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A study of guaiacol, cellulose, and Hinoki wood pyrolysis with silica, ZrO_2 & TiO_2 and ZSM-5 catalysts

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ABSTRACT

Catalytic pyrolysis of biomass is often used to improve bio-oil quality and energy content. In order to better understand the interactions between various catalysts and biomass components, individual components of biomass were isolated and pyrolyzed with different catalysts. Understanding the interactions between pyrolysis vapors and catalysts is important to create catalysts that can improve bio-oil quality and energy content in the future. In this study, cellulose, guaiacol (as a model for lignin), and Hinoki wood were pyrolyzed and catalyzed with silica, ZrO_2 & TiO_2, and ZSM-5 with an SiO_2-to-Al_2O_3 (SAR) ratio of 40 and 1500. GC–MS analysis was used to measure the effects of the different catalysts on the pyrolysis vapors. It was found that silica had a strong interaction with the hydroxyl groups of levoglucosan and significantly decreased sugars in both cellulose and Hinoki wood pyrolysis. ZrO_2 & TiO_2 increased the amount of cyclopentanones and aromatics with Hinoki wood pyrolysis. The ZSM-5 catalysts also increased aromatic hydrocarbons and oxygenated hydrocarbons with Hinoki wood pyrolysis. Based on these results, specific reactions of the catalysts were proposed. Additionally, ZSM-5 with a SAR ratio of 1500 has very few acidic sites, so the steric effects of ZSM-5 could be isolated. These results are discussed and contrasted with ZSM-5 with a SAR ratio of 40. These results show that microporous catalysts and moderate acidity are optimal for improving bio-oil quality.

1. Introduction

The demand for energy increases every year as countries around the world become more industrialized. Due to environmental concerns and limited supply of fossil fuels, scientists are conducting research on alternative energy sources. Biomass is considered as a potential alternative fuel source due to its carbon neutral process and renewability. Biomass can be converted to bio-oil through pyrolysis with high yields of 60–70% by mass [1]. However, the bio-oil is a complex mixture of oxygenated compounds which decreases the energy density and quality of the bio-oil [2]. For this reason, scientists are using various methods to upgrade the bio-oils. One promising method for improving bio-oils is using catalysts in the pyrolysis vapor stream to promote desired reactions.

Scientists have extensively studied and discussed many different types of catalysts for upgrading pyrolysis vapors [2]. Among these, ZSM-5 and zirconia/titania catalysts are considered to be the most promising because they result in a treated bio-oil with reduced oxygen and high aromatics content [3]. However, the catalytic upgrading mechanism is still not fully understood. Biomass is mainly composed of three structural components: cellulose, hemicellulose and lignin. In order to better understand the interactions between the catalyst and biomass vapors, Stefanidis et al. and Zheng et al. pyrolyzed the individual components of biomass with ZSM-5 and compared them to uncatalyzed products [4,5]. Other researchers such as Shoucheng Du et al. have studied model compounds (toluene, furane and miscanthus) from biomass and pyrolyzed them over ZSM-5 to get a better understanding of the catalytic mechanism [6]. Haian Xia et al. studied the effects of ZSM-5 and other catalysts on cellulose pyrolysis [7]. ZSM-5 is often studied; however other catalysts are not as well understood. In this research, we also pyrolyzed biomass components with ZSM-5 to verify the findings for benchmarking, and then expanded the study with other catalysts. The results were compared with uncatalyzed products and other researcher's results. The purpose of this study is to not only to verify the ZSM-5 results, but also understand how other catalysts interact with individual components of biomass.

In this study, cellulose, guaiacol, and Hinoki (Japanese Cypress) wood were chosen as the three types of feed for pyrolysis. Cellulose was chosen because Hinoki wood is composed of about 60% holocellulose (cellulose and hemicellulose). Hemicellulose was not commercially available, so only cellulose was used to model the sugars in the wood. The remaining 40% is composed of lignin and acid-soluble hydrocar-

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bons [8]. Guaiacol was chosen as a model compound for lignin because experimental and computational research has shown that lignin first generates mainly syringol and guaiacol characteristic products [9]. Finally, Hinoki wood was chosen as it was readily available here in Japan for pyrolysis due its use as a building material.

In this study, 4 types of catalysts were used. Two types of ZSM-5 were used. One had a SiO_2-to-Al_2O_3 (SAR) ratio of 40 and the other ZSM-5 catalyst had a SAR ratio of 1500. Lower SAR ratios cause higher acidity. However, changing the SAR ratio does not change the overall structure of the catalyst [10]. By using a ZSM-5 catalyst with high SAR ratio of 1500 we can isolate the steric effects of the catalyst and compare it to the ZSM-5 with increased acid strength and acid site density. ZrO_2 & TiO_2 was chosen as it has been shown to increase hydrocarbon content in bio-oil and improve bio-oil quality [3,11]. Finally, a blank silica catalyst was also used for comparison with the other catalysts. The catalysts were used for the pyrolysis of each feed and the collected bio-oil was analyzed with GC–MS.

