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Selective aromatic production from fast pyrolysis of sugarcane bagasse lignin over ZSM-5 catalyst

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Abstract

Organosolv lignin extracted from sugarcane bagasse (BG-lignin) and commercial grade lignin (Comm-OS) were used as starting materials in this study. From our previous work, aromatic furan (2,3-dihydrobenzofuran) was mainly produced from fast pyrolysis of BG-lignin and Comm-OS at 400–600 °C while alkyl phenol and phenol are more favorable at 700 °C. However, more thermal fragmentation was simultaneously redundant which results in low aromatic selectivity. In this work, aromatic production from lignin with molecular sieve ZSM-5 catalysts was studied using Py-GCMS instrument with biomass to catalyst ratio (B:C) of 1:1, 1:5, and 1:10. Aromatic furan and monolignol (H-unit, G-unit, and S-unit) were transformed to hydrocarbon species with addition of ZSM-5 catalyst according to elimination of side chain by demethoxylation, dehydroxylation, and dealkylation reactions. Maximum aromatic production was found at B:C of 1:10 for both Comm-OS and BG-lignin of 87.31% and 88.22%, respectively, while aliphatic hydrocarbon was more abundant for BG-lignin of 43.21% (1:5). Moreover, ZSM-5 exhibits instinctive performance on MAHs and PAHs production especially at B:C of 1:5 and 1:10. Nevertheless, polymerization between MAHs results in PAHs also observed for both Comm-OS and BG-lignin. From the result, transformation of aromatic furan could be limited by introduction of molecular sieve ZSM-5 which enhances the oxygen elimination from phenol derivative and is favorable for aromatic and BTX production.

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1. Introduction

Biorefinery of lignocellulosic materials focuses on the utilization of cellulose, hemicellulose, and lignin as fine chemical platform to replace petroleum-based counterpart [15]. Though in many instances such as pulp and paper industry, cellulose and hemicellulose are separated and used as pulp leaving lignin as waste and incinerated for power generation [7]. Unquestionably, lignin is promising bio-based aromatic with great potential as a source for

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Nomenclature

Comm-OS	Commercial organosolv lignin
BG-lignin	Bagasse lignin
Py	Pyrolyzer
GC	Gas chromatography
MS	Mass spectrophotometer
O-comp	Oxygen containing compound
OR-Ph-OCH ₃	Oxygenated-alkyl methoxy phenol
R-Ph-OCH ₃	Alkyl methoxy phenol
Ph-OCH ₃	Methoxy phenol
R-Ph	Alkyl phenol
Ph	Phenol
MAHs	Monocyclic aromatic hydrocarbons
PAHs	Polycyclic aromatic hydrocarbons

phenol-derived products and benzene, toluene, and xylene (BTX) that is a key strategic for BCG economy. “*Lignin-first*” process is isolation protocol to preserve lignin by protection-group chemistry for further reaction at the end of biorefinery process [1,12]. Commonly, solvent-based isolation process or organosolv process is preferable for preservation of lignin structure and functional group [1]. On the other hands, the reaction during kraft process is quite vigorous resulting in thiol, organosulfur, that is not suitable for biorefinery process. Soda process using NaOH is also not suitable to refine due to high alkali containing.

Lignin depolymerization to monolignol aromatic structure is one of the valorization strategies to achieve biorefinery competitiveness. Production of phenol-derive compound and aromatic chemicals by degradation of lignin under inert atmosphere is strongly related with raw material, temperature, heating rate, and catalyst [23,27]. Thermal effect plays important role on phenol-derivative selectivity by various reactions. However, undesirable products such as aromatic furan (2,3-dihydrobenzofuran) was found from primary pyrolysis reaction and shown high thermal stability until 700 °C [29]. In the other words, thermal does not promote elimination of hydroxyl side chain of phenol to aromatic hydrocarbon. Zeolite materials is promising catalyst for gas cleaning and oxygen elimination of fuel gas and bio-oil [32]. Resemblance between pore framework and dynamic molecular diameter of benzene, toluene, and xylene (BTX) enhance aromatic selectivity of ZSM-5 have been reported by Yu and co-worker [37]. Mochizuki and co-workers [22] studied fast pyrolysis of jatropha residue under catalytic condition using zeolites H-USY, H-Mordenite, H-Beta, and H-ZSM-5. They reported MAHs and PAHs selectivity when ZSM-5 was introduced with weight ratio of 1:5. To and co-workers [31] studied pyrolysis of m-cresol with HZSM-5 and HY as catalyst at 400–600 °C. They reported higher selectivity on aromatic (20%–30%) compound than HY (10%–15%). Li and co-workers [17] suggest that the mechanism pathway of aromatic production from lignocellulosic materials are mainly contribute by deoxygenation, cracking, hydrocarbon pool, and aromatization. Brønsted acid sites on the ZSM-5 surface donate the acidic proton to diffused molecule and form unstable compounds. The protonated compounds were possibly formed in active carbon species (hydrocarbon pool) which leading to elimination the oxygen atom and were subsequently transformed by aromatization reaction to aromatic structure. The aromatization is supposed to occur at temperature higher than 370 °C [17].

This study aims to minimize the undesirable aromatic furan as major contributor from bagasse lignin (BG-lignin) and commercial organosolv lignin (Comm-OS) pyrolysis and to promote aromatic hydrocarbon generation by using ZSM-5 as catalyst in Py-GCMS instrument at 600 °C. Effect of biomass to ZSM-5 ratio of 1:1, 1:5, and 1:10 on selectivity of chemical compounds such as phenol derivative, aromatic furan, aliphatic hydrocarbon, aromatic hydrocarbon, and oxygenated compound were evaluated and discussed. Moreover, hydrocarbon species were categorized to monocyclic aromatic hydrocarbon (MAHs) and polycyclic aromatic hydrocarbon (PAHs) and examined in detail. The data from this work would be useful for strategize biorefinery process for target chemicals such as BTX or other chemical reactants for many downstream chemical productions.

2. Experimental procedure

2.1. Organosolv lignin

The extraction process of lignin from sugarcane bagasse was explain elsewhere [29]. Essentially, ground and sieved sugarcane bagasse was homogenized with extractive solution (Ethanol:H₂O in ratio 75:25) and transfer into 50 ml PTFE-line stainless steel autoclave and placed into heating oven at 180 °C for 3 h. Lignin was isolated from solution by rotary evaporator and was dried at 60 °C overnight. For comparison, commercial lignin (Comm-OS) was procured from Chemical Point UG (CP8068-03-9).

2.2. ZSM-5 catalysts

Commercial NH₄-ZSM-5 catalysts was supplied by Zeolyst (CBV-3024E) with SiO₂/Al₂O₃ mole ratio of 30 with surface area of 403 m²/g. The commercial ZSM-5 was calcined at 600 °C for 2 h. to eliminate ammonium and form H-ZSM-5 prior to use. The textural properties of ZSM-5 obtained by Surface area analyzer (Quantachrome; Autosorb-1) according to Brunauer–Emmett–Teller (BET) theory and acid site obtained from NH₃-Temperature program desorption (NH₃-TPD) were shown in Table 1.

Table 1. Textural properties of H-ZSM-5 catalyst (Sigma-Aldrich; CBV-3024E).

