

## Production of phenolics and aromatics by pyrolysis of miscanthus

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### ABSTRACT

Upgrading of the vapor-phase products from the pyrolysis of miscanthus was carried out over Al-MCM-41, Al-MCM-48, HZSM-5 and mesoporous MFI (Meso-MFI). The characteristics of the catalysts used in this study were analyzed using N<sub>2</sub>-sorption and NH<sub>3</sub>-TPD. The catalytic activities were evaluated in terms of deoxygenation and the products composition. Catalytic upgrading improved the quality of bio-oil through deoxygenation, although the yield of bio-oil was reduced due to cracking. Mesoporous Al-MCM-41, Al-MCM-48 and Meso-MFI were superior to microporous HZSM-5 in terms of the removal of oxygenates and in the production of phenolics. With respect to the production of aromatics, HZSM-5 and Meso-MFI were more effective due to their high acidity. Of the catalysts tested in this study, Meso-MFI showed the highest activity for the deoxygenation and aromatization. When Pt was loaded onto HZSM-5 and Meso-MFI, both cracking and dehydrogenation were promoted, resulting in enhanced deoxygenation and aromatization.

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### 1. Introduction

With the increasing demand for the development of alternative energy sources, biomass has attracted considerable interest because it is a renewable resource with fewer adverse effects on the environment. Of these biomass sources, miscanthus with high photosynthesis and carbon dioxide fixation rates can be produced by as much as 20–26 dry tons per hectare each year, and is considered one of the most promising energy crops in the EU and US [1–5]. According to their report, the energy production cost of miscanthus was 2.4–3.6 €/GJ, in terms of the higher heating value (HHV), in 2004, which is equivalent to or lower than those of natural gas (3.1 €/GJ) and crude oil (4.6 €/GJ). Given that the price of fossil fuels is expected to double from 2004 to 2030, they argued that miscanthus will achieve sufficient price competitiveness in the future.

As the value of miscanthus as an energy resource has gained prominence, studies on bio-oil production through pyrolysis as a promising thermochemical energy conversion technology have been reported. Jeguirim et al. and Jong et al. used TGA and TG-FTIR,

respectively, to examine the characteristics and kinetics of the pyrolysis of miscanthus [6,7]. Hodgson et al. reported the fast pyrolysis of miscanthus using a fluidized bed reactor, and Heo et al. applied catalytic pyrolysis to miscanthus [8,9]. Nowakowski et al. examined the effect of phosphorous on the pyrolytic behavior of miscanthus using Py-GC-MS and TGA [10]. Yorgun and Simsek produced bio-oil with high aliphatic and aromatic hydrocarbon contents using the catalytic pyrolysis of miscanthus over activated alumina [11]. Khelifa et al. compared the catalytic pyrolysis and steam gasification of a mixture of hematite (Fe<sub>2</sub>O<sub>3</sub>) and miscanthus [12].

Despite the many efforts to produce bio-oil from miscanthus, few studies have examined catalytic upgrading to reduce the oxygen content of bio-oil, which results in a low heating value and instability during long-term storage. The catalytic technologies for bio-oil stabilization include hydrotreatment and catalytic vapor cracking. The latter is favored by many researchers because it is applicable under mild conditions (400–550 °C temperature range and atmospheric pressure) and at low cost. A range of catalysts, including petrochemistry-based zeolite catalysts, such as HZSM-5 and USY, as well as mesoporous MCM-41 catalysts have been applied to the catalytic vapor cracking of bio-oil [13–19]. Zeolite catalysts and mesoporous catalysts have different strengths with respect to bio-oil upgrading. Zeolite catalysts have high acidity,

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which is advantageous for cracking, and excellent hydrothermal stability but mesoporous materials have large pore sizes ( $\geq 2$  nm) that promote mass transfer and/or the diffusion of large molecules. Therefore, if a catalyst possesses high acidity, good stability and large (nanometer-sized) pores, a synergy effect for the upgrading of large molecules produced from the pyrolysis of biomass would be expected. In recent years, there have been reports on the synthesis of aromatics from biomass by catalytic upgrading [20,21]. Carlson et al. evaluated five catalysts, ZSM-5, silicalite, beta, Y and silica–alumina. Among them, ZSM-5 had the highest aromatic yields [20]. Mihalcik et al. screened acidic zeolites for the catalytic pyrolysis of biomass and its components, and reported HZSM-5 to be the most effective in producing aromatic hydrocarbons [21].

