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Low-pressure two-stage catalytic hydropyrolysis of lignin and lignin-derived phenolic monomers using zeolite-based bifunctional catalysts



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ABSTRACT

In the present study, a two-stage catalytic hydropyrolysis of lignin was investigated by converting lignin extracted from corn stover, loblolly pine and red oak using HZSM-5, MoO₃/ZSM-5 and Ni/ZSM-5 as catalysts. Compared to the catalytic pyrolysis with inert gas, the presence of atmospheric-pressure hydrogen significantly enhanced the formation of hydrocarbon from lignin whereas dramatically reducing coke yield. In comparison to HZSM-5, MoO₃/ZSM-5 increased the production of aromatic hydrocarbons, while Ni/ZSM-5 enhanced the formation of aliphatic hydrocarbons. Coke yields decreased with both MoO₃/ZSM-5 and Ni/ZSM-5, which corresponds to the suppression of polyaromatic formation and increased selectivity to single ring aromatics. Corn stover lignin produced the highest yield of aromatic hydrocarbons with all three catalysts, followed by loblolly pine and red oak lignins. Particularly, up to 42.24 C% of corn stover lignin was converted into aromatic and aliphatic hydrocarbons with MoO₃/ZSM-5. In this study, reaction pathways of lignin-derived pyrolysis vapor during catalytic hydropyrolysis were further studied using phenol, guaiacol, and syringol as the model compounds. Results suggest that demethoxylation followed by the hydrodeoxygenation of methoxyl radicals and subsequent alkylation of the phenolic ring to produce cresol, and dimethyl phenol as intermediates prior to the intermediate phenolics were further hydrodeoxygenated to produce benzene and alkylated benzene. MoO₃/ZSM-5 showed strong ability for both demethoxylation and hydrodeoxygenation. In comparison, the ability of Ni/ ZSM-5 for phenolic-hydroxyl removal was much inferior. Based on the results obtained from the conversions of lignin and the model compounds, a negative correlation between the total yields of aromatic hydrocarbons from lignin and the abundancy of phenolic methoxyls in the lignin-derived pyrolysis vapor was found. It was also found that the pyrolysis vapors of simple H, G, or S-based monomers tend to produce more aromatic hydrocarbons than the vapors composed of more complex monomers and oligomers from their corresponding H, G or S group. However, the yield differences were less significant among G and S-based monomers and oligomers.

1. Introduction

Lignin is the second most abundant biopolymer next to cellulose. Isolated lignin is abundantly available as low-cost byproducts from the pulping industry and emerging cellulosic biorefineries [1]. Over 98 % of lignin is currently burned for heat and power, generating very little value. As an increased amount of lignin will become available in the near future, lignin valorization is critical to promoting the economic sustainability of biorefinery. Lignin can be a valuable renewable source of chemicals and fuels. The advantage of catalytic pyrolysis compared to other conversion technologies is that it can complete thermal depolymerization and catalytic upgrading in a single process within seconds. Zeolite is the most popular catalyst used in biomass conversion, featured for its strong cracking and deoxygenation capabilities without requiring hydrogen at high pressure. During the catalytic pyrolysis of biomass, acid-catalyzed dehydration, decarbonylation, decarboxylation, aromatization, and isomerization take place at the active sites of zeolite, producing aromatic hydrocarbons as the targeted chemicals [2–4]. However, the catalytic pyrolysis of lignin using zeolite as the catalyst is usually less effective as it often results in low product yields and severe catalyst coking [5–7].

To improve conversion efficiency, the catalytic pyrolysis of lignin using zeolite-based bifunctional catalysts has been investigated in previous studies. For instance, hydrogenation catalysts, such as noble metals, transitional metals, or metal oxides, have been supported on zeolites [8,9] to promote hydrogenation (HDO) while retaining the

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zeolite's ability for cracking and deoxygenation. The presence of hydrogenation catalysts on zeolites could change the pathway of oxygen removal from decarboxylation and decarbonization to hydro-dehydration, thus improving the efficiency of carbon conversion [10]. Additionally, zeolites supported with metals or metal oxides have shown better thermal stability and tolerance for catalyst deactivation [11]. It has been suggested that the presence of proximal acid sites along with zeolites enhances the deoxygenation ability of the metals through a synergistic action [12]. Jan et al. [13] catalytically hydropyrolyzed lignin using Pd/HZSM-5 under elevated reactor pressures up to 2.58 MPa to report increased hydrocarbon yields compared to that with neat HZSM-5. Cycloalkanes were also observed among the products due to the saturation of the aromatic ring by high reactor pressure. On the other hand, Melligan et al. [14] reported that the catalytic hydropyrolysis of lignin using an Ni-based zeolite catalyst at atmospheric pressure. Due to the low pyrolysis temperature and the low catalyst to biomass ratio adopted, the final products were found to be a mixture of phenolic compounds and aromatic hydrocarbons as a result of an incomplete HDO. Gamliel et al. [15] studied one-step catalytic hydropyrolysis of whole biomass with Ni-based zeolite catalysts using argon and hydrogen gases under different reactor pressures. They found that the presence of Ni on zeolite enhances the formation of single ring aromatic hydrocarbons compared to neat zeolite. They also reported that although switching from argon to hydrogen increased liquid yield, higher hydrogen pressures could not further increase liquid yield, rather increasing the yield of solid residue. A later study shows that the HDO of biomass-derived oxygenates was favored at high pressure and low temperature in the presence of a Ni-zeolite catalyst [16].

Besides the aforementioned metals or metal oxides, molybdenum (Mo) based oxides have received increasing attention as robust, lowpressure HDO catalysts [17-20]. Román-Leshkov et al. [18] converted lignin-derivable phenolic monomers to demonstrate that MoO₃ could achieve high conversion efficiency, high product selectivity, and better catalyst regeneration. Manish et al. [20] dispersed MoO₃ into different catalyst supports, such as SiO₂, γAl₂O₃, TiO₂, ZrO₂, and CeO₂, and found that the supports are vital in maintaining the partially reduced Mo moieties during the HDO of cresol. Molybdenum supported by multiwalled carbon nanotubes was also effective in converting cellulose and biomass into liquid fuel range of hydrocarbons via hydropyrolysis followed by catalytic upgrading [21]. Besides Mo based oxides, other Mo compounds were also found to be effective. A recent study conducted by Marta et al. [22] showed that Mo₂C and Pt have comparably high reactivity for upgrading hydropyrolysis vapor of biomass. In another study, Mo₂C was also used to HDO a mixture of phenolic compounds consisting of m-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol to achieve nearly 90 % conversion into benzene and toluene [23].

In the present study, a two-stage catalytic hydropyrolysis of lignin under atmospheric pressure was investigated by converting three types of lignin derived from hardwood, softwood, and herbaceous biomass using HZSM-5 and ZSM-5 catalysts impregnated with MoO₃ or Ni. In addition to lignin, lignin-derivable phenolic monomers were also converted by same catalysts. The objectives of this work are multifold: a) To compare the performance of different bifunctional catalysts under inert and hydrogen environment in order to determine the effectiveness of low-pressure catalytic hydropyrolysis of lignin; b) To compare the effectiveness of the bifunctional catalysts on upgrading three major lignin species under identical conditions. Hardwood, softwood, and herbaceous lignins have distinctively different molecular structures due to different ratios of H, G and S phenyl-propane units that may affect the conversion outcomes during catalytic hydropyrolysis; c) To convert both lignin and model compounds using same catalysts to better understand reaction mechanisms of low-pressure catalytic pyrolysis of lignin. Previously, either lignin or model compounds were catalytically converted in individual studies [24-29]. From these studies, it was often observed that the conversions of lignins were significantly

different than what were achieved using the model compounds despite of using similar catalysts [18,19]. However, the discrepancies among conversion outcomes from the two types of studies were seldom discussed in literature and thus it was difficult to justify the usefulness of the model compound studies in terms of upgrading lignin. Hereby, we aim to bridge the two-types of studies so the results of model compound studies can be better interpreted during lignin conversion.

2. Materials and methods

2.1. Materials

Lignin was isolated from corn stover (a herbaceous biomass), loblolly pine (a softwood), and red oak (a hardwood) in our laboratory using a milled wood lignin extraction method. An abbreviation of corn stover, loblolly pine and red oak to CS, LP and RO was used in the following discussion. The details of the lignin isolation method can be found in our previous work [30]. Phenol (\geq 99 wt%), guaiacol (\geq 98 wt %), syringol (\geq 99 wt%), and other 1–3 ring aromatic compounds were purchased from Sigma Aldrich. The standard gases (CO, CO₂, CH₄, C₂H₄, C₃H₆ and C₄H₈) diluted in helium were purchased from Praxair, USA. Ammonium form NH₄ZSM-5 (SiO₂/Al₂O₃ = 23) was purchased from Zeolyst Co. Molybdenum (VI) oxide and nickel (II) nitrate hexahydrate were purchased from Sigma Aldrich.