Zeolite	Surface area (m ² /g)			Pore volume (cm ³ /g)			Pore diameter (Å)	Acidic site determined by NH ₃ -TPD (mmol NH ₃ ³ /g)		
	BET	Micropore	External	Micropore	Meso/macopore	Total		Weak acid	Strong acid	Total
ZSM-5	403	310	93	0.17	0.14	0.31	30.28	0.90	1.42	2.32

2.3. Catalytic fast pyrolysis using Py-GC–MS technique

The analytical instrument setup using a Pyrolyzer (Frontier; Py-2020iD) with a auto-shot sampler (Frontier; AS1020E) that interfaced with chromatography unit (Thermo Scientific; TRACE 1300) and mass spectrophotometer detector (Thermo Scientific; ISQLT) is illustrated in Fig. 1. For each run, 0.4 mg of BG-lignin was kept in stainless steel crucible which covered with glass wool to prevent sample loss during the experiment. For catalytic conditions, quantities of ZSM-5 were varied to achieve biomass to catalysts weight ratio (B:C) of 1:1, 1:5, and 1:10 then placed over biomass and cover with glass wool prior to fast pyrolysis at 600 °C. Instruments setup for pyrolyzer (Py), gas

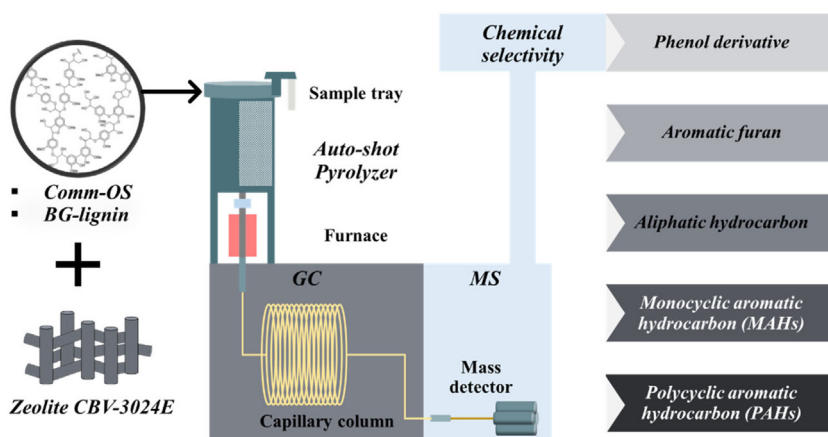


Fig. 1. Py-GCMS experimental set up.

chromatography (GC), and mass spectrophotometer (MS) could be found elsewhere [29]. Identification of each chromatography peak was compared with National Institute of Standards and Technology (NIST) and Wiley mass spectrum libraries. Chemical compound were categorized as Pheol derivative (H-unit, G-unit, and S-unit) Aromatic furan, Aromatic HC, Aliphatic HC, and O-compound with criteria as reported previously [29].

3. Results and discussion

3.1. Organosolv lignin characteristics

Our previous work [29] reported characteristic of extracted lignin by organosolv process from sugarcane bagasse. Basically, they contain 93%–96% of combustible compounds including volatile matters and fixed carbon while ash content is lower than 1.05% for both Comm-OS and BG-lignin. Degradation of lignin analyzed by Thermogravimetric analysis (TGA) found in broad region from 150–800 °C which respond to breakdown of bonding between aromatic structure in lignin and side group such as methoxy, alkyl, and hydroxyl [36]. Functional group of extracted lignin is accordingly with aromatic skeleton of monolignol including H-unit, G-unit, and S-unit with aliphatic structure and non-conjugated carbonyl group which are related to extraction method by organic solvent [30], organosolv process. Properties of lignin raw materials were summarized in Table 2.

Table 2. Properties of lignin raw materials use in this work.

Lignin	Chemical composition (%wt)			Degradation temperature (°C)		Structure (¹ H-NMR)	
	Moisture	VOCs	Fixed CAsh	Onset	Endset	H/G/S	Phe _{OH} /Ali _{OH} ^a
Comm-OS	5.69	56.91	36.35	1.05	140	680	0.26/0.71/0.03
BG-lignin	3.78	67.34	28.80	0.09	140	680	0.16/0.82/0.02

^aPhe_{OH} = Phenolic hydroxyl group, Ali_{OH} = Aliphatic hydroxyl group.

Nuclear magnetic resonance (NMR) is a crucial technique to assess structure of organic substance such as lignin. ¹³C-NMR of Comm-OS and BG-lignin was illustrated in Fig. 2 with signal assignment in Table 3. Chemical shift of aliphatic structure region of 10–35 ppm is a clear difference between Comm-OS and BG-lignin, possibly due to the lignin isolation parameters [2,30]. However, spectra at 40–180 ppm were very similar that possibly results from biomass feedstock of both lignin are herbaceous. Signal according to –OCH₃ side group was found at 55.94 ppm while 3 others majors peak of spectra was detected at 115 ppm (C5, aromatic C–H), 130 ppm (C5, aromatic C–C), and 144 ppm (C3, C4 aromatic ether or hydroxyl) that agree with Casas and co-worker [4] who analyzed lignin extracted from softwood and hardwood lignin. The presence of chemical shift at 115 ppm was corresponding to guaiacylpropane structure [6]. Moreover, present of C β -O, C α -O, and C γ -O signal at 84, 72, and 60 ppm, respectively, identified formation of β -O-4 structure in both Comm-OS and BG-lignin. In addition, C2 and C6 in syringyl structure also presented at 103–105 ppm. Adjaoud and co-worker [2] reported significant

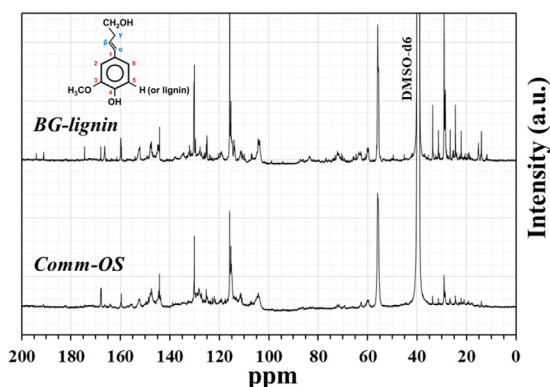
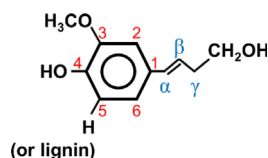


Fig. 2. ¹³C-NMR of organosolv lignin as starting feedstock.

Table 3. ^{13}C -NMR assignment of selected chemical compound [2,6,21].

Signal (ppm)	Assignment
167–178	Unconjugated –COOH
162–168	Conjugated –COOH
140–155	C3, C4 aromatic ether or hydroxyl (etherified)
127–140	C1, aromatic C–C
123–127	C5, aromatic C–C
117–123	C6, aromatic C–H in guaiacyl unit
114–117	C5, aromatic C–H in guaiacyl unit
106–114	C2, aromatic C–H in guaiacyl unit
105–103	C2/C6, aromatic C–H in syringyl unit
78–90	Aliphatic C β -O
67–78	Aliphatic C α -O
60–59	Aliphatic C γ -O
54–57.5	Methoxy (–OCH $_3$)
40	DMSO-d $_6$
36–30	Aliphatic structure

Lignin structure

increase in aliphatic carbon atom signal at low chemical shift after esterification of soda lignin with propionic acid. From the results, characteristics of organosolv lignin extracted from sugarcane bagasse (BG-lignin) seem to be similar to Comm-OS in terms of chemical composition and thermal behavior. However, differences in constituent monolignols and aryl side group were observed (Table 2.) that BG-lignin shows higher guaiacyl (G-unit) type monolignol building unit with same proportion of aliphatic and phenolic hydroxyl group while Comm-OS holds greater aromatic hydroxyl (Phe_{OH}) content. Regarding on high aliphatic hydroxyl fraction as evaluated by ^1H -NMR in Table 2, BG-lignin contains more aliphatic side group than Comm-OS and possible related to chemical compound of pyrolysis products that will describe and discussed in the next section.