A mesoporous MFI (Meso-MFI, hereafter) catalyst is a new material with the advantages of both zeolite catalysts and mesoporous materials [17,19,22]. In addition, Pt exhibited high activity for the cracking and dehydrogenation reactions required for aromatics production from bio-oil [23,24].

In this study, HZSM-5, mesoporous materials (MCM-41 and MCM-48) and Meso-MFI were used to carry out the catalytic upgrading of miscanthus-derived bio-oil. In addition, Pt was added as a bifunctional metal to determine its effects on the characteristics of bio-oil upgrading.

## 2. Experimental

### 2.1. Catalyst preparation

Al-MCM-41, Al-MCM-48 and Meso-MFI catalysts were prepared following the procedures reported in the literature [17,19,22,25]. HZSM-5 was purchased from Zeolyst International Company. For the generation of 0.5 wt.% Pt/HZSM-5 and 0.5 wt.% Pt/Meso-MFI, HZSM-5 and Meso-MFI were impregnated with a  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  water solution and heated in air at 550 °C to load the Pt via  $\text{O}_2$  calcination and  $\text{H}_2$  reduction. 0.5 wt.% Ga/Meso-MFI was prepared following the procedures reported in the literature [17].

### 2.2. Characterization of catalysts

The catalysts used in this study were characterized as follows: the acidity was measured using the  $\text{NH}_3$ -temperature-programmed desorption (TPD) method, employing a TPD/TPR 2900 analyzer (Micromeritics Instrument Co.). Prior to the measurements, the samples were first treated in a He stream at 500 °C. After cooling to 100 °C,  $\text{NH}_3$  adsorption was carried out. After purging samples in the He stream for 2 h, to completely remove the physically adsorbed  $\text{NH}_3$ , the catalysts were heated to 700 °C, at a heating rate of 10 °C/min. The desorbed  $\text{NH}_3$  was detected using a thermal conductivity detector (TCD).  $\text{N}_2$  adsorption/desorption isotherms were obtained at  $-196$  °C, using a Micromeritics ASAP 2000, with the Brunauer–Emmett–Teller (BET) surface area calculated from the linear portion of the BET plot. Inductively coupled plasma analysis was used to determine the Si:Al molar ratio.

### 2.3. Reaction procedure

The *Miscanthus sinensis* var. *purpurascens* used in these experiments was sieved to obtain particles with a mean size of 0.3 mm and; thereafter, dried in an oven (J-NDS1, JISICO) at 110 °C for 24 h to minimize the water content of the oil product. After the miscanthus had been dried, its water content was less than 1 wt.%. The characteristics of miscanthus were reported in the literature [9].

In order to maximize the bio-oil yield, a reaction system with a fluidized bed should be configured [9]. However, the objective of