2.2. Catalyst preparation

Raw zeolite catalyst was activated at 550 °C for four hours to obtain HZSM-5. The MoO₃/ZSM-5 catalyst was prepared by grinding the mixture of MoO₃ (2 %) and zeolite (98 %) followed by calcination in a muffle furnace at 550 °C for four hours. Wetness impregnation was used to prepare the Ni based catalyst. The zeolite was also first activated at 550 °C for four hours. A calculated amount of aqueous solution of 0.01 mol/L Ni (NO₃)₂ was then added into the activated zeolite to obtain HZSM-5 zeolite with 2 % Ni content. The slurry was heated to 80 °C and stirred for three hours. The suspension was then cooled to room temperature and vacuum filtered. The filtered catalyst was washed with deionized water three times and then dried at 110 °C overnight. The dried catalyst was calcined and then reduced at 400 °C for four hours in a hydrogen environment with a flow rate of 150 mL/ min. All catalysts were pelletized into a 50–70 mesh size.

2.3. Temperature programmed desorption (TPD) of catalysts

A Micromeritics Autochem II 2920 with a TCD detector was used to perform the NH₃ temperature-programmed-desorption (NH₃-TPD) analysis. Samples were first treated at 550 °C in 10 mL/min with ultrahigh purity helium for one hour before analysis to remove moisture. After cooling down to 50 °C, the sample was exposed to 10 % NH₃ in helium with the gas flow of 20 mL/min for 30 min. A TCD detector was used to measure the desorbed NH₃ when the sample was heated from 50 to 700 °C with a 10 °C/min ramp in helium with a gas flow rate of 10 mL/min. The signal was offset to zero at 650 °C.

2.4. Pyrolysis of lignin and model monomers

The two-stage catalytic pyrolysis was conducted in a tandem micropyrolyzer (Frontier Laboratory, Japan). In the reactor, two microfurnace ovens were connected in series. The first oven was used as the pyrolysis reactor and its temperature was kept at 600 °C when lignin was pyrolyzed, or 400 °C when the phenolic monomers were vaporized. The second reactor was used as a fixed catalyst-bed and its temperature was kept at 600 °C. The carrier gas in the reactor can be alternated between helium and hydrogen. Each time, 500 µg of lignin or phenolic monomer was placed inside a deactivated stainless cup and then dropped into the preheated reactor. The pyrolysis vapor exiting the first

Table 1

Product distribution during thermal pyrolysis of lignin under helium or hydrogen environments.

Lignin type	Corn stover		Loblolly pine		Red oak	
Carrier gas	He	H ₂	Не	H ₂	He	H ₂
Product yield (C %)						
Light gases						
CO	3.15 ± 0.06	3.08 ± 0.01	3.42 ± 0.03	3.19 ± 0.03	3.75 ± 0.02	3.89 ± 0.06
CO ₂	4.24 ± 0.02	4.35 ± 0.01	2.83 ± 0.05	2.95 ± 0.02	3.26 ± 0.09	3.16 ± 0.05
CH ₄	1.16 ± 0.04	1.17 ± 0.02	1.46 ± 0.05	1.44 ± 0.04	2.17 ± 0.17	2.08 ± 0.10
Sum	8.55 ± 0.12	8.37 ± 0.04	7.71 ± 0.13	7.76 ± 0.09	9.19 ± 0.28	9.30 ± 0.21
Acetic acid	2.41 ± 0.18	2.39 ± 0.00	0.53 ± 0.10	0.41 ± 0.00	1.60 ± 0.06	1.73 ± 0.00
Char	29.10 ± 0.80	28.30 ± 1.20	37.20 ± 0.42	35.20 ± 0.28	37.40 ± 1.37	35.60 ± 0.70
Phenolic monomers						
Phenol	0.41 ± 0.04	0.38 ± 0.01	0.26 ± 0.00	0.28 ± 0.01	0.06 ± 0.00	0.04 ± 0.00
2-Methoxyphenol	0.48 ± 0.01	0.51 ± 0.01	0.67 ± 0.00	0.70 ± 0.03	0.35 ± 0.01	0.36 ± 0.02
m-cresol	0.09 ± 0.00	0.11 ± 0.01	0.13 ± 0.00	0.15 ± 0.01	0.07 ± 0.00	0.08 ± 0.00
p-cresol	0.48 ± 0.02	0.50 ± 0.03	0.36 ± 0.00	0.38 ± 0.02	0.08 ± 0.00	0.07 ± 0.01
Phenol, 2-methoxy-3-methyl-	0.04 ± 0.00	0.04 ± 0.00	0.06 ± 0.00	0.07 ± 0.00	0.05 ± 0.00	0.05 ± 0.00
2-Methoxy-5-methylphenol	-	-	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Creosol	0.64 ± 0.01	0.66 ± 0.01	1.30 ± 0.00	1.32 ± 0.06	0.84 ± 0.03	0.81 ± 0.02
Phenol, 2,5-dimethyl-	0.08 ± 0.00	0.07 ± 0.01	0.18 ± 0.00	0.19 ± 0.00	0.07 ± 0.00	0.07 ± 0.00
4-ethylphenol	0.31 ± 0.02	0.40 ± 0.01	0.07 ± 0.00	0.08 ± 0.00	-	-
Phenol, 4-ethyl-2-methoxy-	0.04 ± 0.00	0.10 ± 0.00	0.08 ± 0.00	0.09 ± 0.00	0.06 ± 0.01	0.06 ± 0.00
Phenol, 4-ethyl-2-methoxy-	0.14 ± 0.01	0.21 ± 0.03	0.37 ± 0.00	0.39 ± 0.01	0.14 ± 0.01	0.15 ± 0.02
4-vinylphenol	6.82 ± 0.32	6.52 ± 0.10	0.37 ± 0.00	0.35 ± 0.01	0.52 ± 0.00	0.50 ± 0.01
2-Methoxy-4-vinylphenol	2.80 ± 0.02	2.85 ± 0.04	0.85 ± 0.00	0.82 ± 0.06	-	-
Eugenol	0.12 ± 0.01	0.09 ± 0.00	0.26 ± 0.00	0.28 ± 0.00	0.14 ± 0.01	0.16 ± 0.00
Phenol, 2-methoxy-4-propyi-	0.03 ± 0.00	0.03 ± 0.00	0.08 ± 0.00	0.15 ± 0.00	0.10 ± 0.01	0.10 ± 0.01
Phenol, 2,0-dimethoxy-	0.57 ± 0.03	0.55 ± 0.02	0.12 ± 0.00	0.17 ± 0.00	0.03 ± 0.03	0.70 ± 0.01
1.2.4 Trimethouse on a	0.44 ± 0.01	0.38 ± 0.00	1.52 ± 0.00	1.45 ± 0.00	0.34 ± 0.02	0.32 ± 0.01
1,2,4-1filleuloxyDelizelle	0.04 ± 0.03	0.62 ± 0.01	0.40 ± 0.00	0.42 ± 0.00	1.43 ± 0.09	1.47 ± 0.00
Valiiiiii Ponzono 1.2.2 trimothovy E mothyl	0.23 ± 0.02	0.20 ± 0.00	0.03 ± 0.00	0.02 ± 0.03	0.21 ± 0.01	0.18 ± 0.02
Phenol 2 methovy 4 propyl	0.19 ± 0.03	0.17 ± 0.00	- 0.24 + 0.00	- 0.20 + 0.01	0.39 ± 0.04	0.42 ± 0.01
Apocynin	- 0.12 + 0.01	- 0.10 + 0.00	0.24 ± 0.00 0.25 ± 0.00	0.29 ± 0.01 0.24 ± 0.06	- 0.21 + 0.02	- 0.23 + 0.00
3' 5'-Dimethoxyacetophenone	0.12 ± 0.01 0.41 ± 0.03	0.10 ± 0.00 0.45 ± 0.00	0.23 ± 0.00 0.13 ± 0.00	0.24 ± 0.00	0.21 ± 0.02 0.65 ± 0.01	0.25 ± 0.00
Phenol 2 6-dimethoxy-4-(2-propenvl)-	0.41 ± 0.05 0.73 + 0.06	0.43 ± 0.00 0.78 + 0.01	0.15 ± 0.00 0.35 ± 0.00	0.13 ± 0.00 0.37 + 0.00	0.03 ± 0.01 0.90 ± 0.06	0.00 ± 0.01 0.93 + 0.03
Benzaldebyde 4-bydroxy-3 5-dimethoxy-	0.18 ± 0.02	0.70 ± 0.01	0.00 ± 0.00 0.12 ± 0.00	0.07 ± 0.00	0.38 ± 0.04	0.90 ± 0.00 0.40 ± 0.00
2-Propanone 1-(4-hydroxy-3-methoxyphenyl)-	-	-	0.12 ± 0.00 0.07 ± 0.00	0.09 ± 0.00	0.00 ± 0.01 0.07 + 0.02	0.10 ± 0.00 0.10 ± 0.01
Ethanone 1-(4-hydroxy-3 5-dimethoxyphenyl)-	0.24 + 0.03	0.22 + 0.00	0.07 ± 0.00	0.05 ± 0.00	0.30 ± 0.02	0.32 ± 0.01
Desaspidinol	0.07 ± 0.01	0.06 ± 0.00	_	-	-	-
3.5-Dimethoxy-4-hydroxyphenylacetic acid	_	_	_	_	0.13 ± 0.04	0.15 ± 0.01
Desaspidinol / 2-Pentanone, 1-(2,4,6-trihvdroxyphenyl)	_	_	_	_	0.10 ± 0.02	0.09 ± 0.01
3,4,5-Trimethoxyphenylacetic acid	-	-	-	-	0.08 ± 0.01	0.09 ± 0.01
3,5-Dimethoxy-4-hydroxycinnamaldehyde	-	-	-	-	0.30 ± 0.04	0.40 ± 0.03
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	-	-	0.15 ± 0.00	0.11 ± 0.01	-	-
Homovanillic acid	-	-	0.12 ± 0.00	0.13 ± 0.00	-	-
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)-	-	-	0.31 ± 0.00	0.39 ± 0.00	-	-
Sum of phenolic monomers	13.34 ± 0.76	13.30 ± 0.30	8.23 ± 0.58	8.40 ± 0.26	7.55 ± 0.00	7.60 ± 0.14
Total phenolic oligomers*	35.98 ± 1.74	36.33 ± 1.54	35.01 ± 1.23	34.87 ± 0.63	38.11 ± 1.71	37.79 ± 1.05