2. Experimental

2.1. Materials and methods

The biomass feed, consisting of Hinoki (Japanese Cypress) wood chips was supplied by a local store. Wako Pure Chemical Industries supplied the 38 μm powdered cellulose and it was used without modification. Guaiacol (99% purity) was supplied by Acros Oganics and it was used without modification. The Hinoki wood chips were sieved through 2.8 mm and 5.0 mm size trays and the 2.8 mm −5.0 mm wood chips were used. Elemental analysis was performed on the Hinoki wood using a Yanaco CHN corder MT-6 elemental analyzer and the results are shown below in Table 1. Oxygen was calculated by subtracting the total of the other compounds from 100%.

The ZrO_2 & TiO_2 (40% Anatase TiO_2) with pore sizes of 11 nm, 16 nm, and 121 nm and surface area of 86.8 m^2/g was supplied by Saint Gobain NorPro and the silica beads with a pore size of 16.1 nm and surface area of 203 m^2/g (CARiACT Q-15) was supplied by Fuji Silysia Chemical LTD. The ZSM-5 with a SAR ratio of 1500 (1500 ZSM-5) and the ZSM-5 with a SAR ratio of 40 (40 ZSM-5) were supplied by Tosoh and used without modification. The 1500 ZSM-5 had a surface area of 310 m^2/g and the 40 ZSM-5 had a surface area of 330 m^2/g. Both ZSM-5 catalysts had a pore size of 0.58 nm. Catalysts were heated in an oven at 80 °C overnight before use.

2.2. Experimental methods

A 50 mm diameter pyrolysis reactor was loaded with Hinoki (12 g) and catalyst (12 g) and then the entire system was purged with flowing nitrogen gas for 5 min. Afterwards, the pyrolysis reactor was heated to the target temperature (500 °C) with a heating rate of 32 °C/min. The pyrolyzed vapors were carried by the nitrogen over the catalyst bed. Guaiacol is a liquid at room temperature and was fed into the top of the reactor at 2 mL/min using a NE-1000 syringe pump made by New Era Pump Systems Inc. after the reactor was held at 500 °C for 10 min. Hence, the heating rate for the guaiacol feed and the other feeds are different. Different heating rates can cause different product distributions; however, if the guaiacol was not heated rapidly, it may evaporate at 205 °C and condense in the condenser rather than pyrolyzing [12]. Rapid heating was used to increase the conversion of guaiacol to pyrolysis products. The vapors were condensed using an ice bath. The resulting bio-oil was collected and analyzed. The char & coke and the bio-oil masses were weighed to obtain an overall mass balance of the system. The char & coke and bio-oil mass subtracted from the initial feed was assumed to be the mass of off-gas (Fig. 1).

Table 1
Elemental analysis of Hinoki wood.

Element	Percent
C	46%
H	6%
N	0.1%
O	48%

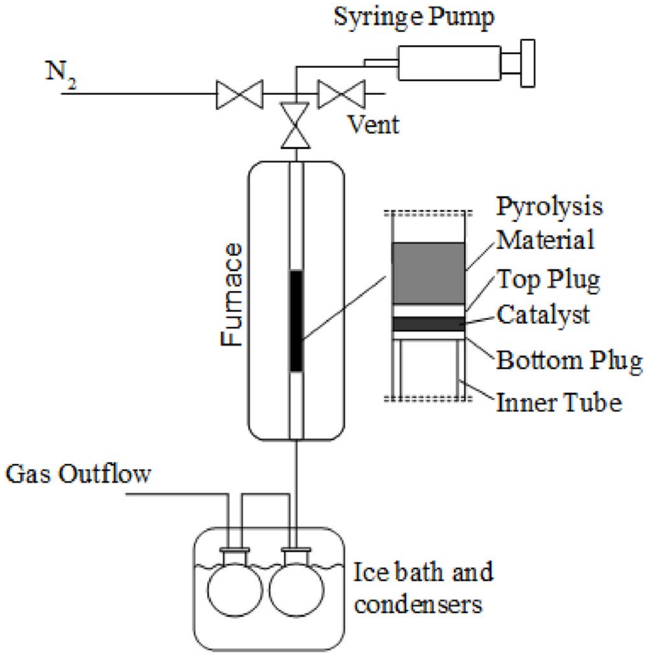

Fig. 1. Experimental set-up for pyrolysis experiment.

2.3. GC–MS methods

In order to identify compounds and qualitatively analyze the bio-oil samples, GC–MS was conducted on all bio-oil samples. Samples were prepared as ∼5% solution mixed with acetone.

The GC–MS analysis was performed on a GC-2010 Plus equipped with a GC–MS-QP2010 SE mass-detector made by Shimadzu. The column used was an Rtx-5MS 30 m x 0.25 mm, 0.25 μm. The analysis was run with a 5–1 split entry. For cellulose and wood samples, the oven temperature was held at 40 °C for 10 min and then ramped to 50 °C at 1 °C/min. Next, it was ramped to 130 °C at 2 °C/min. Finally, the temperature was ramped to 300 °C at 4 °C/min and held for 5 min. Fewer compounds were expected in the guaiacol samples so a faster GC–MS program was used. The oven temperature was held at 40 °C for 10 min and then ramped to 50 °C at 1 °C/min. Next, it was ramped to 100 °C at 2 °C/min. Finally, the temperature was ramped to 270 °C at 20 °C/min and held for 5 min. The compounds were identified by comparing the mass spectra to NIST 11 MS library of compounds using the GC–MS software. A similarity threshold of over 80 was used to identify the compounds. All GC–MS experiments were conducted in duplicates and the standard deviations were calculated.