this study was not to maximize the bio-oil yield but to investigate the basic upgrading behavior of bio-oil over catalysts, which was required as a preliminary study before practical applications to bio-oil upgrading employing a fluidized bed reactor. Therefore, the pyrolysis of miscanthus and the subsequent catalytic upgrading of the pyrolytic vapors were carried out in a fixed bed reactor system. The upgrading system was consecutively installed at the latter part of the main pyrolysis reactor. The main pyrolysis reactor was a quartz reactor into which the miscanthus (5.0 g) was charged. The fixed catalyst bed reactor was a tubular quartz type reactor which was filled with 0.5 g of catalyst. All the catalysts were pelletized, crushed and screened with standard sieves (1.7–2.4 mm) prior to their use in the experiments. For non-catalytic pyrolysis, the catalyst was replaced with quartz beads to maintain the same space velocity within the fixed catalyst bed. Prior to the experiments, all the experimental systems were purged with inert nitrogen, at a flow rate of 50 mL/min, for 1 h. Both reactors were indirectly heated electrically to the desired reaction temperature. Thereafter, the pyrolysis and upgrading reaction continued for 1 h. The temperatures of the experimental systems were adjusted using a PID temperature controller and monitored with two thermocouples (K type). The errors in the average reaction temperatures were within  $\pm 5$  °C. Condensable bio-oil was collected in a glass condenser cooled to a temperature of  $-25$  °C, using a circulator (RW-2025G, JEIO TECH), with ethyl alcohol as the cooling solvent. The non-condensable gases passing through the quenching system were sampled using Teflon gasbags, at 30 min intervals, with their compositions then analyzed. The experiments were conducted at least three times for each catalyst to confirm the reproducibility of the reported procedures. Mass balance for all experiments was calculated as follows: char (wt.%) + bio-oil (wt.%) + gas (wt.%) = 100. The reproducibility of the runs was above 97%.

### 2.4. Product analysis

Because it is difficult to obtain quantitative analytical results from bio-oil with acceptable accuracies using the existing gas chromatography equipment, the area% of a GC–MS chromatogram was considered a good approximation for indicating the amounts of various chemical compounds in the bio-oil [9,13–15,17–19,26–28]. In this study, the quantitative and qualitative analyses of the bio-oil were performed using GC–MS (HP 5973), with an HP-5MS capillary column. For the analysis of chemical composition in bio-oil, the organic fraction was separated from aqueous fraction by centrifuging at 3000 rpm for 5 min. The water content of the bio-oil was measured using the ASTM E 203 method. A Karl Fischer titrator (Metrohm 787 KF Titrimo) was used, with HYDRANAL Composite 5 K (Riedel-de Haen) and HYDRANAL Working Medium K (Riedel-de Haen) used as the titration reagent and the titration solvent, respectively. The analysis was carried out three times to confirm the reproducibility and average values were calculated for each identified product.

The pyrolysis gases were analyzed using GC–TCD and GC–FID (ACME 6000, Young Lin Instruments Co. Ltd.). A Carboxen 1000 column and HP-plot  $\text{Al}_2\text{O}_3/\text{KCl}$  column were used for the TCD and FID, respectively.

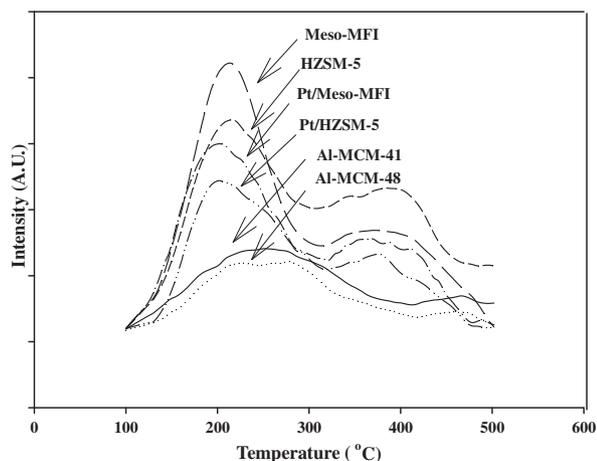
## 3. Results and discussion

### 3.1. Characterization of catalysts

The structural characteristics of the catalysts used in this study are summarized in Table 1. The specific surface areas of the mesoporous materials, Al-MCM-41 and Al-MCM-48, were considerably larger than those of the solid acid catalysts, HZSM-5 and