* Calculated based on carbon mass difference.

reactor was swept into the catalyst bed loaded with a 10 mg catalyst to be upgraded. Three samples of same feedstock were sequentially pyrolyzed using a same catalyst bed. The used catalyst was replaced by a fresh catalyst each time when the feedstock type changed. In the case of non-catalytic pyrolysis, the pyrolysis vapor passed through an empty catalyst bed. After conversion, the products exiting the catalyst bed were analyzed using an online Agilent (7890B) GC/MS-FID-TCD system. Inside the GC, the product vapors were separated into three streams to enter MS, FID, and TCD, respectively. The split ratio in the front inlet of the GC was 50:1 and a total flow rate was 156 mL/min. The GC temperature was initially at 40 °C and increased to 280 °C at a heating rate of 6 °C/min. The composition of the vapor products was identified in the MS and quantified in the FID. For quantification, authentic chemicals were injected into the GC to create calibration curves. Light gases, such as carbon oxides and C₁-C₄ aliphatic hydrocarbons (CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₈) were measured by the TCD. Calibration curves of the gaseous products were generated using the standard gases with different concentrations. The product yields from the three sequential runs with a same feedstock were averaged and the results are reported.

After pyrolysis, the char residue in the sample cup was collected. The used catalysts were also collected from the catalyst bed after three consecutive runs at identical pyrolysis conditions in order to determine the amount of coke formed. The carbon contents in the lignin, char, and catalytic coke were analyzed using a Vario Micro Cube elemental analyzer (Elementar, Germany). The carbon mass balance of the products was reported in this study. The carbon yield of a product and product selectivity were calculated based on the Eq.s (1) and (2) given below:

$$Carbon yield of product (C\%) = \frac{The mole of carbon in product}{The total mole of carbon in feedstock} \times 100\%$$
(1)

Selectivity (%)

The mole of carbon in the aromatic or aliphatic product

The total mole of carbon in the aromatic or aliphatic product group× 100%

3. Results and discussions

3.1. TPD results of catalysts

The results of TPD analysis with the three catalysts are shown in Fig. S1 in the supplemental. Ammonia was used to detect the amount and strength of acid sites in zeolite [31]. Compared to HZSM-5, $MOO_3/ZSM-5$ had decreased low-temperature acid sites (100 - 300 °C). However, the distribution of high-temperature acid sites (300 - 600 °C) of $MOO_3/ZSM-5$ was quite similar to that of HZSM-5. The low-temperature acid sites were also decreased in Ni/ZSM-5. However, there was a significant increase of high-temperature acid sites with Ni/ZSM-5.

Introducing metals to zeolite generally does not change the original physical structure. However, the surface area is reduced due to the agglomeration of metal particles and the blockage of micropores by metals [32,33], which could be the reason for decrease of acid sites. During the wet impregnation of Ni into ZSM-5, the exchange of metal ions and H+ functionality of zeolite could also decrease the low-temperature active sites (i.e., weak acid sites), which can be Brønsted acid sites [33,34]. The MoO₃/ZSM-5 can be synthesized with either wet impregnation or solid exchange [35]. In this study, the solid exchange method (i.e., physical mixing followed by co-activation) was chosen since, according to previous study, the catalysts prepared in this way have a better performance compared to those produced by wet impregnation [36]. During the co-activation process at 550 °C, the MoO₃ species would be dispersed on the ZSM-5 surface, and the solid exchange of MoO₃ with the OH groups of HZSM-5 would result in the reduction of Brønsted acid sites [37]. High-temperature acid sites are usually moderate or strong acid sites. The increase of high temperature acid sites with Ni/ZSM-5 could result from the growth of alumina with low coordination and the dehydroxylation from thermal treatment [38]. Similar changes in the acid sites were previously reported for Ni/ ZSM-5 [12,32].

3.2. Comparison of helium and hydrogen as the carrier gases

Catalytic pyrolysis of lignin with a catalytic bed consists of twostage conversions. In the first stage, lignin undergoes thermal decomposition at the pyrolyzer. In the second stage, the lignin-derived pyrolysis vapor is catalytically upgraded at the catalytic bed. The effect of hydrogen during the first stage of thermal decomposition was evaluated by pyrolyzing lignin using helium or hydrogen gas without catalyst (i.e., no catalyst was loaded in the catalyst bed). The product distributions are given in Table 1. Since phenolic oligomers cannot be detected by GC/MS, their total yield was calculated based on carbon mass difference. Switching the carrier gas from helium to hydrogen had no significant effect on the product distribution in all three lignins. The slightly increased monomer yields and decreased pyrolysis char yields suggest that hydrogen promotes cracking of lignin. However, hydrocracking during thermal decomposition was limited due to low hydrogen pressure and lack of active hydrogen atoms in the absence of catalyst.

The effect of hydrogen during the upgrading of lignin-derived vapor over the catalytic bed (i.e., the second stage of the conversion) can be evaluated by comparing the product distributions from catalytic pyrolysis of lignin under helium (Table 2) or hydrogen environment (Table 3). With same lignin, catalytic hydropyrolysis produced significantly higher amounts of aromatic hydrocarbons and dramatically reduced catalytic coke compared to catalytic pyrolysis with helium at all catalysts. For example, as high as 42.24 C% of total hydrocarbons (i.e., 19.23 C% of aromatic hydrocarbons plus 22.91 C% of aliphatic hydrocarbon) were obtained when CS lignin was converted over MoO₃/ ZSM-5 in the presence of hydrogen, compared to 23.03 C% (i.e., 9.67 C% of aromatic hydrocarbons plus 13.35 C% of aliphatic hydrocarbons) with the same zeolite but in the presence of helium. While both aromatic and aliphatic hydrocarbons were promoted by the

presence of hydrogen gas, the increase in aromatic yield was much more dramatic. Considering hydrogen has no significant effect on thermal decomposition of lignin at the first stage of the conversion as described above, external hydrogen took effect mostly at the catalyst bed by reacting with lignin-derived pyrolysis vapor. While decarbonylation is the main pathway that zeolite deoxygenates biomass, CO yield decreased noticeably during catalytic hydropyrolysis. The alkane yield also increased upon catalytic hydropyrolysis. Thus, it is suggested that the hydrogen dissociated at the catalyst sites suppresses decarbonylation, while promoting HDO and hydrogenation. The dramatic decrease in the catalytic coke is also related by the presence of reactive hydrogen generated at catalyst sites. During catalytic conversion, coke can be formed in both inside and on the surface of catalyst. Generally, the coke formation from lignin is associated with deposition of polyaromatic hydrocarbons resulting from over-aromatization, or polymerization of phenolic compounds due to condensation and coupling reactions [39].