3. Results and discussion

3.1. Yield results of pyrolysis

The catalysts were used to catalyze pyrolysis vapors with various feeds. The bio-oil and char & coke were weighed and the yields were calculated after the pyrolysis process for each experiment. Figs. 2–4 show the mass yields of different feeds. The gas yield is calculated by subtracting the mass of char and oil from the initial mass of wood feed. Each uncatalyzed experiment was conducted 3 times to measure the

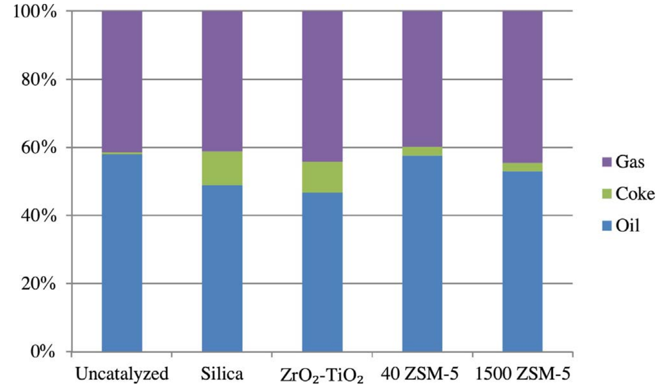

Fig. 2. Gas, coke and oil yields for pyrolysis of guaiacol with different catalysts.

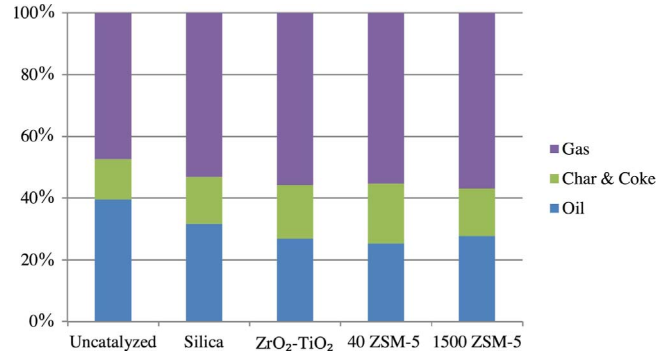

Fig. 3. Gas, char & coke and oil yields for pyrolysis of cellulose with different catalysts.

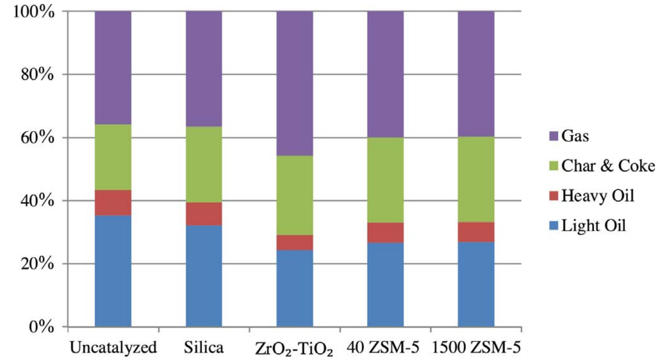

Fig. 4. Gas, char & coke and oil yields for pyrolysis of Hinoki wood with different catalysts.

repeatability of the pyrolysis apparatus.

Guaiacol is a model compound for lignin and was pyrolyzed. The triplicate uncatalyzed bio-oil yields had a standard deviation of 3.3% and the coke had a standard deviation of 0.7%. The bio-oil was created with a 58% yield from guaiacol. When the 40-ZSM-5 catalyst was used the yield slightly decreased to around 55% yield. This is similar to the results observed by other researchers who also observed a slight decrease in bio-oil yield when pyrolyzing lignin with ZSM-5 [4,13]. Guaiacol is expected to have similar reactions as lignin. The silica and ZrO_2-TiO_2 had a more substantial decrease in bio-oil yield and an increased amount of coke build up on the catalyst.

The bio-oil yield from uncatalyzed cellulose pyrolysis was 40% and had a standard deviation of 1.0%. The char had a standard deviation of 0.1%. This yield decreased with all catalysts, especially with 40 ZSM-5 and ZrO_2-TiO_2. The amount of char & coke for catalyzed experiments increased with catalyst used. Again, 40-ZSM-5 and ZrO_2-TiO_2 had the largest increase in char & coke. While, Haian Xia et al. and Xinlai Wei et al. observed an increase in bio-oil yield and a decrease in char & coke when cellulose was pyrolyzed with ZSM-5 catalyst, Stefanidis et al. observed a decrease in bio-oil yield with ZSM-5 catalyst [4,7,14]. The reason behind this discrepancy is not clear but, we also observed a decrease in bio-oil with ZSM-5 catalysts.