**Table 1**  
Textural properties of catalysts.

	$S_{BET}$ (m <sup>2</sup> /g)	$V_{tot}$ (cm <sup>3</sup> /g)	Average pore size (nm)	Si/Al ratio
Al-MCM-41	950	0.93	2.6	20
Al-MCM-48	1350	1.21	2.6	20
HZSM-5	411	0.22	0.51 × 0.55 0.53 × 0.56	15
0.5 wt.% Pt/HZSM-5	386	0.20	0.51 × 0.55 0.53 × 0.56	15
Meso-MFI	567	0.7	4.1	15
0.5 wt.% Pt/Meso-MFI	472	0.6	4.1	15



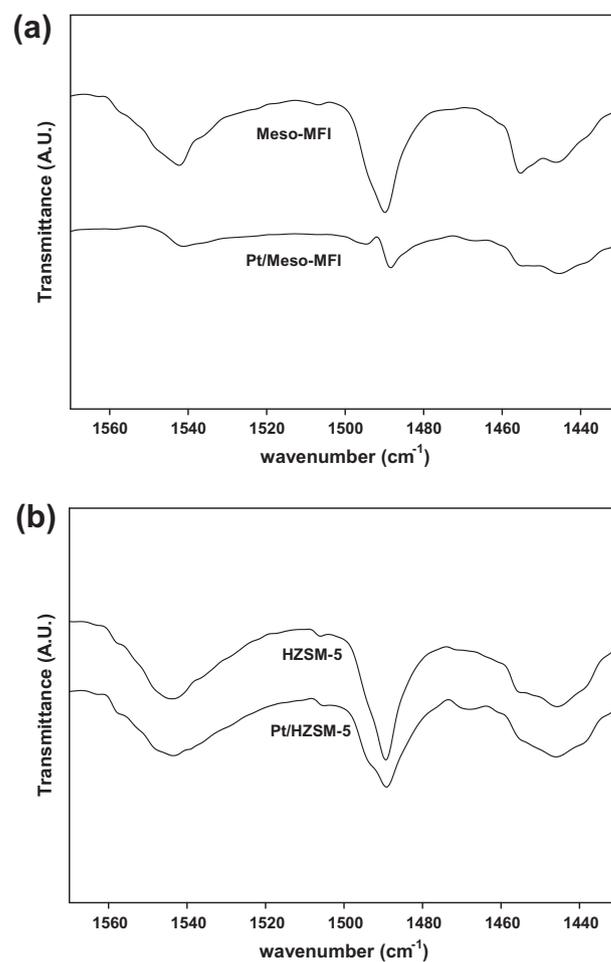
**Fig. 1.** NH<sub>3</sub>-TPD curves of catalysts.

Meso-MFI. In addition, Meso-MFI exhibited a larger specific surface area than HZSM-5, which was attributed to the formation of mesopores [17]. After loading of Pt, the surface areas of the catalysts were reduced, probably due to pore blocking.

Fig. 1 shows the NH<sub>3</sub>-TPD curves of the catalysts used in this study. The zeolite catalysts (HZSM-5 and Meso-MFI) exhibited higher acidities than the mesoporous catalysts (Al-MCM-41 and Al-MCM-48). Also, Fig. 2 shows the pyridine FT-IR spectra of Meso-MFI, Pt/Meso-MFI, HZSM-5 and Pt/HZSM-5. Pyridine produces a band at around 1545 cm<sup>-1</sup> when adsorbed on Brønsted acid sites and a band at around 1454 cm<sup>-1</sup> when adsorbed on Lewis acid sites [29]. It can be shown that zeolite catalysts have Brønsted acid sites and Lewis acid sites. Meanwhile in our previous pyridine FT-IR studies, mesoporous catalysts such as Al-MCM-48 and Al-MCM-41 have mostly weak Lewis acid sites [30,31]. When Pt was loaded onto the zeolite catalysts, the Brønsted acid sites (1545 cm<sup>-1</sup>) were reduced. This result was in good agreement with our previous studies using Ga as a bifunctional metal, which was attributed to the replacement of H<sup>+</sup>, Brønsted acid sites, by the transport of Pt into the pores after hydrogen reduction [17].