3.2. Study on production of aromatic products using ZSM-5 catalyst using Py-GC–MS

Py-GCMS technique is usually employed to study degradation behavior of biomass for renewable substance and value-added chemical production whether thermal or catalytic condition. From our previous work, pyrolysis temperature strongly effect to selectivity of chemical compound produced during fast pyrolysis of Comm-OS and BG-lignin [29]. In brief, distribution of H-unit, G-unit, and S-unit produced from depolymerization of Comm-OS and BG-lignin is significantly affected when pyrolysis temperature is raised from 400 °C to 700 °C. Enhancement of H-unit selectivity is abundant at 700 °C resulting from demethoxylation of S-unit and G-unit [3,8]. However, aromatic furan with high selectivity than 30% was still found at any non-catalytic conditions. Aromatic furan, assigned as 2,3-dihydrobenzofuran, emerged as dominant species from fast pyrolysis of 38.83% and 50.39% at 600 °C for comm-OS and BG-lignin, respective, while aromatic and aliphatic hydrocarbon production lower than 10%. The reaction pathways of aromatic furan from lignin depolymerization is still unclear. However, the suspected reactions are cleavage and structure rearrangement of ether linkage between monolignol unit [9,29] which result in benzene ring coupling with 2,3-dihydrofuran ring. Detection of aromatic furan (12.12% [25] and 24.1% [18]) also reported by researchers who studied pyrolysis of kraft lignin and lignin model compound, respectively. Elimination of benzofuran to aromatic hydrocarbon using molecular sieve catalysts such as ZSM-5 was studied at 600 °C with various catalysts content (1:1, 1:5, and 1:10). Chromatograms of pyrolyzed products analyzed by gas chromatography unit were illustrated in Fig. 3.

From the results, signal of chemical species produced under catalytic condition were dramatically different from thermal condition for both Comm-OS (Fig. 3(a)) and BG-lignin (Fig. 3(b)). Benzofuran was identified at

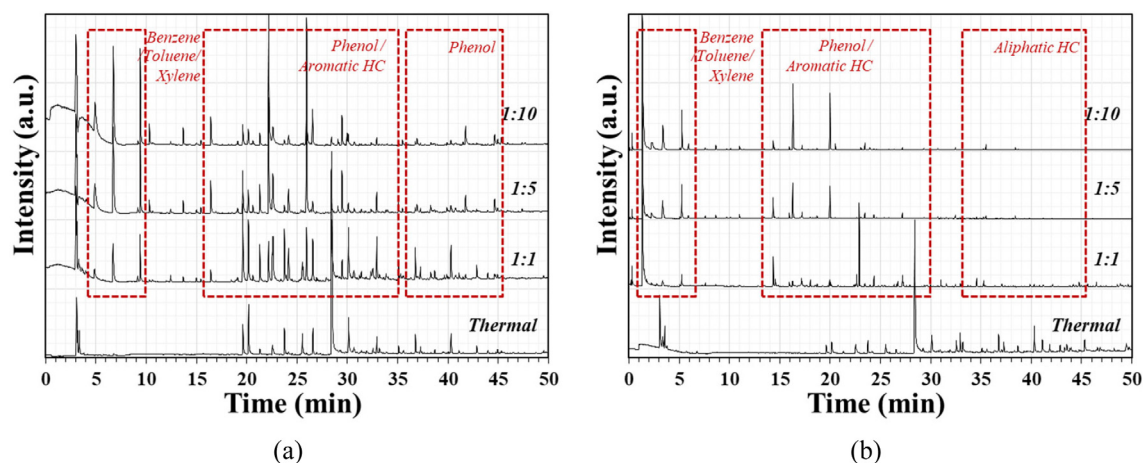


Fig. 3. Chromatogram of pyrolyzed products with (a) Comm-OS and (b) BG-lignin as raw materials.

retention time (RT) of 28 min while phenol and oxygenated compound was identified at RT 30–42 min for thermal condition at 600 °C. Monocyclic aromatic hydrocarbon (MAHs) product such as toluene, benzene, and xylene were detected at RT 5–10 min while polycyclic aromatic hydrocarbon (PAHs) were found at RT 15–35 min. Phenol derivative appeared in wider region from RT 15 min to 45 min as found in non-catalytic condition. Hydrocarbon selectivity is enhanced in proportional with ZSM-5 content. For example, stronger signal of toluene, naphthalene, and 1-methylnaphthalene at RT 6.70, 22.20, and 25.95 min, respectively, were detected with decreasing intensity of benzofuran at RT 28 min. Moreover, intensity of carbon dioxide (CO₂) at RT 1.3 min were distinctly increased which is responsible for oxygen atom elimination from aromatic furan or oxygenated compound by decarbonylation and decarboxylation reaction on the surface of ZSM-5 [33,34].

Selectivity on the chemical compound of pyrolysis products obtained from Comm-OS and BG-lignin were illustrated in Fig. 4. Referring to chromatogram (Fig. 3.), aromatic furan as 2,3-dihydrobenzofuran is the most abundant contributor on pyrolysis products under non-catalytic condition that could possibly produce from cleavage of ether linkage (C α -O, C β -O, and C γ -O) between monolignol compound such as p-hydroxyphenyl, guaiacyl, and syringyl unit and subsequently structural rearrangement of o-quinone methide by radically induced reaction [20]. However, higher pyrolysis temperature has minor effect on conversion of 2,3-dihydrobenzofuran to phenol or

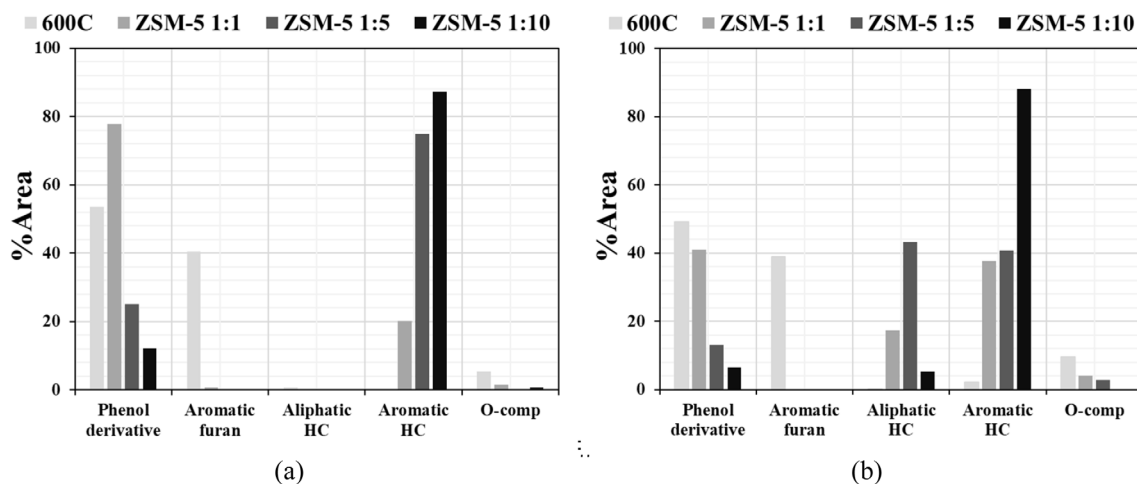


Fig. 4. Chemical selectivity of pyrolysis products under catalytic condition (a) Comm-OS and (b) BG-lignin.

hydrocarbon compound [20,29]. During depolymerization of lignin, intermediate compounds such as ion and radical were produced. Recombination of intermediate radicals such as aryl, alkyl, and methoxy during the lignin pyrolysis at 400–700 °C was dominated and results in lower phenol (Ph) selectivity [29]. Lou and co-workers [20] reported 36.05–66.26% of 2,3-dihydrobenzofuran production from fast pyrolysis of enzymatic/mild acidolysis lignin (EMAL) isolated from moso bamboo at 250–600 °C. At high pyrolysis temperature of 800 °C, thermal effect shows superior reduction of 2,3-dihydrobenzofuran conversion to 19.15%. However, high temperature fast pyrolysis is not practical for upscale biorefinery process due to prohibitive capital investment and cost. Moreover, elimination of aromatic hydroxy group was prohibit with results as coke formation instead of aromatic hydrocarbon which possibly related to the polymerization of o-quinone methide as reported by Hosoya and co-workers [9]. Moreover, they suggested o-quinone methide reactivity is the key intermediate for char formation during pyrolysis of lignin via various complex reactions. Thus, selective molecular sieve catalysts could be overcome this boundary by adsorption of intermediate radicals on acid site and promoted hydrocarbon and others high value chemical substance from lignin.