The bio-oil yield was 45% for uncatalyzed Hinoki wood and had a standard deviation of 1.0% for the light oil and 1.4% for the heavy oil. The char had a standard deviation of 0.1%. The uncatalyzed pyrolysis resulted in the largest yield of bio-oil. When catalyst was used, the yield of the bio-oil decreases and the coke increases. This is the same pattern as cellulose and guaiacol feed. Wood pyrolysis resulted in two phases (organic and aqueous) that were not observed with the other two feeds. Overall, guaiacol pyrolysis results in the highest yield of bio-oil, followed by Hinoki wood and then cellulose. Cellulose is expected to have a higher bio-oil yield than Hinoki wood because it is more easily converted to liquid products. Wood is composed in part of recalcitrant lignin and so lower yield is expected. However, Muley et al. also observed that wood had a higher bio-oil yield than cellulose [15]. This may be due to the high amount of initial biomass used in these experiments, which generally decrease the overall yield.

3.2. GC–MS results of guaiacol pyrolysis

The pyrolyzed guaiacol vapors were catalyzed and the bio-oils were analyzed with GC–MS. The results of the identified peaks are presented below in Table 2. On average, 6% of the peaks were unidentified. Pyrolysis of guaiacol and other feed materials resulted in hundreds of compounds so direct comparison between the catalysts is difficult. To make comparison easier between catalysts, the compounds were classified into different groups based off the work done by others [11,16]. These groups are acids, aldehydes, alcohols, cyclopentanones (CP), furans, hydrocarbons (HC), ketones, phenols, sugars, aromatic hydrocarbons (AR), oxygenated aromatics (OA), and others. Categories with small amounts of compounds were combined and added to the 'others' category to simplify the tables.

Uncatalyzed guaiacol feed resulted in 85% phenolic compound. Minor amounts of various oxygenated aromatics and aromatic hydrocarbons were also detected. Huang et al. had similar experimental results and computatively determined that the initial reaction step of guaiacol pyrolysis is the homolytic cleavage of the $CH_3{-}O$ bond [17]. Also, the addition of an H to the carbon atom of the benzene ring on which the methoxy is connected decreases the activation energy of demethoxy reaction of guaiacol [9,17]. Hence, an acidic catalyst is expected to decrease the activation energy of the demethoxy reaction and increase yields of phenolic products. All catalysts promoted demethoxy reactions and decreased the amount of guaiacol in the final products as shown in Table 3 below.

Table 2
Composition of guaiacol pyrolysis products (peak area% of identified peaks).

Guaiacol Feed	Furan%	HC%	Phenols%	AR%	OA%	Other%
Uncatalyzed	5.1 ± 0.5	0.3 ± 0.1	85.4 ± 2.1	0.6 ± 0.5	7.9 ± 1.1	0.6 ± 0.2
Silica	3.5 ± 1.5	0.3 ± 0.1	86.4 ± 1.1	0.8 ± 0.4	8.2 ± 0.6	0.7 ± 0.0
ZrO_2-TiO_2	3.2 ± 1.0	0.3 ± 0.2	84.3 ± 0.9	2.0 ± 0.8	9.2 ± 0.9	0.8 ± 0.1
40 ZSM-5	4.9 ± 0.2	1.7 ± 0.1	82.8 ± 1.6	2.4 ± 0.6	7.4 ± 0.7	0.6 ± 0.1
1500 ZSM-5	4.7 ± 0.2	0.5 ± 0.1	83.9 ± 1.9	2.2 ± 0.2	7.9 ± 1.6	0.6 ± 0.0

Table 3
Detailed classification of phenolic compounds from guaiacol pyrolysis.

Guaiacol Feed	Catechol%	Cresol%	Ethylphenol%	Guaiacol%	Phenol%	Other%
Uncatalyzed	20.9 ± 0.8	21.8 ± 1.7	9.5 ± 0.2	9.9 ± 2.6	8.8 ± 1.0	28.9 ± 4.7
Silica	24.2 ± 0.9	24.8 ± 0.0	8.9 ± 0.1	2.8 ± 0.4	12.9 ± 0.6	26.4 ± 1.1
ZrO_2-TiO_2	17.9 ± 1.6	21.7 ± 0.3	8.9 ± 0.3	0.4 ± 0.0	21.4 ± 0.6	29.7 ± 1.7
40 ZSM-5	25.9 ± 1.0	25.5 ± 0.7	8.8 ± 0.4	0.5 ± 0.0	11.9 ± 0.0	27.3 ± 2.1
1500 ZSM-5	24.3 ± 1.3	27.3 ± 1.1	9.8 ± 0.4	0.1 ± 0.1	12.6 ± 1.1	26.0 ± 1.7

Uncatalyzed guaiacol pyrolysis had about 10% unconverted guaiacol, which was decreased to 3% with silica. The ZrO_2-TiO_2 and ZSM-5 catalysts decreased the guaiacol to nearly 0% indicating that the catalysts aid in reactions occurring with the methoxy group on the guaiacol. The ZrO_2-TiO_2 caused a decrease in catechol and cresol, which significantly increased phenols when compared with the other catalysts. According to Heejin Lee et.al, phenol can be produced from the deoxygenation of catechol, which is formed by the demethylation of guaiacol, or phenol can be produced from direct demethoxylation of guaiacol [18]. According to our results, the ZrO_2-TiO_2 appears to promote the deoxygenation of catechol, thereby increasing the phenols. ZrO_2-TiO_2 is known to promote deoxygenation reactions and increase hydrocarbons, which supports these results [11].

