

Green Aromatics from Catalytic Fast Pyrolysis of Fast Growing Meranti Biomass

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Abstract

The study on catalytic pyrolysis decomposition of *Shorea leprosula* wood biomass to form aromatic compounds in fast pyrolysis was performed by pyrolytic-gas chromatography/mass spectroscopy (Py-GC/MS) and transmission electron microscope (TEM) - electron energy-loss spectroscopy (EELS) to analyze the chemical compound and solid residue microstructure. Py-GC/MS and TEM-EELS analysis showed that the fast pyrolysis increased the decomposition of hardwood, in which in the presence of ZSM-5 catalyst, the liquid products from wood decomposition was then diffused into the pore of ZSM-5 catalyst to form aromatics including benzene, toluene, styrene, naphthalenes and indanes. The carbonaceous solid compounds or cokes were not deposited on the surface of pores of ZSM-5 catalyst in the fast pyrolysis, as shown by the EELS spectrum that exhibited no detection of any solid carbonaceous compound in the solid residue.

Keywords: Catalytic fast pyrolysis, pyrolytic-gas chromatography/mass spectroscopy, transmission electron microscope, electron energy-loss spectroscopy.

Introduction

Establishment of large area of forest plantation composed of fast growing hardwood species in many tropical countries generates low cost and abundant biomass which is potential for conversion to renewable biofuels and chemicals such as aromatics. One of those species is *Shorea leprosula* which has been planted in the few forest concessions in Indonesia including more than 146,600 acres managed by PT. Sari Bumi Kusuma in Central Kalimantan. The conversion of biomass to aromatics compound is a rational effort for providing green chemicals which are able to substitute various oil derivate chemicals. Aromatics are intensively used in the variety of fields such as in pharmaceutical for solvent (Constable *et al.* 2007) and drugs (Fujita *et al.* 2001) and in chemical industries for food packaging, vehicle tyres, plastics, detergents, dyes, cosmetics, etc [The Aromatics Produces Association (APA) – European Chemical Industry Council (CEFIC). 2001].

Efforts in the development of biomass conversion to aromatics have been carried out. Catalytic upgrading of bio-oil which is produced by fast pyrolysis of biomass is one of the routes considered to obtain aromatic compounds such as reported by Vitolo *et al.* (2001) and Park *et al.* (2010) using HZM-5 catalyst. The other methods are by hydrodeoxygenation which use hydrogen for exclusion of the heteroatom at high pressure and temperature between 250–450°C, forming respectively H₂O and H₂S in the produced aromatic products (Mortensen *et al.* 2011). Fast pyrolysis of biomass is preferred on producing bio-oil due to the feasibility to obtain the high yield at range between 60–75 wt% (Mahon *et al.* 2006). More recently, Carlson *et al.* (2009) have developed a single step catalytic fast pyrolysis to produce aromatics including benzene, toluene and naphthalene from biomass in a single reactor with a short residence time. In this process, biomass was initially decomposed to smaller oxygenates that then enter the

catalyst pores where they are converted to CO, CO₂, water, coke and volatile aromatics through simultaneous dehydration, decarboxylation and decarbonylation. This single step is rapid and shown as promising biomass conversion process to aromatics.

In previous studies, the aromatic production and selectivity was found as a function of catalyst to feedstock weight ratio, heating rate and reaction temperature (Carlson *et al.* 2010). French and Czernik (2010) performed a study on the efficiency of various catalyst for aromatic production and found that the highest yield of aromatics from wood, around 16 wt% including 3.5 wt% of toluene were obtained by ZSM-5 zeolite catalyst. Moreover, Zhang *et al.* (2009) compared the catalytic activation of the fresh and spent catalysts in fast pyrolysis of biomass. However, there is no report on the microstructure of solid residue in relation to the aromatics production from fast catalytic pyrolysis of wood biomass. Kurosaki *et al.* (2003) reported that flash heating results in carbon microstructure with the curved graphene layers that in contrast to conventional heating. It seems that aromatics products which are determined by thermal degradation in catalytic fast pyrolysis, likely correspond to the microstructure of solid residue. In addition, the microstructure of solid residue, especially carbonized wood, is crucial to expand its potential applications. The objectives of this study were to evaluate the aromatic products of catalytic fast pyrolysis of *Shorea leprosula* wood using ZSM-5 catalyst which was analyzed by Py-GC/MS and to observe the microstructure of solid residue of the catalytic fast pyrolysis by TEM and EELS.