Introduction of ZSM-5 catalyst seem to promote conversion of aromatic furan to phenol derivative and hydrocarbon compound especially aromatic structure for both Comm-OS and BG-lignin. Aromatic furan is significantly reduced from 50.39% and 38.83% to lower than 0.70%, for Comm-OS and BG-lignin, respectively, according to higher catalyst content from 1:1 to 1:10. Maximum aromatic production was found at 1:10 for both Comm-OS and BG-lignin of 87.31% and 88.22%, respectively. In addition, dramatically decrease of phenol derivative was found from 77.75% to 12.07% for Comm-OS and 40.89% to 6.51% for BG-lignin with addition of ZSM-5 from 1:1 to 1:10. Elimination of aliphatic side chain was more robust in BG-lignin according to higher aliphatic HC with maximum content at 1:5 of 43.21%. This result is corresponding with ¹H-NMR [29] and ¹³C-NMR spectra that chemical shift signal of aliphatic structure region is superior for BG-lignin. Enhancement of aromatic HC portion was quite straightforwardly with the reduction of phenol derivative and aliphatic furan (2,3-dihydrobenzofuran) by demethoxylation, dihydroxylation, and dealkylation reactions [13,26]. Unfavorable content of oxygen containing compound such as ether, ester, carboxylic acid, and ketone were detected with lower than 10% for catalytic conditions and totally disappeared with excess ZSM-5 (1:5 and 1:10). Advantage of zeolite catalysts on hydrocarbon selectivity have been reported by many researchers [11,13,14,16,25,28,35,39]. Mochizuki and co-worker [22] demonstrate the reaction pathways of lignin component in jatropha under catalytic condition with ZSM-5. During the catalytic pyrolysis of lignin, chemical vapor compounds produced from depolymerization of lignin may accept proton from Brønsted acid site on ZSM-5 surface leading to the formation of carbocation as intermediate products [24]. These compounds were subsequently undergo oxygen elimination by decarbonylation and decarboxylation reaction which results in aromatic and aliphatic hydrocarbons. Adsorption of phenol-like oxygenated compound on acid active site inside pore framework results in hydrocarbon products by decarboxylation and decarbonylation reaction. Furthermore, higher catalyst content from 1:1 to 1:10 lean to conduct production of aromatic HC with highest of 87.31% and 88.22% for Comm-OS and BG-lignin, respectively, by increasing of acid site. Vichaphund and co-worker [33] reports the same fashion on effect of catalyst content 1:5 was remarkably promoted aromatic formation with 94% selectivity of pyrolysis vapors of jatropha at 500 °C. Consideration on hydrocarbon products, different lignin raw materials, Comm-OS and BG-lignin, seem to strongly effect the configuration aromatic formation. For BG-lignin, aliphatic produced is dramatically reduced when ZSM-5 was introduced to 1:10 with higher aromatic formation. This incident should be describe with the same reaction pathway of pyrolysis of cellulose under catalytic condition that demonstrated by Mochizuki and co-worker [22]. Diffusion of intermediate compound through acid catalyst, ZSM-5, pore size results in formation of MAHs and light hydrocarbon by series of oligomerization, cyclization, and aromatization [5,10].

Phenolic selectivity and aromatic structure related with catalysts content were illustrated in Fig. 5. The phenolic compound were categorized as oxygenated-alkyl methoxy phenol (OR–Ph–OCH₃), alkyl methoxy phenol (R–Ph–OCH₃), methoxy phenol (Ph–OCH₃), alkyl phenol (R–Ph), and phenol (Ph) with criteria that reported elsewhere [29] while aromatic is categorized as monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbon (PAHs). It is clearly noticed that ZSM-5 catalysts promoted elimination of phenolic side chain such as methoxy, alkyl, and hydroxyl group by demethoxylation and dealkylation reactions. Kim and co-workers [11] studied pyrolysis of methylated lignin over zeolite Y catalyst. The reaction pathway of lignin inside catalyst pore was discussed with dealkylation of aliphatic alkyl group (R–Ph) to phenol (Ph) with MAHs such as cresols and ethylphenol as products. Combination between neighboring phenol results in PAHs by dihydroxylation, aromatization, isomerization, and oligomerization. Elimination of oxygenated-alkyl group on OR–Ph–OCH₃, primary pyrolysis products, was more

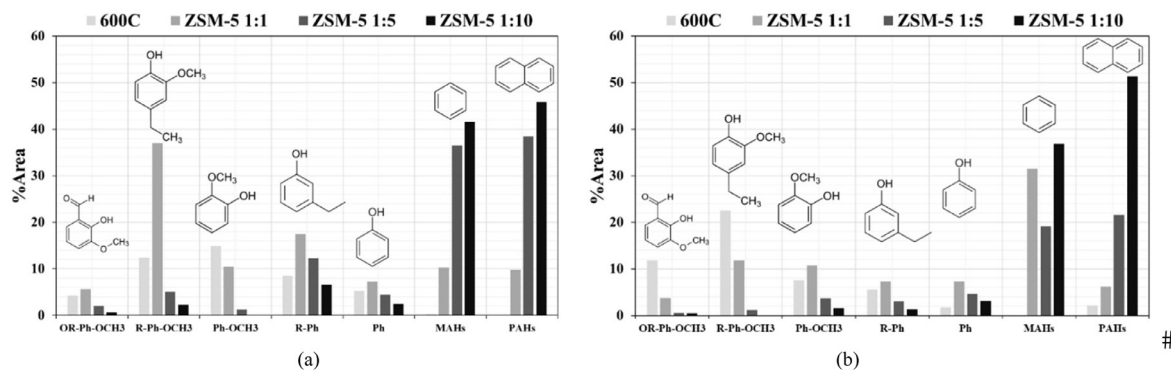


Fig. 5. Selectivity of aromatic compound under catalytic condition. (a) Comm-OS and (b) BG-lignin.

abundant in Comm-OS with 1:5 catalysts with rising of R-Ph-OCH₃ (37.01%) and Ph-OCH₃ (10.44%). Cleavage of methoxy group continuously proceeded with formation of alkyl phenol (R-Ph) and phenol (Ph) of 6.56–17.44% and 2.50–7.26% for Comm-OS, respectively, while BG-lignin was 1.35–7.28% and 1.70–7.29%, respectively.