These results show that the hydroxyl groups on the phenol and catechol are refractory to ZSM-5 because the phenolic compounds were not converted to benzene or other aromatic hydrocarbons in significant amounts. Only a slight increase in toluene, styrene, and azulene was observed with ZSM-5 catalysts. Horne et al. tested ZSM-5 with anisole and Stafanidis et al. tested ZSM-5 with lignin and reported similar findings and also concluded that the ZSM-5 catalyst is refractory to C—O bond between the aromatic ring and the hydroxyl group of phenolic compounds [4,19]. They also reported that the bio-oil remains unaltered with ZSM-5 catalyst with different lignin-type feeds. Finally, the 1500 ZSM-5 catalyst also had no significant change in products. However, the slight increase in hydrocarbons was not observed with the 1500 ZSM-5 indicating the conversion to hydrocarbons is due to the acidic sites on the ZSM-5 catalyst rather than steric effects.

3.3. GC–MS results of cellulose pyrolysis

The pyrolyzed cellulose vapors were catalyzed and the bio-oils were analyzed with GC–MS. The GC curves are shown below in Fig. 5.

While guaiacol pyrolysis had very uniform product distribution regardless of catalysts, cellulose pyrolysis had large changes in product distribution with different catalysts. The major products of uncatalyzed cellulose were levoglucosan (48%), 5-Hydroxymethylfurfural (5%), and furfural (11%). Additionally, many smaller peaks were identified and sorted into the same categories as were used previously. The results of the identified peaks are shown below in Table 4. On average, 12% of the peaks were unidentified.

The catalysts had a significant effect on the sugars, phenols, and furans in our study of cellulose pyrolysis. Some researchers have noted the creation of phenolic compounds in uncatalyzed cellulose bio-oil [15]. However, in this study and others, phenolic compounds were not found in uncatalyzed cellulose pyrolysis [20]. In Fig. 5, the levoglucosan peak formed through depolymerization of cellulose is at 70 min and significantly decreases with silica catalyst. Choi et al. suggest that the silica oxide layer binds to the hydroxyl groups on the levoglucosan molecule thereby decreasing the sugar concentration in the bio-oil [21]. ZrO_2-TiO_2 and 40 ZSM-5 also significantly decreased the sugar concentration in the final bio-oil product from 51% to 27% and 21% respectively. However, 1500 ZSM-5 had no effect on the levoglucosan peak according to the integration results. 40 ZSM-5 had a significant increase in phenols while the ZrO_2-TiO_2 catalyst showed a significant increase in furans. Other researchers also saw a significant increase in phenolic compounds due to ZSM-5 catalysts and suggested that the phenolic compounds are formed from secondary reaction of the cellulose vapors [4,22]. Additionally, as was shown with the guaiacol pyrolysis, ZSM-5 is refractory to conversion of phenols to other compounds so any created phenolic molecules pass unconverted through the catalyst.

3.4. GC–MS results of Hinoki wood pyrolysis

Hinoki wood is a combination of cellulose, hemicellulose, and lignin. As the lignin is modeled by guaiacol, the pyrolysis results of Hinoki wood is expected to be partially a combination of the results of cellulose and guaiacol. The Hinoki wood pyrolysis resulted in two

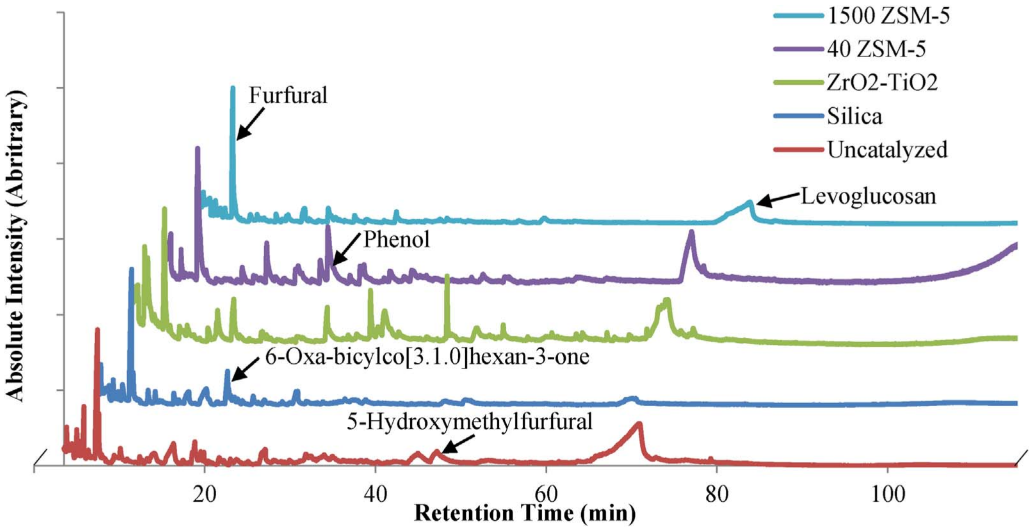

Fig. 5. GC–MS results of pyrolyzed cellulose.