### 3.2. Catalytic upgrading of pyrolytic vapors from miscanthus

The product distribution obtained under various pyrolysis and upgrading temperatures, using the HZSM-5 catalyst, is shown in Table 2. Under non-catalytic pyrolysis conditions, a higher temperature caused more char to be converted into gas via secondary decomposition reactions, but the bio-oil yield maintained more or less unchanged. Based on this result, the pyrolysis temperature was set at 450 °C during the catalytic upgrading experiments. Catalytic upgrading using the HZSM-5 catalyst resulted in a reduction in the bio-oil yield due to cracking, which lead to an increased gas yield. It was proven in our previous study that the main deoxygenation pathway of bio-oil is dehydration, which can be used as a basis for the evaluation of bio-oil produced from lignocellulosic



**Fig. 2.** Pyridine FT-IR spectra of (a) Meso-MFI and Pt/Meso-MFI (b) HZSM-5 and Pt/HZSM-5.

**Table 2**  
Effect of the pyrolysis and upgrading temperature on the product distribution.

	Without catalyst			HZSM-5		
	400	450	500	450	450	450
Reaction temp. (°C)	–	–	–	450	500	550
Catalyst bed temp. (°C)	–	–	–	450	500	550
Water content (wt.% in oil)	34.4	35.3	39.3	45.0	55.1	64.2
Oil	53.8	55.2	54.2	51.0	47.8	46.1
Gas	17.6	18.8	22.0	23.0	26.4	28.1
Char	28.6	26.0	23.8	26.0	25.8	25.8

biomass [17]. On increasing the upgrading temperature, the water content in the bio-oil increased considerably (Table 2). This result was attributed to the deoxygenation of oxygenates in the bio-oil, which contained carbonyl and carboxyl groups, indicating that the catalytic upgrading improved the bio-oil quality.

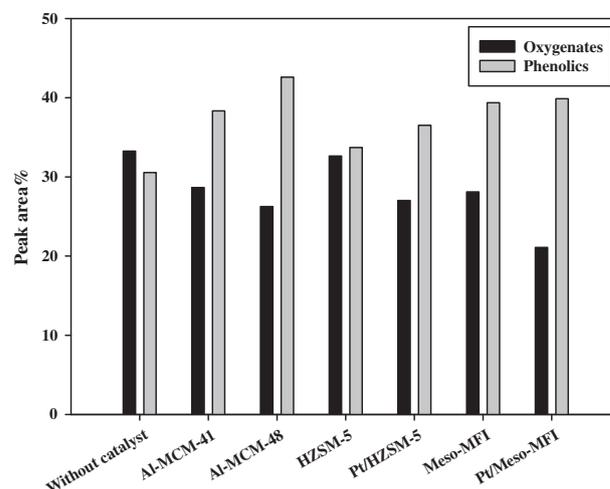
**Table 3**  
Effect of the catalyst type on the product distribution.

Catalyst	Char (wt.%)	Oil (wt.%)	Gas (wt.%)	Water (wt.% in oil)
Without catalyst	26.0	55.2	18.8	35.3
Al-MCM-41	25.8	48.2	26.0	48.5
Al-MCM-48	25.8	49.2	25.0	46.4
HZSM-5	25.8	47.8	26.4	55.1
Pt/HZSM-5	25.4	43.8	30.8	58.9
Meso-MFI	25.8	48.1	26.1	57.6
Pt/Meso-MFI	25.6	44.2	30.2	64.8