From our previous work, non-catalytic condition could not drive the dehydroxylation of phenol to aromatic compound [29]. Regarding on complexity and instability of radical during depolymerization of lignin, intermediate radical and ion may recombine with phenol as aromatic substitution group and result in phenol derivative with low aromatic selectivity. Despite the decomposition of phenol derivative and conversion to aromatic compound at high temperature, lower yield of valuable products also found with decomposed to gas such as CO₂, CO, and alcohol. Thus, selective catalyst could overcome this boundary by transforming phenol derivative and unfavorable aromatic furan to aromatic hydrocarbon. ZSM-5 exhibits instinctive performance on MAHs and PAHs selectivity especially at 1:5 and 1:10. Liu and co-worker [19] reported that ZSM-5 was superior selectivity on aromatic structure than BETA, HY-25 and SAPO-34 with lower coke formation. The advantage of aromatic selectivity is strongly related to ZSM-5 framework that influence on adsorption of precursor [24]. The geometry of ZSM-5 catalyst with sinusoidal and straight channel is similar to dynamic diameter of aromatic such as benzene, Toluene, and xylene (BTX) results in shape selectivity was suggest by Zhang an co-worker [37,38]. Higher aromatic production at B:C 1:5 and 1:10 of 36.48–41.51% and 38.49–45.79% for MAHs and PAHs, respectively was obtained for Comm-OS lignin. Phenol derivative and aromatic products from catalytic fast pyrolysis of Comm-OS was shown in Table 4. At low catalyst content (1:1), phenol, 2-methoxyphenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxyphenol are found in high proportion of 7.26%, 5.29%, 18.51%, and 4.79%, respectively. These phenol derivatives were substantially reduced with excess of catalyst at 1:5 and 1:10 corresponding with rise of aromatics such as benzene, toluene, o-xylene, naphthalene, and 1-methylnaphthalene with total aromatic were 74.97% and 87.31%, respectively. For BG-lignin, difference between MAHs and PAHs is clearly noticed with 19.15–36.86% and 21.59–51.37%, respectively. Lower aromatic selectivity observed on BG-lignin is related to disproportionation of alkyl and oxygenated-alkyl side chain that is more favorable under catalytic condition as shown in Fig. 4(b). Phenol, 2-methoxy-4-methylphenol, p-tert-butylphenol and 1,2,3-Trimethoxybenzene (Table 5.) are major compounds of 7.29%, 2.01%, 3.46%, and 4.17% at 1:1 that were suddenly transform to aromatic products under ZS-5 1:5 and 1:10 such as benzene, toluene, o-xylene, naphthalene, 2-methylnaphthalene, and propylbenzene with total aromatic of 40.75% and 88.22%, respectively.

From the result, formation of aromatic furan could be limited by introduction of molecular sieve ZSM-5 catalyst which enhance the oxygen elimination from phenol derivative as described pathway. However, yield of phenol as high value chemical substance is directly reduced. The data from this work is valuable information for biorefinery process design for consideration of the proper process for target chemical. For example, ZSM-5 is more favorable for aromatic and BTX production while thermal condition is more appropriate for phenol and its derivative production for fine chemical substance.

4. Conclusion

Organosolv lignins, Comm-OS and BG-lignin, were pyrolyzed using ZSM-5 as catalysts to curtail the formation of aromatic furan (2,3-dihydrobenzofuran), undesirable products, and to promote aromatic hydrocarbon. Py-GCMS

Table 4. Pyrolysis products obtained from fast pyrolysis of Comm-OS using ZSM-5 catalyst.

RT	Formula	Compound	%Area			
			Thermal	1:1	1:5	1:10
<i>Phenol and derivative</i>						
19.62	C6H6O	Phenol	5.28	7.26	4.44	2.50
20.18	C7H8O2	Phenol, 2-methoxy-	8.08	5.29	–	–
21.31	C7H8O	Phenol, 2-methyl-	0.86	2.95	2.80	1.24
22.61	C7H8O	p-Cresol	–	6.48	6.05	3.93
22.54	C7H8O	Phenol, 3-methyl-	2.51	–	–	–
23.76	C8H10O2	Creosol	4.05	3.70	0.68	0.45
23.94	C8H10O	Phenol, 3-ethyl-	0.46	–	–	–
24.15	C8H10O	Phenol, 3,4-dimethyl-	0.44	2.89	2.59	1.05
25.53	C8H10O	Phenol, 4-ethyl-	3.48	2.67	–	–
26.56	C9H12O2	Phenol, 4-ethyl-2-methoxy-	–	3.34	–	–
28.46	C9H10O2	2-Methoxy-4-vinylphenol	–	18.51	1.18	1.08
29.07	C10H14O	2,5-Diethylphenol	–	0.74	–	–
29.82	C9H10O	2-Allylphenol	0.22	–	–	–
30.13	C8H10O3	Phenol, 2,6-dimethoxy-	6.44	4.79	1.28	–
30.65	C11H16O	Benzene, 1-methoxy-4-methyl-2-(1-methylethyl)-	–	1.19	–	–
31.41	C9H10O4	Benzoic acid, 2-hydroxy-4-methoxy-6-methyl-	0.37	0.69	0.34	–
32.56	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	0.78	1.64	–	–
32.93	C9H12O3	Phenol, 4-methoxy-3-(methoxymethyl)-	2.16	3.06	1.63	0.68
33.18	C8H8O3	4-Hydroxy-2-methoxybenzaldehyde	–	0.39	–	–
33.85	C9H12O2	Phenol, 5-methoxy-2,3-dimethyl-	–	0.55	–	–
33.87	C10H12O3	Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	0.22	–	–	–
35.11	C10H14O3	5-tert-Butylpyrogallol	1.04	1.26	0.85	0.34
35.59	C10H14O2	Phenol, 3-methoxy-2,4,6-trimethyl-	0.40	0.52	–	–
36.76	C11H16O2	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	2.93	2.52	0.38	0.29
37.28	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.94	0.80	–	–
38.28	C10H8O	2-Naphthalenol	–	0.84	1.25	0.20
38.70	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.51	0.55	0.39	–
40.31	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	2.76	2.51	0.72	0.31
40.77	C11H10O	1-Naphthalenol, 4-methyl-	–	0.35	0.46	–
41.10	C9H10O4	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	0.44	0.41	–	–
42.88	C10H12O4	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.09	1.05	–	–
43.97	C11H14O4	trans-Sinapyl alcohol	0.34	0.36	–	–
Total			24.12	48.74	8.48	2.90
<i>Aromatic</i>						
4.86	C6H6	Benzene	–	1.24	6.52	7.73
6.76	C7H8	Toluene	0.30	3.72	12.11	14.43
9.17	C8H10	o-Xylene	–	–	0.40	0.19
9.40	C8H10	o-Xylene	–	3.27	7.70	8.96
10.32	C8H10	o-Xylene	–	–	0.99	1.88
12.43	C9H12	Benzene, 1-ethyl-3-methyl-	–	–	0.34	0.25
13.68	C9H12	Benzene, 1-ethyl-3-methyl-	–	–	0.93	1.40
15.44	C9H10	Indane	–	–	0.41	0.38
16.42	C9H8	Indene	–	0.96	3.07	3.07
19.10	C10H12	Benzene, 4-ethenyl-1,2-dimethyl-	–	–	0.44	0.28
20.14	C10H10	Benzene, 1-methyl-4-(1-propynyl)-	–	–	2.29	1.86
20.62	C10H10	Benzene, 1-methyl-4-(1-propynyl)-	–	0.45	0.77	0.66
22.17	C10H8	Naphthalene	–	3.52	13.32	16.74
25.95	C11H10	Naphthalene, 1-methyl-	–	4.18	13.19	13.76
26.54	C11H10	Naphthalene, 1-methyl-	–	–	1.22	3.53
29.07	C12H12	Naphthalene, 2-ethyl-	–	–	0.59	0.60
29.48	C12H12	Naphthalene, 1,7-dimethyl-	–	1.51	4.18	3.21
29.96	C12H12	Naphthalene, 1,7-dimethyl-	–	–	–	2.50

(continued on next page)

Table 4 (continued).

