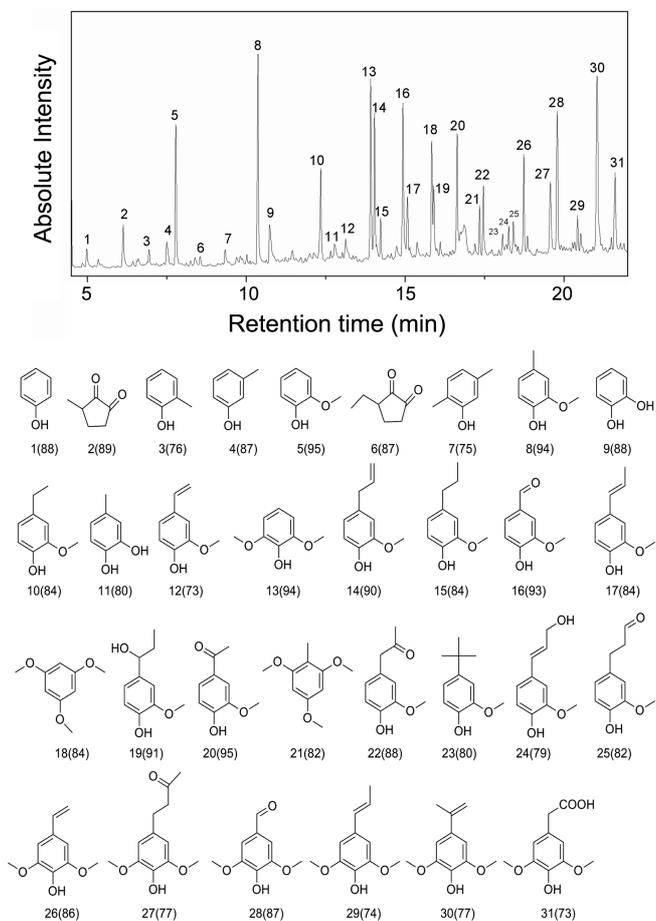


Figure 2. GC-MS spectrum of HFBO and chemical structural formulas detected by GC-MS.^a Values in parentheses indicate similarities (%).

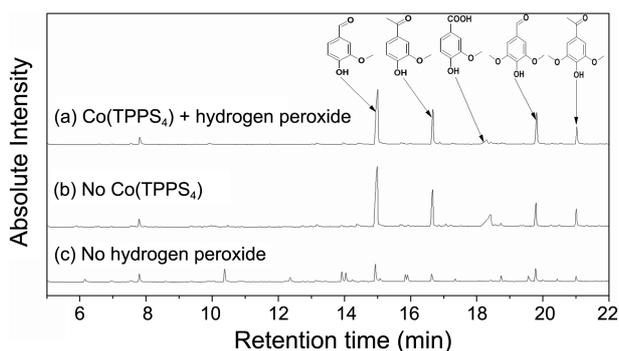


Figure 3. GC-MS spectrum of blank test product comparisons (0.1 g HFBO, 10 mL NaOH solution, reaction temperature 150 °C, reaction time 120 min).

were aromatic compounds, as shown in Figure 2.

Catalytic Oxidation of HFBO to Produce Aromatic Aldehydes. The solvent system was primarily selected because HFBO and Co(TPPS₄) were completely soluble in alkaline medium, making it possible to perform oxidation experiments in homogeneous phase. According to the analysis of the extracted liquor products by GC-MS, the main products were all aromatic compounds, they were vanillin, acetovanillone (4-hydroxy-3-methoxyacetophenone), vanillic acid (4-hydroxy-3-methoxybenzoic acid), syringaldehyde, and acetosyringone (2,6-dimethoxy-4-acetylphenol), as shown in Figure 3(a). In this study, vanillin and syringaldehyde were selected to determine the effects of reaction condition.

The reaction temperature was observed as an important factor for the aromatic aldehydes yields. The reaction temperature ranged from 140 to 180 °C in this work. The effect of reaction temperature on yields of aromatic compounds is shown in Figure 4. The maximum yields of vanillin and syringaldehyde were 4.36 wt % and 1.56 wt % at 150 °C, respectively. Moreover, the maximum total yield of aromatic compounds was 8.86 wt % at 150 °C. The increase in total yield of aromatic compounds from 140 to 150 °C could indicate that the catalytic oxidation was promoted at a higher temperature to overcome the activation energy for the reaction, while the subsequent decrease in the yields of vanillin, acetovanillone, syringaldehyde, and acetovanillone from 150 to 180 °C might be caused by polymerization of some aromatic compounds in HFBO. It was worth noting that the yield of vanillic acid still increased from 150 to 160 °C, which indicated that vanillin was prone to oxidation to produce vanillic acid at a higher temperature. So, high temperature (above 150 °C) would result in excessive oxidation, which is one of the reasons for the decrease of vanillin yield. Thus, considering the yield of the main products, we conclude that 150 °C is the optimal temperature for the catalytic oxidation process of HFBO.