In the absence of external hydrogen, there was nearly no benefit of using bifunctional catalysts over neat HZSM-5. In Table 2, more coke and fewer hydrocarbons were produced in several of the cases with bifunctional catalysts compared to the cases using neat HZSM-5. It has also been reported previously that Mo added zeolite promotes coking when methane was converted under inert environment [35]. In the absence of hydrogen, the presence of the metal or metal oxides on the zeolite may reduce the effective active sites of zeolite to lower the conversion efficiency of the lignin-derived pyrolysis vapor.

3.3. Catalytic hydropyrolysis of different types of lignin over zeolite-based catalysts

From the results shown in Table 3, the effects of lignin species and catalyst type on the product distribution during catalytic hydropyrolysis can be evaluated further.

When HZSM-5 was employed, the highest yield of aromatic hydrocarbons (i.e., 20.52 C%) was observed with CS lignin followed by the yields from LP lignin and RO lignin. The yields of catalytic coke were only slightly different among different lignins (i.e., 9.01-9.64 C%). The yield of total phenolic vapor before the catalytic upgrading (i.e., the total sum of phenolic monomers and oligomers given in Table 1) was highest with CS lignin and lowest with RO lignin. Thus, the results imply that the pyrolysis vapor of CS lignin has the lowest tendency to form coke. In comparison, the pyrolysis vapor of RO lignin forms coke profoundly. The highest alkane yield was observed with RO lignin followed by the yields from LP lignin and CS lignin. Methane selectivity was higher with LP lignin and RO lignin compared to CS lignin due to higher methoxyl content in woody biomass-based lignins. On the other hand, the CO₂ yield was highest with CS lignin since herbaceous biomass-based lignin contains more carboxylic groups on its aromatic side chains.

Employing MoO₃/ZSM-5 instead of HZSM-5 increased the yields of aromatic hydrocarbons from all three lignins. Coke formation was significantly suppressed as the yields were only 1.83-3.80 C% for the different types of lignin. Alkane yield increased whereas alkene yield decreased due to enhanced hydrogenation by MoO₃/ZSM-5. The yields of carbon oxides further decreased, indicating that HDO reactions replaced decarbonylation and decarboxylation reactions at a greater extent. Among aromatic hydrocarbons, the selectivity for benzene increased significantly at the expense of decreased selectivity for polyaromatic hydrocarbons. Since polyaromatic hydrocarbons are known as a precursor of catalytic coke [40], this result is consistent with the decreased coke yield with MoO₃/ZSM-5. Among the three types of lignin, the highest aromatic hydrocarbons yield of 27.06 C% was reported from the CS lignin, followed by 22.86 C% from LP lignin and 20.67 C% from RO lignin. The increase in benzene selectivity by MoO₃/ZSM-5 was the most noticeable with LP lignin. LP lignin also produced the least amount of catalytic coke (1.83 C%) with MoO₃/ZSM-

Table 2

Lignin type	Corn stover			Loblolly pine			Red oak		
Catalyst type Product yield (C%)	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5
Aromatics	10.99 ± 0.29	9.67 ± 1.34	10.00 ± 0.91	7.59 ± 0.02	7.97 ± 1.60	6.75 ± 0.08	9.46 ± 0.29	7.81 ± 1.26	7.72 ± 0.09
Aliphatics	14.42 ± 0.39	13.35 ± 0.46	13.05 ± 0.72	12.72 ± 0.18	12.39 ± 0.17	12.85 ± 1.08	14.36 ± 0.39	13.49 ± 0.49	14.00 ± 0.09
Alkane (C \leq 4)	6.51 ± 0.06	6.35 ± 0.10	7.77 ± 0.33	7.01 ± 0.15	6.87 ± 6.16	8.55 ± 0.08	7.53 ± 0.06	7.39 ± 0.10	8.92 ± 0.09
Alkene (C \leq 5)	7.91 ± 0.34	7.00 ± 0.37	5.27 ± 0.39	5.71 ± 0.03	5.53 ± 7.01	4.30 ± 0.08	6.83 ± 0.34	6.10 ± 0.39	5.08 ± 0.09
Total hydrocarbons	25.41 ± 0.68	23.12 ± 1.80	23.05 ± 1.63	20.31 ± 0.20	20.36 ± 1.77	19.60 ± 1.16	23.82 ± 0.68	21.30 ± 1.75	21.72 ± 0.18
CO	7.86 ± 0.10	7.67 ± 0.21	10.34 ± 0.12	7.00 ± 0.07	7.34 ± 0.07	10.36 ± 0.08	9.02 ± 0.10	8.94 ± 0.21	12.81 ± 0.09
CO_2	5.66 ± 0.21	5.35 ± 0.09	5.80 ± 0.61	3.89 ± 0.27	3.52 ± 0.10	4.68 ± 0.08	4.52 ± 0.21	4.31 ± 0.04	4.46 ± 0.09
Pyrolysis char	29.14 ± 1.52	29.14 ± 1.52	29.14 ± 1.52	37.20 ± 1.18	37.20 ± 1.18	37.20 ± 1.18	37.43 ± 5.75	37.43 ± 5.75	37.43 ± 5.75
Catalytic coke	16.91	17.76	15.90	16.26	17.90	11.07	16.38	19.59	17.69
Sum	84.98 ± 2.51	82.94 ± 3.62	84.23 ± 3.88	84.65 ± 1.72	86.32 ± 3.11	82.91 ± 1.84	91.17 ± 6.78	91.56 ± 7.75	94.11 ± 6.98

Production distribution from catalytic pyrolysis of lignin under helium environment (pyrolyzor temperature: 600 °C, catalytic bed temperature: 600 °C).

5.

Opposite to that which was observed with MoO₃/ZSM-5 and HZSM-5, the yields of aromatic hydrocarbons decreased with Ni/ZSM-5 compared to that with HZSM-5 for all three lignins. However, the selectivity to benzene among aromatic hydrocarbon was greatly enhanced by Ni/ZSM-5. The yield of aliphatic hydrocarbons also increased dramatically with Ni/ZSM-5 with methane as the major product. Methane can be produced by the hydrogenolysis of the aliphatic side chain or hydrocracking of the aromatic ring. CO₂ yields only slightly decreased with Ni/ZSM-5. Also, the yields of CO were similar to the yields obtained with HZSM-5 for the same type of lignin. Thus, the suppression of decarbonization and decarboxylation was not as significant as it was observed with MoO₃/ZSM-5. Although the coke yields reduced with Ni/ZSM-5 for all three lignins, the extent of the decrease was not as significant as it was observed with the MoO₃/ZSM-5 catalyst. For CS lignin, the yield of aromatic hydrocarbon was 19.23 C%, only a slight decrease from 20.52 C% with HZSM-5. CS lignin also produced the highest yield of total aliphatic hydrocarbons (22.91 C%) among all lignins. However, the highest coke yield with Ni/ZSM-5 was also observed with CS lignin. Although the yields of total aliphatics were slightly lower with LP lignin and RO lignin in comparison to CS lignin,

methane selectivity was higher from the wood-based lignins. LP lignin also produced aromatic hydrocarbons with the highest selectivity to benzene (34.97 %).

3.4. Catalytic hydropyrolysis of phenolic model monomers

Lignin is composed of three basic units, which are p-hydroxylphenyl (H), guaiacyl (G) and syringyl (S) units. Accordingly, phenol, guaiacol, and syringol are the three simplest monomers that can be produced when lignin thermally decomposes. Thus, those three monomers were used as model compounds to study the reaction mechanisms of lignin-derived pyrolysis vapors during catalytic hydropyrolysis.