RT	Formula	Compound	%Area			
			Thermal	1:1	1:5	1:10
30.68	C12H10	Hexa-2,4-dien-1-ylbenzene	–	–	0.51	0.42
32.37	C13H14	Naphthalene, 1,4,5-trimethyl-	–	–	0.38	0.18
35.29	C11H14	2,2-Dimethylindene, 2,3-dihydro-	–	0.65	–	–
35.48	C13H10	1H-Phenalene	–	–	0.33	0.50
36.92	C13H10	1H-Phenalene	–	–	0.89	0.65
39.91	C14H12	9H-Fluorene, 4-methyl-	–	–	0.57	0.13
41.50	C14H10	9H-Fluorene, 9-methylene-	–	–	–	0.16
41.75	C14H10	Phenanthrene	–	–	1.93	2.29
44.66	C15H12	Naphtho [2,3-b] norbornadiene	–	0.56	1.52	1.06
44.95	C15H12	Naphtho [2,3-b] norbornadiene	–	–	0.36	0.48
Total			0.30	20.05	74.97	87.31

Table 5. Pyrolysis products obtained from fast pyrolysis of BG-lignin using ZSM-5 catalyst.

RT	Formula	Compound	%Area			
			Thermal	1:1	1:5	1:10
<i>Phenol and derivative</i>						
13.39	C10H10O2	Benzene, 1,2-(methylenedioxy)-4-propenyl-, (E)-	–	–	0.09	0.11
14.35	C6H6O	Phenol	–	7.29	4.64	3.12
14.56	C7H8O2	Phenol, 2-methoxy-	–	1.80	–	–
15.94	C7H8O	Phenol, 3-methyl-	–	1.23	1.30	0.97
16.96	C8H10O2	2-Methoxy-5-methylphenol	–	–	0.11	–
17.15	C7H8O	Phenol, 3-methyl-	–	1.84	0.46	0.39
17.24	C7H8O	Phenol, 3-methyl-	–	1.28	1.58	1.20
18.03	C8H10O2	Phenol, 2-methoxy-4-methyl-	–	2.01	0.27	–
18.70	C8H10O	Phenol, 2,6-dimethyl-	–	0.68	0.51	0.38
19.62	C6H6O	Phenol	1.70	–	–	–
20.06	C8H10O	Phenol, 3-ethyl-	–	1.21	–	–
20.14	C8H10O	Phenol, 2,6-dimethyl-	–	0.71	0.17	–
20.16	C7H8O2	Phenol, 2-methoxy-	2.16	–	–	–
21.31	C7H8O	Phenol, 2-methyl-	0.24	–	–	–
22.54	C7H8O	Phenol, 3-methyl-	2.10	–	–	–
22.65	C10H14O	Phenol, p-tert-butyl-	–	3.46	0.10	–
23.76	C8H10O2	Creosol	2.30	–	–	–
24.15	C8H10O	Phenol, 3,4-dimethyl-	0.34	–	–	–
24.36	C9H10O4	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	–	3.25	–	0.34
25.53	C8H10O	Phenol, 4-ethyl-	1.91	–	–	–
26.58	C9H12O2	Phenol, 4-ethyl-2-methoxy-	0.57	–	–	–
26.72	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	–	1.80	0.08	–
27.21	C9H12O3	1,2,3-Trimethoxybenzene	–	4.17	1.31	–
29.23	C10H12O2	Phenol, 2-methoxy-3-(2-propenyl)-	0.88	–	–	–
29.38	C9H10O4	3,4-Dimethoxy-5-hydroxybenzaldehyde	–	–	0.41	–
31.03	C10H14O2	Phenol, 2-methoxy-4-propyl-	–	2.47	–	–
30.11	C8H10O3	Phenol, 2,6-dimethoxy-	3.71	–	–	–
30.95	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	0.30	–	–	–
31.55	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	–	1.02	0.19	–
31.93	C9H10O	Phenol, 4-(2-propenyl)-	0.40	–	–	–
32.56	C10H12O2	Phenol, 2-methoxy-6-(1-propenyl)-	2.48	–	–	–
32.93	C9H12O3	Phenol, 4-methoxy-3-(methoxymethyl)-	3.19	–	–	–
33.20	C8H8O3	Vanillin	2.41	–	–	–
32.95	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	–	0.79	–	–
33.71	C10H10O2	Benzene, 1,2-(methylenedioxy)-4-propenyl-, (E)-	–	0.50	–	–

(continued on next page)

Table 5 (continued).

RT	Formula	Compound	%Area			
			Thermal	1:1	1:5	1:10
33.73	C15H14O	Benzene, 1-methoxy-4-(2-phenylethenyl)-	–	–	0.17	–
34.19	C15H14O	Benzene, 1-methoxy-4-(2-phenylethenyl)-	–	–	0.10	–
34.58	C10H12O2	Phenol, 2-methoxy-4-(1-propenyl)-	–	2.84	0.37	–
35.11	C10H14O3	5-tert-Butylpyrogallol	0.56	–	–	–
35.29	C9H10O4	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	–	1.65	0.30	–
35.59	C10H14O2	Phenol, 3-methoxy-2,4,6-trimethyl-	0.55	–	–	–
36.36	C11H12O4	Glycidic acid, trans-3-[4-methoxyphenyl]-, methyl ester	0.40	–	–	–
36.76	C11H16O2	Phenol, 3-(1,1-dimethylethyl)-4-methoxy-	3.11	–	–	–
37.07	C10H12O3	Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	0.43	0.90	0.12	–
37.28	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.68	–	–	–
38.43	C14H22O	Phenol, 2,4-bis(1,1-dimethylethyl)-	–	–	0.63	–
38.68	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.08	–	–	–
40.31	C11H14O3	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	4.53	–	–	–
41.10	C9H10O4	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2.75	–	–	–
41.21	C14H22O	Phenol, 2,4-bis(1,1-dimethylethyl)-	–	–	0.09	–
41.84	C12H16O3	1,2-Dimethoxy-4-(1-methoxy-1-propenyl) benzene	1.23	–	–	–
42.88	C10H12O4	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.27	–	–	–
43.32	C10H12O3	(E)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol	1.00	–	–	–
43.55	C12H16O4	Ethyl 3-(4-hydroxy-3-methoxyphenyl) propionate	1.82	–	–	–
43.97	C11H14O4	trans-Sinapyl alcohol	1.25	–	–	–
46.60	C12H14O4	Ethyl ferulate	0.68	–	–	–
46.85	C11H12O3	p-Hydroxycinnamic acid, ethyl ester	0.86	–	–	–
48.25	C13H18O4	1,2-Dimethoxy-4-(1,3-dimethoxy-1-propenyl) benzene	0.36	–	–	–
49.74	C11H14O4	trans-Sinapyl alcohol	0.94	–	–	–
Total			49.20	40.89	13.01	6.51
<i>Aromatic</i>						
2.23	C6H6	Benzene	–	0.88	1.81	4.38
3.34	C7H8	Toluene	–	2.15	5.38	11.41
5.07	C8H10	o-Xylene	–	0.57	0.68	0.67
5.26	C8H10	o-Xylene	–	3.55	7.62	13.59
5.91	C8H10	o-Xylene	–	–	0.81	1.94
6.14	C8H8	Styrene	–	–	0.09	–
7.60	C9H12	Benzene, 1,2,4-trimethyl-	–	0.90	0.59	0.60
8.65	C9H12	Benzene, 1,2,4-trimethyl-	–	–	0.70	1.51
10.11	C9H10	Indane	–	–	0.20	0.41
10.99	C9H8	Indene	–	–	1.07	1.44
13.45	C9H10	Benzene, 1-propenyl-	–	–	0.21	0.27
14.87	C10H8	Naphthalene	–	–	0.34	0.29
16.27	C10H8	Naphthalene	–	1.95	9.19	22.13
18.30	C10H8	Naphthalene	–	–	0.13	–
19.95	C11H10	Naphthalene, 2-methyl-	–	2.11	8.66	16.28
20.52	C11H10	Naphthalene, 2-methyl-	–	–	–	2.26
20.52	C11H10	Naphthalene, 2-methyl-	–	–	0.22	–
22.38	C9H12	Benzene, propyl-	–	0.49	–	–
22.90	C9H12	Benzene, propyl-	–	22.29	–	–
23.05	C11H10	Naphthalene, 1-methyl-	–	–	–	0.60
23.15	C13H14	Naphthalene, 1-(1-methylethyl)-	–	–	–	0.12
23.44	C13H14	Naphthalene, 1-(1-methylethyl)-	–	1.47	1.70	2.62
23.92	C13H14	Naphthalene, 1-(1-methylethyl)-	–	–	–	0.84
24.01	C13H14	Naphthalene, 1-(1-methylethyl)-	–	–	–	0.56
24.61	C12H10	Acenaphthene	–	–	–	0.20
26.37	C13H14	Naphthalene, 2-(1-methylethyl)-	–	–	–	0.19
27.18	C13H12	1,1'-Biphenyl, 2-methyl-	–	–	–	0.63