**Table 4**  
Main compounds identified in the non-catalytic bio-oil.

RT (min)	Compounds	Area (%)
5.23	Acetic acid	6.49
12.34	2-Furancarboxaldehyde	7.78
12.45	2-Cyclopenten-1-one	0.56
13.28	2-Furanmethanol	1.26
15.4	2-Methyl-2-cyclopenten-1-one	0.54
15.56	1-(2-Furyl)-ethanone	0.30
15.67	2(5H)-Furanone	1.30
16.18	1,2-Cyclopentanedione	2.24
16.72	5-Methyl-2-(5H)-furanone	0.20
17.66	5-Methyl-2-furancarboxaldehyde	1.18
17.91	3-Methyl-2-cyclopenten-1-one	0.34
18.45	Phenol	1.68
20.3	2-Hydroxy-3-methyl-2-cyclopenten-1-one	1.53
20.87	2,3-Dimethyl-2-cyclopenten-1-one	0.21
21.2	2-Methyl-phenol	0.35
21.99	4-Methyl-phenol	1.35
22.41	2-Methoxy-phenol	2.43
23.49	Maltol	0.36
23.56	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.43
24.54	2,4-Dimethyl-phenol	0.22
25.15	4-Ethyl-phenol	2.31
25.52	2-Methoxy-4-methyl-phenol	1.41
26.41	1,2-Benzenediol	1.75
26.85	4-Vinylphenol	5.61
27.28	5-(Hydroxymethyl)-2-furancarboxaldehyde	1.79
28.32	3-Methoxy-1,2-benzenediol	1.67
28.67	4-Ethyl-2-methoxy-phenol	1.48
29.84	2-Methoxy-4-vinylphenol	2.51
30.88	2,6-Dimethoxy-phenol	3.06
31.05	2-Methoxy-4-(2-propenyl)-phenol	0.67
31.5	4-Hydroxy-benzaldehyde	0.68
32.47	4-Hydroxy-3-methoxy-benzaldehyde(vanillin)	1.38
33.52	4-Hydroxy-3-methoxy-benzoic acid	0.25
33.81	2-Methoxy-4-propyl-phenol	0.36
34.86	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	0.32
35.65	Levogluconan	12.92
37.63	2,6-Dimethoxy-4-(2-propenyl)-phenol	1.16
39.24	4-Hydroxy-3,5-dimethyl-benzaldehyde	0.47

The product distributions obtained with the different types of catalyst are summarized in Table 3. In general, catalytic upgrading reduced the bio-oil yield, while increasing the gas yield, but the effects of the different catalyst types on the product yield were not large. However, there was a distinct difference in the water content of the bio-oils produced via the use of the different catalysts. Compared to Al-MCM-41 and Al-MCM-48 which have mostly weak acid sites, HZSM-5 and Meso-MFI having strong acid sites showed better cracking performances and lead to higher deoxygenation capacities. Another interesting finding was that the loading of Pt onto the HZSM-5 and Meso-MFI catalysts resulted in enhanced deoxygenation capacities, despite of the decreased number of Brønsted acid sites participating directly in the cracking reactions; as mentioned above in the NH<sub>3</sub>-TPD and pyridine FT-IR results, unfortunately leading to an additional reduction in the bio-oil yield. This was contrary to the results of catalytic pyrolysis of miscanthus



**Fig. 3.** Main chemical compounds in upgraded bio-oils.

**Table 5**  
Main aromatics identified in upgraded bio-oils.

Compounds	Peak area (%)			
	HZSM-5	Pt/HZSM-5	Meso-MFI	Pt/Meso-MFI
Toluene	0.4	0.5	0.6	1.3
Ethyl-benzene	0.4	0.3	0.4	0.5
<i>p</i> -Xylene	1.7	1.8	2.6	3.9
C <sub>9</sub> + mono aromatics	1.8	2.7	4.2	7.4
C <sub>10</sub> + PAHs	2.3	3.3	0.8	2.1

over Ga/Meso-MFI where the yield of bio-oil (48.3 wt.%) was similar to that for Meso-MFI (48.1 wt.%). This difference may stem from the different catalytic behaviors of Ga and Pt. Ga only plays a role as a co-catalyst, which enhances the rate of specific reactions, such as dehydrogenation, while not participating in the cracking reactions. Pt, on the other hand, takes part in the cracking, hydrogenolysis, hydrocracking and dehydrogenation reactions [23]. Therefore, in this study, Pt may have cracked some larger molecules of the bio-oil into smaller gas molecules, eventually increasing the gas yield. This has also been confirmed by other investigators. Jongpatiwut et al. carried out the aromatization of *n*-octane and *n*-hexane over Pt/SiO<sub>2</sub> and Pt/KL catalysts [24]. In their results, significant cracking products, such as C<sub>1</sub>–C<sub>5</sub> hydrocarbons, were obtained. Shabaker et al. also confirmed that Pt participated in simultaneous C–C bond cleavage and dehydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> via the aqueous-phase reforming of ethylene glycol [32].