The influence of reaction time on yields of aromatic compounds was investigated at 150 °C. As shown in Figure 5, the maximum yields of vanillin and syringaldehyde were 4.57 wt % and 1.58 wt %, respectively, after 120 min of the catalytic process. The maximum total yield of aromatic

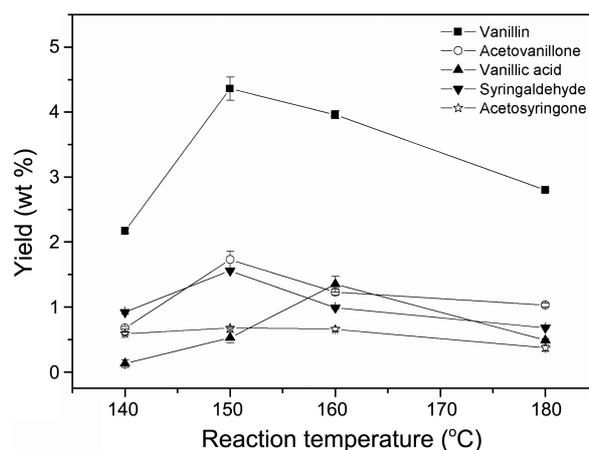


Figure 4. Effect of reaction temperature on aromatic compounds yields (0.1 g HFBO, 0.01 g Co(TPPS₄), 0.5 mL H₂O₂, 10 mL NaOH solution, reaction time 180 min).

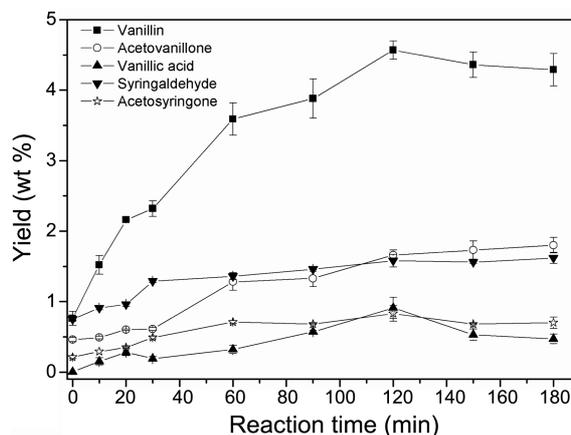


Figure 5. Effect of reaction time on aromatic compounds yields (0.1 g HFBO, 0.01 g Co(TPPS₄), 0.5 mL H₂O₂, 10 mL NaOH solution, reaction temperature 150 °C).

compounds was also obtained at a reaction time of 120 min, with a yield of 9.55 wt %. As reaction time increased, HFBO was probably depolymerized during oxidation, forming aldehydes, acids, and other products. However, too long reaction time would promote polymerization of HFBO derived products, which results in low yield of the main products. The quantity of aromatic compounds accumulated during the reaction and there was a balance between formation and consumption of the aromatic compounds. Thus, the reaction time is critical for the catalytic process. 120 min would be a desirable reaction time for the catalytic oxidation process of HFBO at 150 °C.

As shown in Figure 3 and Figure 6, comparing the results obtained at 150 °C with or without catalyst, it is clear that Co(TPPS₄) catalyst had significant effects on the yields of vanillin and syringaldehyde. With the addition of Co(TPPS₄), the yields of vanillin and syringaldehyde increased from 2.6 to 4.57 wt % and from 0.86 to 1.58 wt %, respectively. At the same time, the yield of vanillic acid decreased from 1.41 to 0.91 wt %. The results clearly show that deep oxidation of

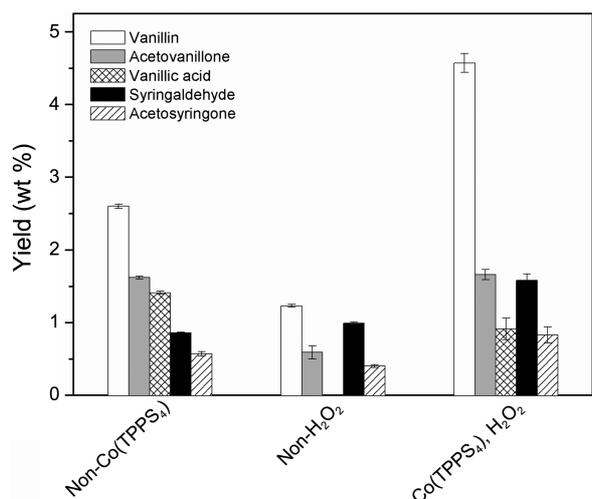


Figure 6. Yields of blank test aromatic compounds comparisons (0.1 g HFBO, 10 mL NaOH solution, reaction temperature 150 °C, reaction time 120 min).