(continued on next page)

Table 5 (continued).

RT	Formula	Compound	%Area			
			Thermal	1:1	1:5	1:10
27.94	C12H18	Benzene, hexyl-	–	0.62	0.13	–
29.32	C13H10	Fluorene	–	–	–	0.53
30.72	C13H10	Fluorene	–	–	0.38	0.56
32.47	C9H8	Benzene, 1-ethynyl-4-methyl-	–	–	–	0.64
35.25	C14H10	Phenanthrene	–	–	–	0.28
32.47	C9H8	Benzene, 1-ethynyl-4-methyl-	–	0.70	–	–
35.48	C14H10	Phenanthrene	–	–	0.84	1.84
38.43	C13H10	Fluorene	–	–	–	0.99
38.72	C13H10	Fluorene	–	–	–	0.35
39.83	C16H10	Pyrene	–	–	–	0.09
49.47	C26H38	Benzene, 1,1'-tetradecylidenebis-	2.15	–	–	–
Total			2.15	37.67	40.75	88.22

chromatogram clearly indicated the transformation of pyrolyzed products from non-catalytic condition such as aromatic furan and monolignol (H-unit, G-unit, and S-unit) to hydrocarbon species with addition of ZSM-5 catalyst. The decreasing of phenol derivative was found from 77.75% to 12.07% for Comm-OS and 40.89% to 6.51% for BG-lignin with addition of ZSM-5 from 1:1 to 1:10 according to elimination of aliphatic side chain by demethoxylation, dihydroxylation, and dealkylation reactions. Aliphatic hydrocarbon was more abundant for BG-lignin that contains more aliphatic side chain which observed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra. However, aliphatic produced from BG-lignin is dramatically reduced when ZSM-5 was introduced to 1:10 with higher aromatic formation. ZSM-5 exhibits instinctive performance on MAHs and PAHs selectivity especially at 1:5 and 1:10. Comm-OS seem to be suitable for aromatic compound generation than BG-lignin with the latter is more favorable on aliphatic hydrocarbon. Nevertheless, polymerization between MAHs to PAHs also observed for both Comm-OS and BG-lignin. From the result, transformation of aromatic furan could be limited by the introduction of molecular sieve ZSM-5 which enhance the oxygen elimination from phenol derivative and favorable for aromatic and BTX production.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Abu-Omar MM, Barta K, Beckham GT, Luterbacher JS, Ralph J, Rinaldi R, et al. Guidelines for performing lignin-first biorefining. | Energy Environ. Sci. 2021;14:262. <http://dx.doi.org/10.1039/d0ee02870c>.
- [2] Adjaoud A, Dieden R, Verge P. Sustainable esterification of a soda lignin with phloretic acid. Polymers (Basel) 2021;13:1–19. <http://dx.doi.org/10.3390/polym13040637>.
- [3] Asmadi M, Kawamoto H, Saka S. Thermal reactions of guaiacol and syringol as lignin model aromatic nuclei. J. Anal. Appl. Pyrolysis 2011;92:88–98. <http://dx.doi.org/10.1016/j.jaap.2011.04.011>.
- [4] Casas A, Oliet M, Alonso MV, Rodríguez F. Dissolution of Pinus Radiata and Eucalyptus Globulus Woods in Ionic Liquids Under Microwave Radiation: Lignin Regeneration and Characterization. Sep. Purif. Technol., vol. 97, Elsevier; 2012, p. 115–22. <http://dx.doi.org/10.1016/j.seppur.2011.12.032>.
- [5] Chang Z, Qu Y, Gu Z, Zhou L, Li R, Sun Z, et al. Production of aromatic hydrocarbons from catalytic pyrolysis of huadian oil shale using ZSM-5 zeolites as catalyst. J. Anal. Appl. Pyrolysis 2020;104990. <http://dx.doi.org/10.1016/j.jaap.2020.104990>.
- [6] Chen CL, Robert D. Characterization of lignin by ^1H and ^{13}C NMR spectroscopy. Methods Enzymol. 1988;161:137–74. [http://dx.doi.org/10.1016/0076-6879\(88\)61017-2](http://dx.doi.org/10.1016/0076-6879(88)61017-2).
- [7] Chen X, Zhang K, Xiao LP, Sun RC, Song G. Total utilization of lignin and carbohydrates in Eucalyptus grandis: An integrated biorefinery strategy towards phenolics, levulinic acid, and furfural. Biotechnol. Biofuels 2020;13. <http://dx.doi.org/10.1186/s13068-019-1644>.