The conversions and product distributions of the phenolic monomers during catalytic hydropyrolysis are given in Table 4. Aromatic hydrocarbons were major products from all the conversion cases, but their total yields and the selectivity of individual aromatics highly depended on both feedstock monomers and catalyst types. Aliphatic yields from the conversions of guaiacol and syringol were constantly higher compared to the conversion of phenol. Also, the aliphatics produced from syringol were found to be composed of only alkanes. Carbon oxides were more prominently produced from guaiacol. Coke formation

Table 3

Production distribution from catalytic hydropyrolysis of lignin (pyrolyzor temperature: 600 °C, catalytic bed tempera

Lignin type	Corn stover			Loblolly pine			Red oak		
Catalyst type	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5	HZSM-5	MoO ₃ / ZSM-5	Ni/ZSM-5
Product yield (C%)									
Aromatics	20.52 ± 0.37	27.06 ± 0.11	19.23 ± 0.84	18.57 ± 0.03	$22.86~\pm~0.20$	14.19 ± 0.78	17.31 ± 0.39	20.67 ± 0.64	14.96 ± 1.51
Aliphatics	18.23 ± 0.14	18.66 ± 0.36	22.91 ± 0.02	16.74 ± 0.57	$18.07~\pm~0.18$	19.92 ± 2.12	19.25 ± 0.57	16.85 ± 0.42	21.83 ± 0.53
Alkane (C \leq 4)	9.37 ± 0.03	12.23 ± 0.14	17.42 ± 0.28	9.81 ± 0.30	12.99 ± 0.29	16.24 ± 1.76	11.91 ± 0.10	12.89 ± 0.26	20.10 ± 3.90
Alkene (C \leq 5)	$8.86~\pm~0.11$	6.43 ± 0.21	5.49 ± 0.74	6.93 ± 0.27	5.08 ± 0.37	3.68 ± 0.36	7.34 ± 0.46	$3.96~\pm~0.16$	1.73 ± 0.63
Total hydrocarbons	38.75 ± 0.51	35.72 ± 0.47	42.24 ± 0.86	36.31 ± 0.60	40.93 ± 0.38	34.11 ± 2.90	36.56 ± 0.96	37.52 ± 1.06	36.79 ± 2.04
CO	4.82 ± 0.02	4.14 ± 0.29	$4.82~\pm~0.10$	4.28 ± 0.07	3.59 ± 0.05	$4.04~\pm~0.81$	5.61 ± 0.14	3.86 ± 0.24	$5.21~\pm~0.38$
CO ₂	$5.01~\pm~0.08$	3.44 ± 0.03	4.38 ± 0.17	2.85 ± 0.05	2.13 ± 0.07	2.50 ± 0.12	3.15 ± 0.05	$2.17~\pm~0.02$	2.51 ± 0.13
Pyrolysis char	28.33 ± 0.79	28.33 ± 0.79	28.33 ± 0.79	35.23 ± 0.79	35.23 ± 0.79	35.23 ± 0.79	35.64 ± 0.79	35.64 ± 0.79	35.64 ± 0.79
Catalytic coke	9.34	2.56	7.45	9.01	1.83	4.33	9.64	3.80	4.32
Sum	86.25 ± 1.40	84.19 ± 1.58	87.12 ± 4.93	86.68 ± 1.51	83.71 ± 1.78	80.21 ± 9.62	90.60 ± 1.95	82.99 ± 2.12	84.47 ± 7.1
Aromatic selectivity (%)									
Benzene	23.30	37.54	28.34	21.28	34.97	26.88	19.39	26.62	23.72
Toluene	22.94	32.01	22.78	26.28	37.96	27.92	27.41	39.48	27.30
Xylene	8.56	9.74	7.45	11.31	14.30	11.10	14.17	18.32	14.02
Alkylated benzene	8.98	7.10	7.56	9.08	4.86	6.67	9.00	7.67	5.76
Naphthalene	11.20	5.28	12.34	8.42	2.40	10.15	7.77	2.47	12.70
Polyaromatics (C_{10+})	25.01	8.32	21.54	23.63	5.52	17.27	22.26	5.46	16.50
Aliphatic selectivity (%)									
Methane	54.08	64.42	75.50	61.92	70.32	85.11	65.26	77.05	90.16
Ethane	2.79	4.09	3.99	2.73	4.29	3.78	2.56	2.10	3.00
Ethylene	22.84	14.11	10.41	19.55	10.74	6.02	17.00	8.12	2.63
Propane	1.09	2.64	0.95	0.74	2.18	0.61	0.75	1.52	0.48
Propene	16.23	11.82	7.50	12.98	9.87	3.48	12.33	8.87	3.04
Butane	0.57	0.54	0.30	0.34	0.46	0.21	0.38	0.49	0.18
Butene	1.97	1.88	1.03	1.30	1.66	0.64	1.29	1.57	0.39
Pentene	0.42	0.50	0.31	0.44	0.47	0.15	0.44	0.29	0.12

Table 4

roduct distribution from catalytic hydropyrolysis of phenolic monomer	rs (pyrolyzor temperature: 400 °C, catalytic bed temperature	e: 600 °C).
-----------------------------------------------------------------------	--------------------------------------------------------------	-------------

Monomer type	Phenol			Guaiacol			Syringol		
Catalyst type Conversion (C%) Product yield based on	HZSM-5 53.14 ± 0.91	MoO ₃ / ZSM-5 92.27 ± 1.23	Ni/ZSM-5 56.86 ± 3.04	HZSM-5 96.97 ± 0.86	MoO ₃ / ZSM-5 99.31 ± 0.42	Ni/ZSM-5 96.62 ± 0.48	HZSM-5 100.00 ± 0.00	MoO ₃ / ZSM-5 100.00 ± 0.00	Ni/ZSM-5 100.00 ± 0.00
converted feedstock (C%)									
Phenol	-	-	-	14.33 ± 1.51	4.02 ± 0.10	14.23 ± 1.27	8.03 ± 0.24	4.68 ± 0.51	13.21 ± 0.31
Guaiacol	-	-	-	-	-	-	-	-	1.41 ± 0.05
Cresol	-	-	-	15.88 ± 3.69	3.66 ± 0.80	8.16 ± 1.63	1.76 ± 0.11	2.21 ± 0.21	2.24 ± 0.13
Dimethyl phenol	-	-	-	-	-	-	9.24 ± 0.34	1.89 ± 0.04	1.36 ± 0.06
Aromatic hydrocarbons	73.63 ± 1.03	91.65 ± 1.19	63.59 ± 1.76	34.78 ± 4.32	62.91 ± 1.60	37.60 ± 0.04	24.28 ± 0.97	41.82 ± 0.65	29.67 ± 1.23
Coke	21.43 ± 0.00	4.63 ± 0.00	14.26 ± 0.11	$9.98~\pm~0.00$	$1.89~\pm~0.00$	4.05 ± 0.00	40.44 ± 0.00	25.63 ± 0.00	33.12 ± 0.00
CO	1.55 ± 1.10	1.37 ± 0.15	2.93 ± 0.13	2.51 ± 0.14	1.31 ± 0.12	3.22 ± 1.00	$0.80~\pm~0.01$	0.60 ± 0.22	0.90 ± 0.19
CO ₂	0.04 ± 0.03	-	-	2.84 ± 0.99	1.31 ± 0.10	2.80 ± 0.23	0.83 ± 0.02	1.00 ± 0.32	1.24 ± 0.01
Aliphatic hydrocarbons	1.68 ± 0.74	0.81 ± 0.22	14.56 ± 0.63	11.55 ± 6.08	13.31 ± 0.85	19.32 ± 2.93	12.28 ± 0.22	11.85 ± 0.42	12.90 ± 0.05
Alkane	1.03 ± 0.43	0.36 ± 0.04	14.56 ± 0.63	4.21 ± 2.96	9.10 ± 0.27	13.90 ± 2.41	12.28 ± 0.22	11.85 ± 0.42	12.90 ± 0.05
Alkene	0.65 ± 0.31	0.45 ± 0.18	-	7.33 ± 3.13	4.18 ± 0.58	5.42 ± 0.53	-	-	-
Aromatic Selectivity (%)									
Benzene	26.38	95.75	76.67	16.87	51.72	35.30	14.65	39.96	24.09
Toluene	1.65	1.01	2.64	23.34	30.53	28.56	28.66	38.04	32.39
Xylene	0.54	0.09	0.24	9.57	6.53	8.88	20.29	11.73	19.52
Alkylated benzene	2.82	0.08	0.30	5.27	1.58	2.65	4.77	1.66	1.35
Naphthalene	17.15	0.41	3.40	14.66	4.30	10.94	8.64	3.42	12.22
Polyaromatics (C_{10+})	51.46	2.68	16.75	30.29	5.34	13.67	22.99	5.18	10.43
Aliphatic Selectivity (%)									
Methane	-	-	73.15	26.88	65.01	64.02	55.95	75.47	100.00
Ethane	61.58	44.82	15.58	7.37	2.23	6.30	14.32	-	-
Propane	-	-	14.27	1.44	1.13	1.40	29.73	44.53	-
Butane	-	-	-	0.80	-	0.23	-	-	-
Ethylene	-	-	-	37.22	22.12	14.62	-	-	-
Propene	38.42	55.18	-	20.82	9.51	10.68	-	-	-

was the lowest with guaiacol for all of the catalysts, with that of phenol slightly higher. In comparison, coke formation was strongly favored with syringol.