Materials and Methods

A wood strip sample was collected from the bottom part of a ten years old *Shorea leprosula* tree grown in the line planting of forest concession area managed by PT. Sari Bumi Kusuma, Central Kalimantan, Indonesia. Part of the

wood strip sample was milled into powder and sieved with wire mesh screens to obtain particles with size range of 0.25 ~ 0.42 mm (passing through 40 mesh sieve and retained by 60 mesh sieve). ZSM-5 catalyst was used in this study.

The pyrolysis of wood (0.1 mg) or the mixture of 1 (wood) : 9 (ZSM-5) (1 mg) was performed with a single-shot (denoted as fast pyrolysis) and a double-shot (denoted as slow pyrolysis) by a double shot pyrolyzer (PY-2020, Frontier Lab.) directly connected to a GC/MS system Shimadzu (QP-5000) equipped with a fused silica capillary column (30 m x 0.25 μ m inner diameter). The fast pyrolysis was performed by raising the temperature of pyrolyzer furnace to 400°C without heating the sample. When the condition had stabilized, then the sample in steel sampling cup, 5 mm in diameter and 7 mm in height, was dropped to the furnace and kept at 400°C for 3 min under the He gas flow rate of 50 ml/min. The slow pyrolysis was conducted by placing the sample in steel sampling cup in furnace. The sample was then pre-heat treated at temperature of 100°C for 3 min followed by heating at 100°C/min to 400°C. The reaction time was 3 min under the same condition as during the fast heating process.

The GC/MS condition was the same for both slow and fast pyrolysis experiments. Oven temperature was held at 90°C for 3 min and then increased up to 190°C at 10°C/min and kept for 5 min. The temperature increased from 190°C to 320°C at 10°C/min and isothermal at 320°C for 35 min. The carrier gas used was helium with a controlled flow of 50

ml/min.

The microstructure and chemical composition of ZSM-5 and the solid residue from the catalytic and non-catalytic slow and fast pyrolysis was analyzed using TEM (JEOL-JEM-2100F), equipped with electron energy-loss spectroscopy (EELS, GATAN).

Results and Discussion

Figure 1 (A) and (B) show the total ion chromatogram of liquid products from slow pyrolysis of wood and the mixture of wood and ZSM-5 [1 (wood) : 9 (ZSM-5)], respectively. The slow pyrolysis of wood produced liquid products constituted hundreds of chemical compounds as shown by hundreds of peaks detected on the total ion chromatogram (top). These chemical compounds include hundreds of low molecular weight compounds and molecular aggregates of higher molecular weights which are from the thermal degradation of three main wood constituents: cellulose, hemicellulose and lignin (Meier 1999). Figure 1 (B) shows that catalyst added in wood slightly influenced the chemical compounds in liquid products. The little change in the chemical composition in liquid products indicated that ZSM-5 catalyst performed less efficiency in slow pyrolysis of wood. In the slow pyrolysis of biomass, the vapors do not escape as rapidly as in fast pyrolysis (Mahon *et al.* 2006). Therefore, fewer vapors diffuse in ZSM-5 catalyst.