### 3.3. Chemical composition of upgraded bio-oils

The composition of the bio-oil obtained from non-catalytic pyrolysis is shown in Table 4. Acids, carbonyls, carboxyls, phenolics and levoglucosan were shown to be the main products, which were in accordance with previous studies [9].

Thus far, a number of researchers have compared the chemical compositions of bio-oils after catalytic upgrading as another criterion for evaluation. In this study, phenolics and aromatics, regarded as desirable chemicals, as well as oxygenates were chosen as the criteria species to assess the degree of deoxygenation. Changes in the bio-oil composition as a result of catalytic upgrading are shown in Fig. 3. In general, catalytic upgrading resulted in a reduction of the oxygenates content and an increase in the phenolics content, with high value-added. In this study, main oxygenate

**Table 6**  
Yields and composition of gas products.

	Without catalyst	Al-MCM-41	Al-MCM-48	HZSM-5	Pt/HZSM-5	Meso-MFI	Pt/Meso-MFI
<i>Yield (wt.%)</i>							
CO	5.0	9.1	8.9	9.1	12.2	9.1	13.1
CO <sub>2</sub>	12.2	14.2	13.6	14.6	15.0	13.9	14.0
C <sub>1</sub> –C <sub>4</sub>	1.3	1.9	1.8	1.9	2.7	2.1	3.2
<i>Selectivity (wt.% in gas)</i>							
CO	27.0	36.2	35.7	35.7	40.9	36.2	45.6
CO <sub>2</sub>	65.9	56.4	54.7	56.8	50.0	55.6	48.4
CH <sub>4</sub>	3.5	3.2	3.2	1.8	2.7	2.5	2.2
C <sub>2</sub> H <sub>4</sub>	0.7	0.8	0.8	1.5	1.9	1.0	1.5
C <sub>2</sub> H <sub>6</sub>	1.0	0.9	0.9	0.5	1.0	0.7	0.7
C <sub>3</sub> H <sub>6</sub>	0.8	1.1	1.0	2.0	2.2	2.1	2.9
C <sub>3</sub> H <sub>8</sub>	0.4	0.4	0.4	0.3	0.3	0.3	0.3
C <sub>4</sub> H <sub>8</sub>	0.5	0.7	0.6	0.9	0.8	1.1	1.4
C <sub>4</sub> H	0.1	0.1	0.1	0.1	0.2	0.1	0.1

and phenolic compounds are levoglucosan and alkylated phenols and guaiacol derivatives, respectively. With the use of catalysts, levoglucosan decreased from 13% for non-catalytic pyrolysis to 10.9% (HZSM-5) > 8.4% (Pt/HZSM-5) > 6.5% (Meso-MFI) > 5.3% (Pt/Meso-MFI) > 1.8% (Al-MCM-41) > 1.6% (Al-MCM-48), while alkylated phenols and guaiacol derivatives increased from 20.2% for non-catalytic pyrolysis to 21.9% (HZSM-5) < 22.2% (HZSM-5) < 25.3% (Al-MCM-41) < 26.2% (Pt/Meso-MFI) = 26.5% (Meso-MFI) < 27.1% (Al-MCM-48). Al-MCM-41, Al-MCM-48 and Meso-MFI catalysts which possess mesopores were superior to HZSM-5 having micropores in terms of the removal of oxygenates and the production of phenolics. This agrees with the results of previous studies that used mesoporous catalysts. Adam et al. performed catalytic upgrading of bio-oil, using mesoporous catalysts, such as Al-MCM-41 and SBA-15, and concluded that these catalysts were the most effective for removing oxygenates, such as acids, alcohols, carbonyls, and producing phenolics [13,14]. Another interesting result was that among the mesoporous materials, Al-MCM-48, which possesses a 3-dimensional structure, exhibited the best performance in terms of both oxygenates removal and phenolics selectivity as a result of its outstanding mass transfer and diffusion rates, while the 2-dimensional Al-MCM-41 exhibited a lower performance with respect to bio-oil upgrading. When Pt was loaded onto the zeolite, its contribution was very small with respect to increasing the phenolics selectivity, while being effective at removing oxygenates, which may be attributed to the cracking ability of Pt itself, as mentioned above.