Table 4
Composition of cellulose pyrolysis products (peak area% of identified peaks).

Cellulose Feed	Acid%	CP%	Furan%	Ketone%	Phenols%	Sugar%	Other%
Uncatalyzed	2.9 ± 2.4	6.6 ± 2.9	26.5 ± 0.0	5.7 ± 3.4	0.6 ± 0.5	51.1 ± 4.9	6.7 ± 3.5
Silica	3.5 ± 0.1	17.3 ± 4.9	47.6 ± 3.5	10.6 ± 1.8	1.1 ± 0.7	10.4 ± 4.0	9.5 ± 7.8
ZrO_2-TiO_2	5.5 ± 0.6	10.6 ± 3.3	38.4 ± 2.4	5.5 ± 0.7	1.9 ± 1.4	26.5 ± 2.1	11.7 ± 5.1
40 ZSM-5	1.7 ± 1.3	16.0 ± 1.4	30.1 ± 3.9	2.7 ± 1.9	17.9 ± 2.3	21.0 ± 2.7	10.7 ± 4.4
1500 ZSM-5	3.2 ± 0.9	8.3 ± 2.9	24.9 ± 2.6	5.2 ± 2.3	1.0 ± 0.2	50.5 ± 2.9	6.9 ± 3.7

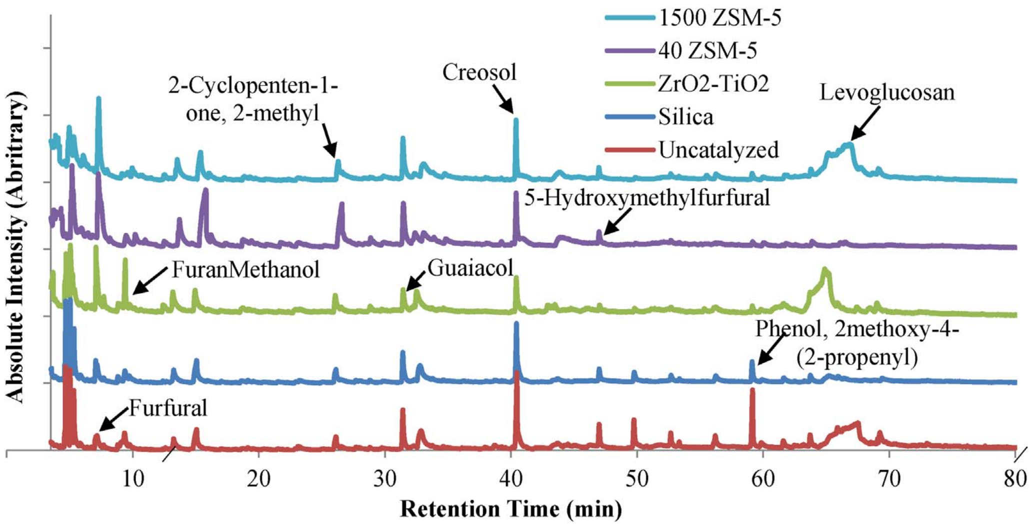

Fig. 6. GC–MS results of pyrolyzed Hinoki wood (aqueous phase).

Table 5
Composition of aqueous-phase bio-oil products (peak area% of identified peaks).

Hinoki Feed	Acid %	Aldehyde %	Alcohol %	CP %	Furan %	Ketone %	Phenols %	Sugar %	Other %
Uncatalyzed	5.5 ± 0.1	5.1 ± 2.5	3.1 ± 2.9	4.3 ± 1.1	7.3 ± 5.2	4.7 ± 0.9	35.7 ± 2.1	27.0 ± 1.9	7.4 ± 2.7
Silica	7.1 ± 4.6	6.7 ± 2.6	9.8 ± 1.1	10.5 ± 1.7	7.9 ± 2.0	11.1 ± 0.1	31.6 ± 0.4	5.7 ± 0.9	9.7 ± 2.8
ZrO_2-TiO_2	6.2 ± 3.9	5.7 ± 1.1	4.9 ± 1.4	18.1 ± 2.2	6.0 ± 5.0	5.4 ± 3.3	16.3 ± 4.6	31.8 ± 8.4	5.5 ± 3.2
40 ZSM-5	7.5 ± 2.0	3.3 ± 3.6	5.4 ± 2.7	24.3 ± 5.8	7.3 ± 0.4	7.1 ± 1.3	23.0 ± 2.9	1.7 ± 0.1	20.4 ± 6.6
1500 ZSM-5	7.5 ± 5.2	3.7 ± 1.9	2.7 ± 1.4	13.4 ± 3.7	6.3 ± 0.8	6.3 ± 2.6	15.9 ± 1.8	40.8 ± 7.8	3.4 ± 3.6

Table 6
Composition of organic-phase bio-oil products (peak area% of identified peaks).