HFBO was restrained and the selectivity of vanillin and syringaldehyde was improved when Co(TPPS₄) was added. Depth of oxidation inhibition may be manifested in two aspects, one was restrained the cleavage of large π bond of aromatic ring, the other one was restrained the production of vanillic acid.

Comparing the results with or without H₂O₂, it is clear that H₂O₂ was effective in the catalytic process of HFBO. With the addition of H₂O₂, the yields of vanillin and syringaldehyde increased from 1.23 to 4.57 wt % and from 0.99 to 1.58 wt %, respectively. Moreover, the residue which can't be extracted with ethyl acetate was decreased, the yield of residue decreased from 52.3% to 24.7%. The M_w of residue was 13340 g/mol which was much higher than the M_w of HFBO (1394 g/mol). The results indicate that polymerization of many aromatic compounds in HFBO happened when H₂O₂ was not added. After adding H₂O₂, monomeric aromatic compounds were apt to form aromatic aldehyde, meanwhile, the bonds of oligomer in HFBO were easy to rupture to produce monomeric aromatic compounds, and then to form aromatic aldehydes.

Catalyst Stability During Catalytic Oxidation of HFBO.

The reusability or recyclability of the catalyst is very important. The repetitive use of the catalyst Co(TPPS₄) was performed to test its stability. Figure 7 shows the yields of vanillin, acetovanillone, vanillic acid, syringaldehyde, and acetosyringone in the recycling experiments. The yield of vanillin was decreased slightly for the 5 successive catalyst reuses. However, no obvious change in the yields of acetovanillone, vanillic acid, syringaldehyde, and acetosyringone was shown for the 5 successive catalyst reuses. Moreover, the UV spectrum of the fresh and the recovered Co(TPPS₄) were compared, and the results showed that there was no obvious change for the main peaks, suggesting that few change of the catalyst occurred after the reactions.

Possible Reaction Mechanism During Catalytic Oxidation of HFBO. According to the composition analysis of

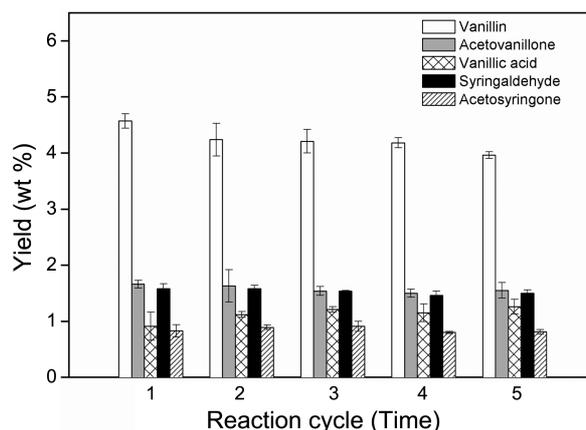


Figure 7. Yields of aromatic compounds when catalyst was reused five successive times (0.1 g HFBO, 0.01 g Co(TPPS₄), 0.5 mL H₂O₂, 10 mL NaOH solution, reaction temperature 150 °C, reaction time 120 min).

HFBO, aromatic compounds in HFBO could be separated into two types, which were unsaturated side chain of aromatic compounds (e.g. 12, 14, 17, 19, 22, 24, 26, 29, 30 in Figure 2) and saturated side chain of aromatic compounds (e.g. 3, 4, 7, 8, 10, 11, 15, 21, 23 in Figure 2 and larger (≥ 2 rings) aromatic compounds). In order to research the reaction mechanism of catalytic oxidation in Co(TPPS₄)/H₂O₂ system, 4-ethylguaiaicol and ferulic acid were chosen as saturated and unsaturated side chain of aromatic compounds model compounds, respectively. 4-ethylguaiaicol almost didn't react, only few vanillin was found, as shown in Figure 8. But vanillin, 4-vinylguaiaicol, and acetovanillone were found in the catalytic oxidation of ferulic acid, as shown in Figure 8. Vanillin was main product among these products. 4-vinylguaiaicol was reaction intermediate from ferulic acid removing carboxyl under alkaline conditions. Acetovanillone was by-products. The results indicated that unsaturated side chain of aromatic compounds were apt to produce aromatic aldehydes by catalytic oxidation in Co(TPPS₄)/H₂O₂ system.