Phenol conversion over HZSM-5 was 53.14 %, implying some phenol molecules diffused through the catalytic bed without reacting. Aromatic hydrocarbons and catalytic coke were main products as their respective yields were 73.63 C% and 21.43 C%. The phenol conversion increased to 92.27 % when MoO_3/ZSM -5 was the catalyst. The yield of aromatic hydrocarbons was 91.65 C% with the selectivity to benzene to be as high as 95.75 %. On the other hand, polyaromatic selectivity decreased from 51.46 % with HZSM-5 to 2.68 % with MoO_3/ZSM -5. The decreased polyaromatic formation is accordant with the decreased coke yield (4.63 C%).

Phenol conversion over Ni/ZSM-5 was 56.86 %, only a slight increase compared to that with HZSM-5. While the yield of alkane was negligible with both HZSM-5 and $MoO_3/ZSM-5$, it accounted for 14.56 C% with Ni/ZSM-5. On the other hand, the aromatic yield decreased to 63.59 C%, which is even lower than the yield obtained with HZSM-5. However, single-ring aromatics were preferentially produced with Ni/ZSM-5. The coke formation was also suppressed, although the yield was much higher than that with $MOO_3/ZSM-5$.

It has been proposed that the metal or metal oxides catalyzed HDO process follows a reverse Mars-van Krevelen Mechanism [19,41]. It was also suggested that Mo based catalysts have higher HDO efficiency than other transitional metals because the oxygen-vacancy creation and diffusion occur faster with Mo than with other metals [42]. Based on the results described above, it is reasonable to infer that the HDO of phenolic hydroxyl could rapidly occur at the catalyst bed of MoO₃/ZSM-5 to produce benzene without causing ring-opening. Phenolic hydroxyl is usually highly reactive toward repolymerization and condensation reactions. Thus, the removal of hydroxyl by HDO largely suppressed the formation of phenolic oligomers and catalytic coke. On the other hand, a high yield of aliphatic hydrocarbons was produced when phenol was converted over Ni/ZSM-5, indicating that ring opening occurred due to the hydrocracking ability of Ni [43]. Methane

selectivity among aliphatic hydrocarbons was high at 73.15 % with Ni/ ZSM-5. Therefore, a significant amount of methane was likely produced from the hydrocracking of the phenol ring. Methane and other cracking fragments would subsequently form a "hydrocarbon pool" inside the zeolite catalyst pores to produce aromatic hydrocarbons. In addition to aromatics, C₂ and C₃ hydrocarbons could also form during the process. Since its molecular size is smaller than the zeolite pores, phenol can be converted at both the catalyst surface and inside of zeolite pores. However, the conversion at the zeolite surface is likely to play a critical role with the bifunctional catalysts due to the presence of the MoO₃ or Ni and hydrogen accessibility on the catalyst surface. In the case of HZSM-5, phenol molecules mostly convert at active sites inside the zeolite pores to form a "hydrocarbon pool". Although the presence of external hydrogen would enhance HDO, hydrogen dissociation at HZSM-5 was less effective due to the absence of the hydrogenation catalyst. Therefore, acid-catalyzed dehydration and repolymerization which usually occur under inert environments can still take place during catalytic hydropyrolysis with HZSM-5. As a result, more polyaromatics were produced with HZSM-5. The conversion networks of phenol with different catalysts are illustrated in Fig. 1.

The guaiacol conversion was much higher than the phenol conversion, probably because guaiacol diffuses through the catalyst bed much slower due to its larger molecular size and the presence of a methoxyl group. Phenol and cresol were found among the products in addition to hydrocarbons. These partially deoxygenated phenolics are intermediates of guaiacol during catalytic hydropyrolysis. According to the model proposed by Popov et al. [44], both methoxyl and hydroxyl groups can be adsorbed on Brønsted acid sites during the gas phase conversion of guaiacol with zeolite. The dissociation energies of hydroxyl aryl-O, methoxyl aryl-O and methyl-O in guaiacol are 111, 97.4 and 52.8 kcal/mol, respectively [45]. Thus, demethylation of guaiacol should preferentially occur from the perspective of the dissociation energy. It has been suggested that demethylation is followed by two possible reaction pathways. In the first pathway, the detached methanium ion attacks the aryl-O bond, at which the demethylation occurred



Fig. 1. Reactions of phenol during catalytic hydropyrolysis with different catalysts.

previously, and produces a benzaldehyde group via dehydrogenation. The benzaldehyde group later decarbonylates to form benzene and CO. In this pathway, guaiacol is first converted into 2-hydroxybenzaldehyde and later phenol with a decarbonylation [46]. Based on this pathway, the theoretical yield of CO from guaiacol is 14.3 C%. However, the CO vields given in Table 4 are far below the theoretical vield with all three catalysts. Hydroxybenzaldehyde was also not observed among the products. In the second pathway of Popov's model, the methanium ion possibly attaches to the aromatic ring instead of the hydroxyl group, and thus guaiacol is converted to methyl catechol. The two hydroxyl groups on the methyl catechol later undergo sequential deoxygenation reactions to form toluene with cresol as the intermediates. However, both catechol (without methanium ion attachment) and methyl catechol were not observed in the present study. Therefore, neither of the two pathways proposed in Popov's model were supported by the results obtained in this study. It has been experimentally proven in previous studies that lignin pyrolysis involves the formation of free-radical intermediates [47-49], while many short-lived reactive free radicals are produced from the side chain cleavage of phenolic compounds through demethoxylation reactions [50]. Our results suggest that guaiacol is demethoxylated rather than demethylated during catalytic hydropyrolysis, and the resulting phenolic radical is further hydrogenated to produce phenol as the intermediate. Since no methanol was detected among the products, it can be inferred that the methoxyl radical was further HDO to become either methane or methyl radicals. The methyl radical can be involved in the alkylation reactions predominantly at the ortho position of the phenol radical to produce o-cresol, which was detected among the products in a significant amount. When active hydrogen is sufficiently present, the hydroxyl groups in the phenol and cresol are removed through one-step HDO to produce benzene and toluene, so no carbon oxides would be formed. However, carbon oxides were still observed among the conversion products of guaiacol in this study although their yields decreased. Thus, the results suggest that phenol and cresol intermediates were partly converted under a hydrogen-lean condition, which is mostly likely to take place inside of zeolite pores due to mass transfer limitation of hydrogen. Due to their smaller molecular sizes, phenol and cresol are able to enter the pores of HZSM-5 [51]. Under the hydrogen-lean condition, phenol and cresol mostly underwent decarbonylation and ring opening reactions to produce CO and other intermediate radicals including methylene, ethylene, and propene radicals. Once transferred out of the pores, these radicals further combine with reactive hydrogen to form corresponding stabilized alkenes. The selectivity of both ethylene and propene among aliphatic hydrocarbons were high during catalytic hydropyrolysis of guaiacol, which support the proposed pathway. The CO₂ formation from guaiacol may be attributed to the water-gas shift reactions between CO and H₂O molecules (H₂O as a byproduct of HDO reaction) and the Boudouard reaction [52].

As given in Table 4 above, the combined yield of phenol and cresol was as high as 30.21 C% when guaiacol was converted over HZSM-5. In comparison, the combined yield decreased to 7.68 C% when the conversion was carried out with MoO₃/ZSM-5. Also accompanied were a significantly reduced coke yield and the aromatic yield increasing from 34.78 C% with HZSM-5 to 62.91 C% with MoO₃/ZSM-5. Benzene and toluene were the dominant aromatics with their combined selectivity among total aromatics to be over 82 %. Methane selectivity among aliphatic hydrocarbons increased significantly due to the effective HDO of methoxyls. Overall, MoO₃/ZSM-5 was highly effective in promoting the several reactions described above, including demethoxylation, HDO of methoxyl radicals, alkylation, as well as the HDO of phenolic hydroxyl.

In the case of guaiacol conversion with Ni/ZSM-5, the yield of phenol did not change whereas cresol yield decreased noticeably compared to the conversion over HZSM-5. Alkane yield increased significantly with Ni/ZSM-5, mainly due to increased methane formation. Aromatic yield only slightly increased, however the selectivity to benzene increased noticeably. The results suggest that although demethoxylation was promoted in the presence of Ni, alkylation was suppressed since methoxyls were fully HDO to methane. The selectivity to polyaromatics with Ni/ZSM-5 was lower than that with HZSM-5, but higher than it was observed with MoO₃/ZSM-5. Clearly, the ability of Ni/ZSM-5 for HDO phenolic hydroxyl was poor compared to MoO₃/ZSM-5.