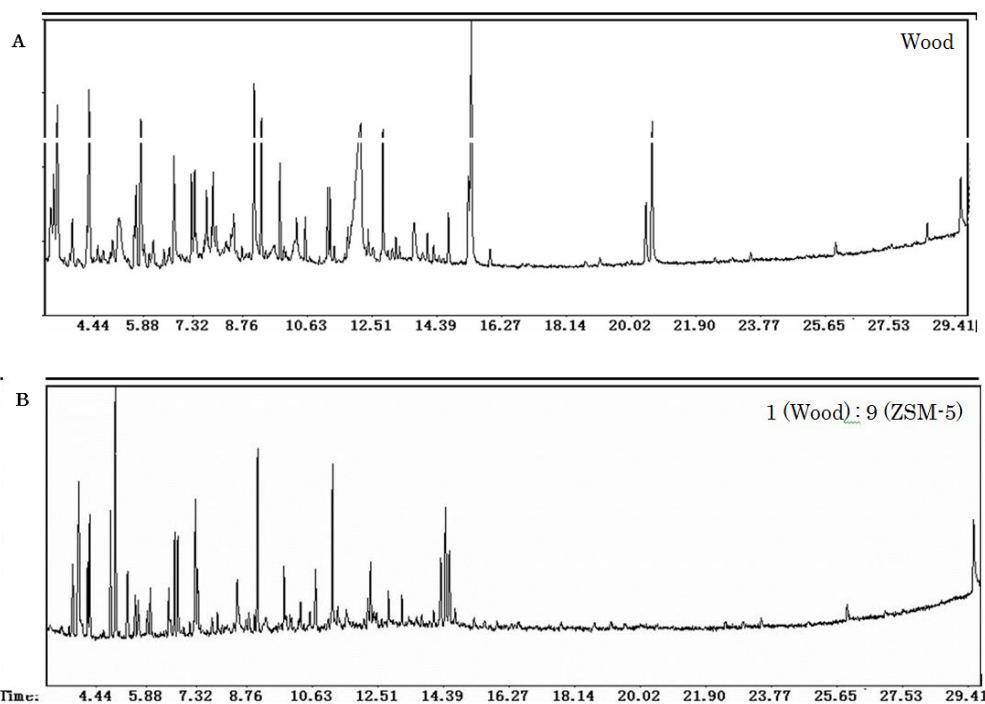


Figure 1. Total ion chromatogram of liquid products from (A) slow pyrolysis of wood and (B) that of the mixture of wood and ZSM-5 [1 (wood) : 9 (ZSM-5)].

Figure 2 (A) and (B) show the total ion chromatogram of liquid products for fast pyrolysis of wood and the mixture of 1 (wood) : 9 (ZSM-5), respectively. The estimated chemical compounds such as furfural and levoglucosan decomposed from cellulose and guaiacol and 4-vinylguaiacol decomposed from lignin were detected (Azeez *et al.* 2010; Shen and Gu 2009). The peaks of carbohydrate derivatives at retention time in ranges up to 5 min (Arias *et al.* 2006) and those of lignin derivatives at retention time in ranges of 6 ~ 15 min (Arias *et al.* 2006; Oasmaa *et al.* 2003) became more abundant compared to that from slow pyrolysis of wood. Fast pyrolysis increased the decomposition of wood through rapid and simultaneous depolymerizing and fragmenting of cellulose, hemicellulose and lignin with rapid increase in temperature (Mahon *et al.* 2006).

The presence of ZSM-5 catalyst reduced the number of chemical compound in the liquid products of fast pyrolysis of wood. Figure 2 (B) shows that the estimated aromatics peaks such as benzene, toluene, styrene, naphthalenes and indanes (Tsuge *et al.* 2011) were detected in fast pyrolysis of the mixture of wood and ZSM-5 [1(wood) : 9(ZSM-5)]. The release of aromatic compounds was along with the disappearing of cellulose and lignin derivatives such as furfural and levoglucosan; and guaiacol and 4-vinylguaiacol, respectively. Therefore catalytic fast pyrolysis decomposed carbohydrates and lignin to produce bio-oil (Mahon *et al.* 2006) containing furfural, levoglucosan, guaiacol and