Hinoki Feed	Acid %	CP %	Furan %	HC %	Ketone %	Phenols %	AR %	OA %	Other %
Uncatalyzed	3.5 ± 0.6	4.0 ± 1.3	11.4 ± 2.3	5.8 ± 1.4	6.0 ± 0.3	51.7 ± 2.2	2.6 ± 2.9	2.4 ± 1.2	12.6 ± 0.5
Silica	1.6 ± 0.5	1.1 ± 1.6	7.7 ± 1.0	4.7 ± 1.1	3.5 ± 0.3	66.9 ± 0.6	5.8 ± 1.3	7.2 ± 2.5	1.4 ± 0.5
ZrO_2-TiO_2	2.4 ± 0.6	9.4 ± 0.2	9.3 ± 1.5	4.0 ± 0.1	1.6 ± 0.0	58.0 ± 0.4	6.8 ± 0.2	5.2 ± 2.4	2.8 ± 0.4
40 ZSM-5	0.8 ± 0.0	2.6 ± 2.6	2.4 ± 2.5	4.6 ± 5.2	0.3 ± 0.4	61.8 ± 4.5	14.3 ± 3.5	11.4 ± 2.0	1.6 ± 0.9
1500 ZSM-5	2.0 ± 0.1	4.2 ± 0.3	9.0 ± 1.9	2.7 ± 0.2	1.3 ± 0.0	58.6 ± 5.7	5.4 ± 0.6	10.2 ± 3.2	5.6 ± 0.2

different phases that could be separated by decantation. The upper layer was labelled as the aqueous phase, while the more viscous, darker layer was labelled as the organic phase. The GC curve of the aqueous phase is shown below in Fig. 6. The summarized data for the aqueous phase and the organic phase of the bio-oil are shown below in Tables 5 and 6.

The levoglucosan peak from the cellulose within the Hinoki wood is clearly seen in the graph above. However, the peak shape is not as clean as with the cellulose pyrolysis indicating additional sugars that may have been derived from hemicellulose within the wood. Hemicellulose contains many different sugar monomers such as arabinose, galactose, mannose, rhamnose, and xylose. Cellulose, on the other hand, only contains anhydrous glucose. Other major peaks such as the creosol and guaiacol are from the pyrolysis of the lignin found within the Hinoki wood. The peaks were integrated and classified into different compound groups. The aqueous-phase composition of the bio-oil is shown below in Table 5 and the organic-phase composition of the bio-oil is shown below in Table 6. The aqueous-phase bio-oil had 18% unidentified peaks on average and the organic-phase bio-oil had 30% unidentified peaks.

Due to the two bio-oil phases, which is commonly observed with wood pyrolysis, analysis of the products is more difficult than with single phase bio-oil from the cellulose and guaiacol pyrolysis [23,24]. The effects of the catalyst cannot be fully observed just by looking at the results of the aqueous phase of the bio-oil. The catalysts cause reactions affecting both the aqueous and organic-phase simultaneously. The

Table 7
Main effects of the catalyst on the different feed materials.

	Guaiacol	Cellulose	Hinoki (Aqueous)	Hinoki (Organic)
Silica	No Change	Removed Sugars Increased Furans	Removed Sugars Increased Ketones	Increased Phenols
ZrO_2-TiO_2	Increased Phenols	Decreased Sugars Increased Furans	Decreased Phenols Increased CP	Increased CP
40 ZSM-5	No Change	Decreased Sugars Increased Phenols	Removed Sugars Increased CP	Decreased Acids and Ketones Increased Aromatics
1500 ZSM-5	No Change	No Change	Decreased Phenols	Increased OA

aqueous-phase contains many sugars and phenols while the organic-phase has more hydrocarbons, aromatic hydrocarbons and phenols.

Silica catalyzed aqueous-phase bio-oils had an increased amount of ketones and aldehydes when compared with other catalyzed products. These oxygenated compounds are detrimental to the quality of bio-oil because they decrease energy density, and lead to corrosion and instability [25]. From the GC–MS spectra in Fig. 6, the effect of the silica can be clearly seen. Silica caused the levoglucosan sugar peak to decrease due to the hydroxyl group binding to the silica oxide layer, while the other peaks remained constant. This pattern was also seen with the cellulose feed. Hence, in the results, the integrated sugars decreased and the remaining groups tend to increase.

ZrO_2-TiO_2 is expected to increase hydrocarbons and cyclopentanones [11]. The results in this study show that the cyclopentanones increase from 4% to 18%. However, hydrocarbons did not increase in either the aqueous-phase or the organic-phase. While the silica oxide layer had strong affinity to the sugar in the bio-oil, the ZrO_2-TiO_2 catalyst had no reduction in sugar indicating that there was not strong interaction with the ZrO_2-TiO_2 oxide layer and sugar.

With cellulose pyrolysis, 40 ZSM-5 caused a decrease in sugar while 1500 ZSM-5 did not. This pattern is also seen with Hinoki wood pyrolysis. The 1500 ZSM-5 actually showed an increase in sugar concentration with Hinoki pyrolysis. This is due to the decomposition of other compounds increasing the yield of gas and char & coke as shown by the decrease in bio-oil yield in Fig. 4 and the decrease in peaks between 45 and 60 min as shown in Fig. 6. Hence, the percent of sugar in the products increased. Finally, the 40 ZSM-5 catalyst caused an increase in cyclopentanones in the aqueous-phase. ZSM-5 has been shown to convert cyclopentanones into napththalene and benzene products thereby increasing aromatics hydrocarbons [19]. This increase in aromatic hydrocarbons can be seen in the organic-phase results below in Table 6.