The intermediates produced during syringol conversion were phenol, cresol and dimethyl phenol. Guaiacol was also observed in a small quantity when syringol was converted by Ni/ZSM-5. During catalytic hydropyrolysis, the two methoxyl groups in syringol were demethoxylated to produce a phenolic radical and two methoxyls. The stabilization of the phenol radical by active hydrogen produces phenol, while the HDO of methoxyls followed by alkylations of the phenol radical produces alkylated phenols as intermediates. Finally, the hydroxyls in the phenolic intermediates are removed by HDO to produce corresponding aromatic hydrocarbons. Of course, alkylated benzene could also be formed by alkylation of benzene after phenol was HDO. Dimethyl phenol was observed with syringol, but it was not seen with guaiacol. When syringol was demethoxylated, the radicals were located on the two ortho positions of the phenolic ring. The phenol radicals at the two ortho positions could both combine with methyl to form a dimethyl phenol. When only one of the radicals at an ortho position combines with a methyl and the remaining radical is stabilized by hydrogen, cresol is formed. If the radicals at both ortho positions are stabilized by hydrogen, phenol is formed. For guaiacol conversion, cresol and phenol are the intermediates in Table 4 since only one ortho position was occupied by methoxyl in guaiacol.

Guaiacol was not observed when syringol was converted by HZSM-5 and MoO_3/ZSM -5. Since the two methoxyl groups are at symmetric

positions, they can be removed from syringol at the same time to avoid guaiacol formation. However, double-demethoxylation of syringol will be more challenging than single-demethoxylation of guaiacol as a syringol molecule has to interact with the active site of the catalysts twice. Considering the fact that syringol produced lower aromatic yields and more coke than guaiacol, demethoxylation could be the rate limiting step in the HDO of syringol. If not removed, the two methoxyl groups of syringol will end in radical induced rearrangement to form o-quinonemethide, which is a key intermediate for coke formation from methoxylated phenols [26]. This supposition was also supported by the significantly higher yield of coke from syringol than those from phenol and guaiacol. As mentioned above, the decarbonvlation and ring opening reactions to produce CO and alkene mostly occur under hydrogen-lean environment inside the catalyst pores. However, syringol is unable to enter the catalyst pores due to its large molecular size. Also, CO yield from syringol conversion was much lower compared to the yield produced from guaiacol. Therefore, the results suggest that syringol conversion was mostly likely to have occurred on the catalyst surface. On the catalyst surface, syringol can either be demethoxylated and subsequently HDO, or polymerized. The polymerized syringol can further be dehydrated to coke or deoxygenated to mainly polyaromatics. The alkanes produced from syringol had a higher selectivity to methane because of the increased number of methoxyl groups. Noteworthy, no alkenes were produced from syringol. Alkenes formed during the conversion of polymerized syringol could be rapidly hydrogenated to alkane on the catalyst surface where active hydrogen is more easily accessible. The conversion pathways for syringol and guaiacol during catalytic hydropyrolysis are illustrated in Fig. 2.

Similar to what was observed with guaiacol conversion, the yields of intermediate phenolics from syringol were noticeably lower with MoO_3/ZSM -5 compared to that with HZSM-5. Aromatic yields increased significantly from 24.28 C% with HZSM-5 to 41.82 C% with MoO_3/ZSM -5, which was also accompanied by the coke yield decreasing from 40.44 C% to 25.63 C%. Benzene, toluene, and xylene were major products, with their combined selectivity among total aromatic hydrocarbons to be 90 %. There was no significant decrease in the yield of aliphatic hydrocarbons with MoO_3/ZSM -5.

When syringol was converted over Ni/HZSM-5, the yields of phenol and cresol increased significantly whereas the yield of dimethyl phenol decreased in comparison to the conversions over HZSM-5 and MoO₃/ ZSM-5. The decreased yield of dimethyl phenol confirms that alkylation of phenol radicals was inhibited with Ni/ZSM-5. Methane was the only aliphatic hydrocarbon product with Ni/ZSM-5 due to its strong hydrocracking ability and HDO of methoxyls. Guaiacol was only found with syringol conversion over Ni/ZSM-5. Thus, the results suggest that a partially demethoxylated syringol was quickly hydrogenated to form guaiacol with Ni/ZSM-5 before the second methoxyl on the symmetric ortho position was removed. However, the probability of this pathway is low since the yield of guaiacol was very low. Total aromatic yield was 29.67 C%, lower than the yield produced from MoO₃/ZSM-5. However, the selectivity of single aromatics increased with Ni/ZSM-5, due to hydrocracking. The coke formation was suppressed by Ni/ZSM-5, but the yield was still high at 33.12 C%. From Table 4, phenol yield during syringol conversion was particularly high with Ni/HZSM-5, indicating that Ni/HZSM-5 is not effective in removing phenolic hydroxyl. Nevertheless, Ni/ZSM-5 still outperformed HZSM-5 due to the enhanced hydrocracking of syringol. The fragments produced from the hydrocracking could enter the catalyst pores to be aromatized to form aromatic hydrocarbons.

3.5. Effect of pyrolysis vapor composition during catalytic hydropyrolysis of lignin

In general, hardwood lignin mainly consists of S and G units and softwood lignin contains mostly G units. Herbaceous lignin, on the other hand, consists of H, G, and S units. Accordingly, pyrolysis vapors derived from CS, LP, and RO lignin prior to entering the catalytic bed consisted of different amounts of H, G, and S based compounds. As shown in Section 3.4, the yields of aromatic hydrocarbons from phenol, guaiacol, and syringol were significantly different from each other due to the variations in the number of methoxyl group attached on the phenolic ring. Therefore, the yield of aromatic hydrocarbons produced from lignin could be correlated to the contents of H, G, and S-based compounds in the lignin-derived pyrolysis vapor prior to the catalytic conversion. To study this relationship, the phenolic monomers produced from CS, LP, and RO lignin during non-catalytic hydropyrolysis given in Table 1 were categorized into H, G, and S-based monomer groups. The relative fractions of the H, G, or S compound group were then calculated by dividing the yields of the H. G. or S -based monomers by the total monomer yields and the results are given in Table S1 for different types of lignin. As shown, while CS lignin-derived monomers consisted of comparable fractions of H, G, and S based monomers, the fraction of H-based monomers was the highest, accounting for 47 %. On the other hand, LP lignin-derived monomers included over 73 % of Gbased monomers and the rests were nearly equally distributed between H and S-based monomers. RO lignin-derived monomers, on the other hand, consisted of about 64 % of S-based monomers. The fraction of total G-based monomers was 28 % and H-based monomers only accounted for 8 %. Therefore, the distributions of H, G, and S-based monomers among total monomers produced from CS, LP, or RO lignins upon thermal hydropyrolysis prior to catalytic conversions agree with general distributions of H, G, and S units in herbaceous, softwood, and hardwood-based lignin feedstocks. As shown in Table 1, lignin-derived pyrolysis vapors also contain phenolic oligomers. Although the specific structures of the phenolic oligomers are impossible to determine analytically, it is reasonable to assume that the relative distributions of H, G, and S-based compounds among oligomers and monomers are the same for a lignin. Accordingly, the yields of H, G, and S-based compounds (including both monomers and oligomers) prior to the pyrolysis vapors of the ligning entering the catalytic bed were calculated and the results are also given in Table S1 for different types of lignin.

To evaluate the effect of methoxyl groups, it was assumed that phenol and other H-based individual compounds in the pyrolysis vapor would produce the same yield of total aromatic hydrocarbons when they were converted over the same type of catalyst. Similar assumptions were also made with the guaiacol and other G-based compounds, as well as with the syringol and other S-based compounds. "Calculated" total yields of aromatic hydrocarbons produced from different types of lignin were then determined using following Eq. (3) and the results given in Table 4 and Table S1:

 $Y_{cal} = Y_H \times Y_{phenol} + Y_G \times Y_{guaiacol} + Y_S \times Y_{syringol}$ (3)

 Y_{cal} - "calculated" carbon yield of total aromatic hydrocarbons from lignin upon catalytic hydropyrolysis;

 Y_{H} - the carbon yield of H-based compounds from thermal hydropyrolysis of lignin;

 Y_G - the carbon yield of G-based compounds from thermal hydropyrolysis of lignin;

 Y_S - the carbon yield of S-based compounds from thermal hydropyrolysis of lignin;

 Y_{phenol} - the carbon yield of total aromatic hydrocarbons from catalytic hydropyrolysis of phenol;

 $Y_{guaiacol}$ - the carbon yield of total aromatic hydrocarbons from catalytic hydropyrolysis of guaiacol;

Y_{syringol} - the carbon yield of total aromatic hydrocarbons from catalytic hydropyrolysis of syringol;

The "calculated" yields of aromatic hydrocarbons were further compared with their corresponding experimental yields previously given in Table 4 for different types of lignin with different types of catalysts and the comparison results are shown in Fig. 3.