- [8] Harman-Ware AE, Crocker M, Kaur AP, Meier MS, Kato D, Lynn B. Pyrolysis-GC/MS of sinapyl and coniferyl alcohol. *J. Anal. Appl. Pyrolysis* 2013;99:161–9. <http://dx.doi.org/10.1016/j.jaap.2012.10.001>.
- [9] Hosoya T, Kawamoto H, Saka S. Role of methoxyl group in char formation from lignin-related compounds. *J. Anal. Appl. Pyrolysis* 2009;84:79–83. <http://dx.doi.org/10.1016/j.jaap.2008.10.024>.
- [10] Jin F, Zhang P, Wu G. Fundamental kinetics model of acidity-activity relation for ethylene oligomerization and aromatization over ZSM-5 zeolites. *Chem. Eng. Sci.* 2021;229:116144. <http://dx.doi.org/10.1016/j.ces.2020.116144>.
- [11] Kim JY, Heo S, Choi JW. Effects of phenolic hydroxyl functionality on lignin pyrolysis over zeolite catalyst. *Fuel* 2018;232:81–9. <http://dx.doi.org/10.1016/j.fuel.2018.05.133>.
- [12] Korányi TI, Fridrich B, Pineda A, Barta K. Development of ‘Lignin-First’ approaches for the valorization of lignocellulosic biomass. *Molecules* 2020;25. <http://dx.doi.org/10.3390/molecules25122815>.
- [13] Kumar A, Anushree, Kumar J, Bhaskar T. Utilization of lignin: A sustainable and eco-friendly approach. *J. Energy Inst.* 2020;93:235–71. <http://dx.doi.org/10.1016/j.joei.2019.03.005>.
- [14] Lago A, Hernando H, Moreno JM, Serrano DP, Feroso J. Valorisation of a lignin-rich residue via catalytic pyrolysis over ZrO₂/ZSM-5 technical catalyst. *Fuel Process. Technol.* 2021;215:106746. <http://dx.doi.org/10.1016/j.fuproc.2021.106746>.
- [15] Lan W, Luterbacher JS. A road to profitability from lignin via the production of bioactive molecules. *ACS Cent. Sci.* 2019;5:1642–4. <http://dx.doi.org/10.1021/acscentsci.9b00954>.
- [16] Li S, Luo Z, Wang W, Sun H, Xie J, Liang X. Catalytic fast pyrolysis of enzymatic hydrolysis lignin over lewis-acid catalyst niobium pentoxide and mechanism study. *Bioresour. Technol.* 2020;316:123853. <http://dx.doi.org/10.1016/j.biortech.2020.123853>.
- [17] Li J, Wei Y, Liu G, Qi Y, Tian P, Li B, et al. Comparative Study of MTO Conversion Over SAPO-34, H-ZSM-5 and H-ZSM-22: Correlating Catalytic Performance and Reaction Mechanism to Zeolite Topology. *Catal. Today*, vol. 171, Elsevier; 2011, p. 221–8. <http://dx.doi.org/10.1016/j.cattod.2011.02.027>.
- [18] Liu JY, Bin Wu S, Lou R. Chemical structure and pyrolysis response of β -o-4 lignin model polymer. *BioResources* 2011;6:1079–93. <http://dx.doi.org/10.15376/biores.6.2.1079-1093>.
- [19] Liu SN, Cao JP, Zhao XY, Wang JX, Ren XY, Yuan ZS, et al. Effect of zeolite structure on light aromatics formation during upgrading of cellulose fast pyrolysis vapor. *J. Energy Inst.* 2019;92:1567–76. <http://dx.doi.org/10.1016/j.joei.2018.07.017>.
- [20] Lou R, Bin Wu S, Dong HL, Lü GJ. Fast pyrolysis of enzymatic/mild acidolysis lignin from moso bamboo. *Ranliao Huaxue Xuebao/J. Fuel Chem. Technol.* 2015;43:42–7.
- [21] Lu Y, Lu YC, Hu HQ, Xie FJ, Wei XY, Fan X. Structural characterization of lignin and its degradation products with spectroscopic methods. *J. Spectrosc.* 2017;2017. <http://dx.doi.org/10.1155/2017/8951658>.
- [22] Mochizuki T, Chen SY, Toba M, Yoshimura Y. Pyrolyzer-GC/MS system-based analysis of the effects of zeolite catalysts on the fast pyrolysis of *Jatropha* husk. *Appl. Catal. A Gen.* 2013;456:174–81. <http://dx.doi.org/10.1016/j.apcata.2013.02.022>.
- [23] Pandey MP, Kim CS. Depolymerization and conversion: A review of thermochemical methods. *Chem. Eng. Technol.* 2011;34:29–41. <http://dx.doi.org/10.1002/ceat.201000270>.
- [24] Rahman MM, Liu R, Cai J. Catalytic fast pyrolysis of biomass over zeolites for high quality bio-oil – A review. *Fuel Process. Technol.* 2020;180:32–46. <http://dx.doi.org/10.1016/j.fuproc.2018.08.002>.
- [25] Ryu HW, Lee HW, Jae J, Park YK. Catalytic pyrolysis of lignin for the production of aromatic hydrocarbons: Effect of magnesium oxide catalyst. *Energy* 2019;179:669–75. <http://dx.doi.org/10.1016/j.energy.2019.05.015>.
- [26] Shen D, Liu G, Zhao J, Xue J, Guan S, Xiao R. Thermo-chemical conversion of lignin to aromatic compounds: Effect of lignin source and reaction temperature. *J. Anal. Appl. Pyrolysis* 2015;112:56–65. <http://dx.doi.org/10.1016/j.jaap.2015.02.022>.
- [27] Son D, Gu S, Choi JW, Suh DJ, Jae J, Choi J, et al. Production of phenolic hydrocarbons from organosolv lignin and lignocellulose feedstocks of hardwood, softwood, grass and agricultural waste. *J. Ind. Eng. Chem.* 2019;69:304–14. <http://dx.doi.org/10.1016/j.jiec.2018.09.009>.
- [28] Soongprasit K, Sricharoenchaikul V, Atong D. Pyrolysis of *milletia* (*pongamia*) pinnata waste for bio-oil production using a fly ash derived ZSM-5 catalyst. *J. Anal. Appl. Pyrolysis* 2019;139:239–49. <http://dx.doi.org/10.1016/j.jaap.2019.02.012>.
- [29] Soongprasit K, Sricharoenchaikul V, Atong D. Phenol-derived products from fast pyrolysis of organosolv lignin. *Energy Rep.* 2020;6:151–67. <http://dx.doi.org/10.1016/j.egy.2020.08.040>.
- [30] Tejado A, Peña C, Labidi J, Echeverria JM, Mondragon I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresour. Technol.* 2007;98:1655–63. <http://dx.doi.org/10.1016/j.biortech.2006.05.042>.
- [31] To AT, Resasco DE. Role of a phenolic pool in the conversion of *m*-cresol to aromatics over HY and HZSM-5 zeolites. *Appl. Catal. A Gen.* 2014;487:62–71. <http://dx.doi.org/10.1016/j.apcata.2014.09.006>.
- [32] Vichaphund S, Sricharoenchaikul V, Atong D. Utilization of fly ash-derived HZSM-5: catalytic pyrolysis of *jatropha* wastes in a fixed-bed reactor. *Environ. Technol. (U. K.)* 2017;38:1660–72. <http://dx.doi.org/10.1080/09593330.2016.1244567>.
- [33] Vichaphund S, Sricharoenchaikul V, Atong D. Selective aromatic formation from catalytic fast pyrolysis of *Jatropha* residues using ZSM-5 prepared by microwave-assisted synthesis. *J. Anal. Appl. Pyrolysis* 2019;141:104628. <http://dx.doi.org/10.1016/j.jaap.2019.104628>.
- [34] Wang K, Kim KH, Brown RC. Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chem.* 2014;16:727–35. <http://dx.doi.org/10.1039/c3gc41288a>.
- [35] Wang S, Li Z, Bai X, Yi W, Fu P. Catalytic pyrolysis of lignin in a cascade dual-catalyst system of modified red mud and HZSM-5 for aromatic hydrocarbon production. *Bioresour. Technol.* 2019;278:66–72. <http://dx.doi.org/10.1016/j.biortech.2019.01.037>.
- [36] Wang G, Li W, Li B, Chen H. TG Study on pyrolysis of biomass and its three components under syngas. *Fuel* 2008;87:552–8. <http://dx.doi.org/10.1016/j.fuel.2007.02.032>.
- [37] Yu Y, Li X, Su L, Zhang Y, Wang Y, Zhang H. The role of shape selectivity in catalytic fast pyrolysis of lignin with zeolite catalysts. *Appl. Catal. A Gen.* 2012;447–448:115–23. <http://dx.doi.org/10.1016/j.apcata.2012.09.012>.

- [38] Zhang B, Zhong Z, Ding K, Song Z. Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: Analytical Py-GC/MS study. *Fuel* 2015;139:622–8. <http://dx.doi.org/10.1016/j.fuel.2014.09.052>.
- [39] Zou R, Wang Y, Jiang L, Yu Z, Zhao Y, Wu Q, et al. Microwave-assisted co-pyrolysis of lignin and waste oil catalyzed by hierarchical ZSM-5/MCM-41 catalyst to produce aromatic hydrocarbons. *Bioresour. Technol.* 2019;289:121609. <http://dx.doi.org/10.1016/j.biortech.2019.121609>.