The heavy compounds in bio-oil were also analyzed by GC–MS and the classification data is shown above. Overall, the organic-phase of the bio-oil had large amount of phenols (52%) and furans (11%), as well as some hydrocarbons (6%), aromatic hydrocarbons (3%), and oxygenated aromatics (2%). This is similar to results in literature [26,27]. Phenols are important industrial chemicals and could be used to produce solvents or resins [28]. The organic-phase of the bio-oil had 250–350 peaks as opposed to the aqueous-phase of the bio-oil which had 50–100 peaks showing that many more compounds are present in the organic-phase of the bio-oil. The high number of peaks also leads to more unidentified peaks.

As there were no sugars observed in the organic-phase of the bio-oil, the silica catalyst had minimal effect on the results. Only an increase in phenols and a slight increase in oxygenated aromatics and aromatic hydrocarbons were observed with the silica catalyst. The main effect of the ZrO_2-TiO_2 was to increase the cyclopentanones from 4% to 9% as well as decrease ketones. The 40 ZSM-5 catalyzed organic-phase bio-oils had decreased acid and ketone concentration compared to uncatalyzed bio-oil thereby increasing the bio-oil quality. 1500 ZSM-5 also caused a decrease in acid and ketone, but not to the extent as 40 ZSM-5. The ZSM-5 catalysts increased the oxygenated aromatics and the 40 ZSM-5 catalyst increased aromatic hydrocarbons from 2% to 11%. This indicates that oxygenated aromatics are formed through the steric effects of the ZSM-5 catalysts; however, the acid sites are necessary to convert those oxygenated aromatics into aromatic hydrocarbons. 40-ZSM-5 had the largest percent of aromatic hydrocarbons increasing them from 3% to 14%. A summary of the effects can be seen in Table 7.

The increase in aromatic hydrocarbons from ZSM-5 catalyst is often observed in literature [28–30]. The ZrO_2-TiO_2 has pore sizes of 11 nm, 16 nm, and 121 nm, which is much larger than the ZSM-5 catalysts' pore size of 0.58 nm. The large pore sizes are said to facilitate coke formation [31]. This supported by the fact that ZrO_2-TiO_2 catalyst decreased the yield of bio-oil to the highest extent and had only a slight increase in aromatics. From these results we conclude that micropores and a moderate level of acid sites increase the bio-oil quality. The micropores increase the oxygenated aromatics and the acidic active sites convert the oxygenated aromatics into aromatic hydrocarbons. Overall, 40 ZSM-5 was the best catalyst at converting pyrolysis vapors into desired products and had a higher yield than ZrO_2-TiO_2 catalyst.

4. Conclusion

Hinoki wood, cellulose, and guaiacol (as a model compound for lignin) were pyrolyzed with different catalysts to get a better understanding of the catalysis process. The pyrolysis of guaiacol resulted in many different phenolic compounds with very high bio-oil yields of up to 60% with minimal coke formation. Silica, ZrO_2-TiO_2, ZSM-5 with a SiO_2-to-Al_2O_3 (SAR) ratio of 40, and ZSM-5 with a SAR ratio of 1500 were tested as catalyst; however, the pyrolysis products of guaiacol were remarkably unchanged. Only 40 ZSM-5 had a slight increase in hydrocarbons and ZrO_2-TiO_2 had an increase in phenols. These results indicate that the hydroxyl group on the benzene ring is resistant to the catalysts that were used in this study. Cellulose was pyrolyzed and resulted in about 40% bio-oil yield, which decreased when all catalysts were used. Cellulose formed mainly levoglucosan through transglycosylation, as well as furans and cyclopentanones. The silica catalyst significantly decreased the levoglucosan due to strong interactions of the hydroxyl groups on the levoglucosan and the oxide layer on the silica catalyst. ZrO_2-TiO_2 catalyst and 40 ZSM-5 catalyst also decreased the levoglucosan and 40 ZSM-5 caused an increase in phenolic compounds. The 1500 ZSM-5 catalyst had no change in levoglucosan indicating that the decrease in sugar with the 40 ZSM-5 catalyst was due to the acid sites on the catalyst surface. Finally, Hinoki wood was catalyzed and resulted in a two-phase oil. Levoglucosan and similar phenolic compounds as with guaiacol pyrolysis were formed during Hinoki pyrolysis because Hinoki is composed of cellulose, hemicellulose, and lignin. The 1500 ZSM-5 had an increase in oxygenated aromatics; however, only 40 ZSM-5 was able to convert these oxygenated aromatics into aromatic hydrocarbons due to the acidic active sites. The 40 ZSM-5 was overall the best with higher yields of bio-oil than ZrO_2-TiO_2 and also conversion of products to aromatic hydrocarbons and hydrocarbons. Based on these results, further research should be conducted on microporous catalysts with acid sites to deoxygenated bio-oil.

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