There are some reports about the nature of the high valent

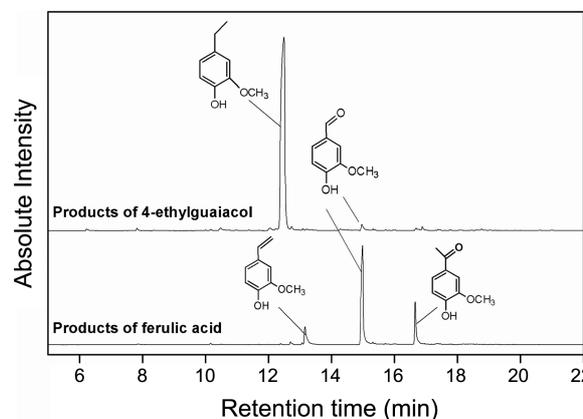


Figure 8. GC-MS spectrum of 4-ethylguaiaicol and ferulic acid oxidation products (0.1 g 4-ethylguaiaicol or ferulic acid oxidation, 0.01 g Co(TPPS₄), 0.5 mL H₂O₂, 10 mL NaOH solution, reaction temperature 150 °C, reaction time 120 min).

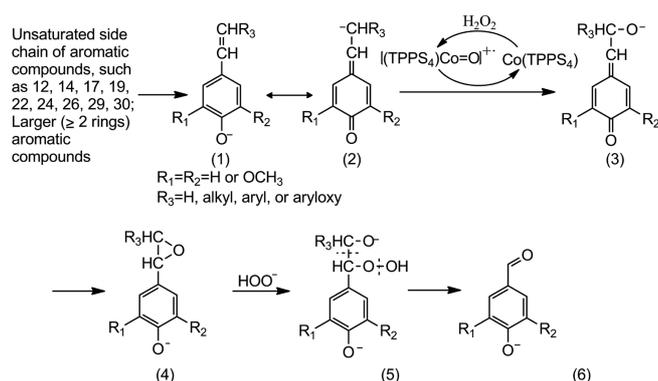


Figure 9. Possible mechanism of HFBO catalytic oxidation using $Co(TPPS_4)/H_2O_2$.

(most probably oxoferryl $Fe=O$) heme intermediate²⁴⁻²⁶ arising from the action of hydrogen peroxide on ferriheme – and by analogy, on Co porphyrins. Thus, a $[(TPPS_4)Co=O]^{+\bullet}$ intermediate could well be the first product arisen by hydrogen peroxide action. Based on the experimental results and the product characterizations as discussed previously, a possible mechanism of unsaturated side chain of aromatic compounds oxidation using $Co(TPPS_4)/H_2O_2$ can be proposed, as shown in Figure 9. Unsaturated side chain of aromatic compounds could be classified as 4-vinylphenol compounds (1), which as phenolate anion (1) and quinone methide anion (2) existed in alkaline solution. $[(TPPS_4)Co=O]^{+\bullet}$ can transfer the oxygen atom to quinone methide anion (2), and be back to its original structure. Meanwhile, quinone methide anion (2) converted to quinone methide oxide anion (3). The quinone methide oxide anion (3) can be rapidly converted to phenyl epoxyethane anion (4), which can be attacked by HOO^- , resulting in the formation of phenolate anion (5). The phenolate anion (5) degrades by the synchronous cleavage of C-C and O-O bonds to form aromatic aldehyde ions (6). In the oxidation mechanism, intermediates (1), (2) and (3) are the key intermediates and rate-determining steps, which is similar to the literature.²⁷ Hence, the improvement of aldehyde yield can be attributed to the $[(TPPS_4)Co=O]^{+\bullet}/Co(TPPS_4)$ redox turnover, which can increase the formation rate of intermediate (2), resulting in an increase in the overall rate of unsaturated side chain of aromatic compounds oxidation.

Conclusion

HFBO was obtained from bio-oil by separation and high value-added aromatic aldehydes were selectively produced from HFBO in a catalytic oxidation process using $Co(TPPS_4)$ as catalyst. 4.57 wt % vanillin and 1.58 wt % syringaldehyde were obtained from catalytic oxidation of HFBO, compared to 2.6 wt % vanillin and 0.86 wt % syringaldehyde without $Co(TPPS_4)$. $Co(TPPS_4)$ showed high catalytic activity and stability in the recycling experiments, and the $Co(TPPS_4)$ catalytic mechanism was discussed. Considering the relative high yield and high selectivity of the main products, the

catalytic oxidation of HFBO by $Co(TPPS_4)/H_2O_2$ system has strong potential for future industrialization.

Supporting Information. Catalyst preparation and characterization were presented in supplementary.

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