It should be noted that assuming any individual phenolic compound to produce same yield of total aromatic hydrocarbons as that would be



Fig. 2. Reaction pathways of guaiacol (upper) and syringol (lower) during catalytic hydropyrolysis.

produced from either phenol, guaiacol or syringol is ideal. Most ligninderived phenolic monomers and oligomers are much more complex than phenol, guaiacol, or syringol due to the presence of additional side-chain functionalities and/or higher degree of polymerization. However, the overall effects of the methoxyl content in the pyrolysis vapor associated to the compositions of H, G, and S-based compounds could still be evaluated using the present assumption.

From Fig. 3 (a), (b) and (c), the "calculated" yield of the total aromatic hydrocarbons is highest with CS lignin, followed by LP lignin, and RO lignin with all three types of catalysts. This trend well agrees with the trend observed among the experimental yields of total aromatic hydrocarbons produced from CS, LP, and RO lignins. As described above, the content of H-based compounds was highest in CS ligninderived pyrolysis vapor. G-based compounds were abundant in LP lignin-derived vapor, while S-based compounds were dominant in RO lignin-derived vapor. Thus, the yields of total aromatic hydrocarbons produced from lignin were reversely correlated to the abundancy of methoxyls in the pyrolysis vapor.

By comparing the "calculated" yield and experimental yield, it was also possible to investigate the conversion of complex monomers and oligomers compared to the conversion of simple monomers during catalytic hydropyrolysis. Other than feedstock lignin type, the composition of lignin-derived pyrolysis vapor can also be affected by various factors, such pyrolysis temperature, vapor residence time, and the presence of additives [53]. Overall, the high pyrolysis temperature and

longer vapor retention time at high reaction temperatures promote the vapor cracking and therefore increase the production of smaller and simpler phenolics [54]. The lignin-derived phenolic oligomers are usually considered difficult to catalytically upgrade. It was reported that phenolic oligomers are the main source of catalytic coke because they mostly adsorb on the zeolite surface to polymerize due to large molecular sizes [51]. From such a point of view, the lignin-based pyrolysis vapors containing smaller phenolics compounds should be more preferred in order to produce more aromatic hydrocarbons upon catalytic conversion. In this study, the "calculated" yields were obtained from Eq. (3) using the aromatic yields that would be produced from phenol, guaiacol, or syringol for all other compounds. Thus, if "calculated" yield is higher than the experimental yield, it can be implied that the pyrolysis vapor consisting of simple monomers (e.g., phenol, guaiacol or syringol) would produce higher aromatic yields than the pyrolysis vapor containing more complex phenolics from their corresponding H, G, or S groups. If the experimental yield is higher than the "calculated" yield, then it means that the pyrolysis vapors containing complex monomers and oligomers would produce more aromatic hydrocarbons than the vapors composed of simple monomers. In Fig. 3, the "calculated" yields of aromatic hydrocarbons are higher than their respective experimental yields for most of the cases. In the cases of catalytic conversions with MoO₃/ZSM-5 or Ni/ZSM-5, the "calculated" vields were always higher than experimental yields for all three lignin. Thus, it can be suggested that the pyrolysis vapors containing simple



Fig. 3. Comparison of "calculated" yield and experimental yield of total aromatic hydrocarbons produced from catalytic hydropyrolysis of lignin. CS, LP and RO represent lignin from corn stover, loblolly pine and red oak, respectively.

monomers produce higher yields of aromatic hydrocarbons than the vapors containing complex monomers and larger oligomers when catalvtically hydropyrolyzed over the bifunctional catalysts. The difference between the "calculated yield" and experimental yield was the most significant with CS lignin-derived vapor, followed by LP ligninderived vapor, and smallest for RO lignin-derived vapor. CS lignin-derived vapor contains the highest amount of H-based compounds. Not only phenol is HDO at the catalyst surface benefited by the metal or metal oxide catalyst, but it also can be converted at the active sites inside the zeolite pores assisted by external hydrogen. In comparison, most other H-based compounds may not be able to directly enter the catalyst pores due to their larger molecular sizes, and thus mainly convert on the catalyst surfaces. Since the active sites on zeolite pores could not be utilized effectively, H-based complex monomers and oligomers would have overall lower conversion efficiency than phenol conversion. Accordingly, the difference between the "calculated" yield and experimental yield was noticeable with CS lignin. On the other

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hand, guaiacol and syringol cannot directly enter the catalyst pores due to their molecular sizes being larger than the pores, as such with the other G-based or S-based compounds. Therefore, they were both converted at the catalyst surfaces. Only some intermediates formed at the surface reactions, such as phenol, cresol, or side chain fragments from the hydrocracking could enter the catalyst pores. The reactions on the catalytic surface are particularly dominant when syringol and other Sbased compounds were converted. Since LP lignin-derived vapor contains mostly G-based compounds and RO lignin-derived vapor contains more S-based compounds, the differences between the "calculated" vields and experimental vields were smaller in LP lignin and RO lignin. The "calculated" vield was even slightly lower than the experimental vield in LP lignin and RO lignin in the case of HZSM-5, implying no advantage in upgrading the pyrolysis vapor composed of simple monomers as opposed to the pyrolysis vapors containing complex monomers and oligomers. Due to the absence of a hydrogenation catalyst, G or S-based compounds including guaiacol and syringol would be easily adsorbed on the zeolite surface of HZSM-5 and polymerize to form coke rather than hydrocarbons. The experimental yield was slightly higher than the "calculated" yield, probably because side chain fragments from the cracking of the oligomers or the monomers with complex side chains can enter the zeolite pores to form aromatic hydrocarbons. With MoO₃/ZSM-5 or Ni/ZSM-5, the fragments with short carbon numbers would be more easily hydrogenated at the catalyst surface to form aliphatic hydrocarbons rather than aromatic hydrocarbons.

4. Conclusions

The present study showed that the catalytic hydropyrolysis of lignin under atmospheric pressure is highly effective in converting various lignin into valuable hydrocarbons compared to catalytic pyrolysis with inert gas. MoO₃/ZSM-5 outperformed HZSM-5 and Ni/ZSM-5 by increasing the yield of aromatic hydrocarbons and significantly reducing catalyst coke. On the other hand, Ni/ZSM-5 mainly promoted the production of aliphatic hydrocarbons. The aromatic yields were highest with CS lignin followed by LP lignin and RO lignin with all three catalysts. The studies using phenol, guaiacol, and syringol as model monomers showed that demethoxylation, HDO of methoxyls, and ring alkylation occurred during catalytic hydropyrolysis to produce phenol, cresol, and dimethylphenol as the intermediates. Subsequent removal of hydroxyls from the phenolic intermediates by HDO produces benzene and alkylated benzene. MoO3/ZSM-5 could rapidly hydrodeoxygenate phenol to produce benzene at selectivity over 92 %. The ability of Ni/ZSM-5 for phenolic-hydroxyl HDO was less effective, but the catalyst could promote hydrocracking and hydrogenation reactions. The study also showed that the aromatic yield produced from different types of lignin is reversely correlated to the abundancy of methoxyl phenols in their pyrolysis vapors. It was further found that the pyrolysis vapors rich in phenol produces higher yield of total aromatic hydrocarbons compared to the pyrolysis vapors containing more complex Hbased monomers and oligomers. However, there was no significant variation on the yields of total aromatic hydrocarbons produced from the vapors containing guaiacol and syringol compared to the yield produced from the vapor composed of complex G or S-based monomers and oligomers.

CRediT authorship contribution statement

Yuan Xue: Conceptualization, Writing - original draft, Investigation. Ashokkumar Sharma: Investigation, Formal analysis. Jiajie Huo: Investigation, Writing - original draft. Wangda Qu: Methodology, Software. Xianglan Bai: Conceptualization, Supervision.

Declaration of Competing Interest

The authors confirm that there are no known conflicts of interest associated with this publication.

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Appendix A. Supplementary data

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