The composition of aromatic compounds, another desirable species aside from phenolics, is summarized in Table 5. Aromatics, as distinct from phenolics, were mainly produced when the acidic catalyst, zeolite, was used. Because, as shown in our previous study, the production of aromatics are favored on the strong acid sites, the yields of aromatics over Al-MCM-41 and Al-MCM-48, which do not contain strong acid sites, were negligible in this study [17]. Among the MFI zeolites, Meso-MFI, which has mesopores, was shown to be favorable for the production of aromatics because of the synergy effect of its strong acid sites and large pore size. When Pt was added to the zeolites, the production of aromatics was significantly enhanced, similar to our previous study where Ga was loaded onto the catalysts. The role of Pt in aromatization has been known to be similar to that of Ga in *n*-paraffin aromatization. Therefore, in bio-oil upgrading, the role of Pt seems to be similar to that of Ga. The incorporation of Pt cations into the Meso-MFI zeolite increased the initial dehydrogenation rates of alkanes, as well as the subsequent dehydrogenation rates needed to more rapidly transform the alkenes to aromatics, leading to considerably more aromatics compared to those produced by the parent Meso-MFI zeolite [17]. Meanwhile, the reported average composi-

tions of *Miscanthus sinensis* var. *purpurascens* were lignin 96.45 g/kg, cellulose 471.23 g/kg and hemicellulose 328.43 g/kg [33], which implies that significant amount of aromatics may come from cellulose and hemicellulose rather than from lignin.

### 3.4. Gas products

The composition of gaseous products obtained by catalytic upgrading is shown in Table 6. The formation of CO and CO<sub>2</sub> is another well known pathway of the deoxygenation of bio-oil. Employing a catalyst considerably increased the concentrations of CO and CO<sub>2</sub>. In addition, Pt seemed to increase the reaction rates via the two pathways relevant to decarbonylation and decarboxylation. However, further study on the detailed mechanism of the role of Pt on the high yields of CO and CO<sub>2</sub> will be required. There was an observable difference in the composition of hydrocarbons. Zeolite catalysts were shown to be superior to Al-MCM-41 and Al-MCM-48 in terms of the selectivity of C<sub>2+</sub>; in particular, of alkenes because some alkanes were converted to alkenes via the dehydrogenation caused by the attack of H<sup>+</sup> [17]. Pt further promotes the dehydrogenation of alkanes. The C<sub>2</sub>–C<sub>4</sub> alkenes produced in such a way are eventually converted to aromatic compounds on zeolite catalysts possessing strong acid sites, as determined from the yield of aromatics shown in Table 5.

## 4. Conclusions

Mesoporous Al-MCM-41 and Al-MCM-48 catalysts exerted high selectivities toward the production of phenolics while HZSM-5 and Meso-MFI, which possess strong acid sites, showed high selectivities to aromatics. Considering the deoxygenation of oxygenates and the selectivity for desirable products, such as phenolics and aromatics, the most adequate catalyst for the upgrading of miscanthus bio-oil was shown to be Meso-MFI zeolite, which has both mesopores and high acidity. The loading of Pt on catalysts promoted cracking and dehydrogenation, resulting in enhanced deoxygenation and aromatization.

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