4-vinylguaiacol, which were then diffused into ZSM-5 pores and through a series of decarbonylation, decarboxylation, dehydration and oligomerization reactions, aromatics were formed (Carlson *et al.* 2010) which were not detected on the non-catalytic fast pyrolysis of wood. ZSM-5 catalyst with a potential ideal pore size in the range of 0.52 ~ 0.55 nm (Mihalcik *et al.* 2011) and Brønsted acid sites (Corma *et al.* 2009) leads to the production of aromatics in this study. The mechanism of aromatic formation from carbohydrates and lignin through a catalytic fast pyrolysis was explained elsewhere (Shen and Gu 2009; Carlson *et al.* 2010; Shen *et al.* 2010; Mullen and Boateng 2010). Analysis of the aromatic compound in liquid products of catalytic fast pyrolysis of wood in this study is still ongoing.

Transmission electron microscope of carbonized wood from non-catalytic fast pyrolysis is shown in Figure 3 (A). A typical of turbostratic microstructure with random orientation of crystallite was found in the carbonized wood from fast pyrolysis. On the edge of the turbostratic microstructure, well developed graphitic structures with circular body form are clearly visible. The fast pyrolysis with rapid and simultaneous depolymerizing and fragmenting of wood through a rapid increase in temperature (Mahon *et al.* 2006) lead to the formation of curvy stacked graphitic structure, as shown previously (Kurosaki *et al.* 2003) which is found different with the microstructure in carbonized wood from slow pyrolysis.

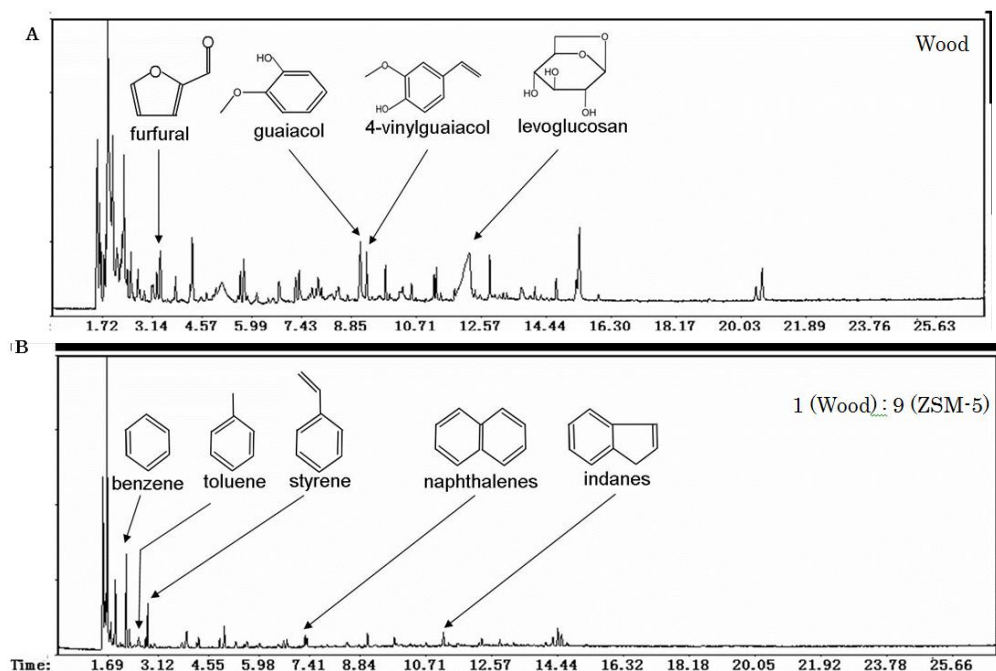


Figure 2. Total ion chromatogram of liquid products from (A) fast pyrolysis of wood and (B) that of the mixture of wood and ZSM-5 [1 (wood) : 9 (ZSM-5)].

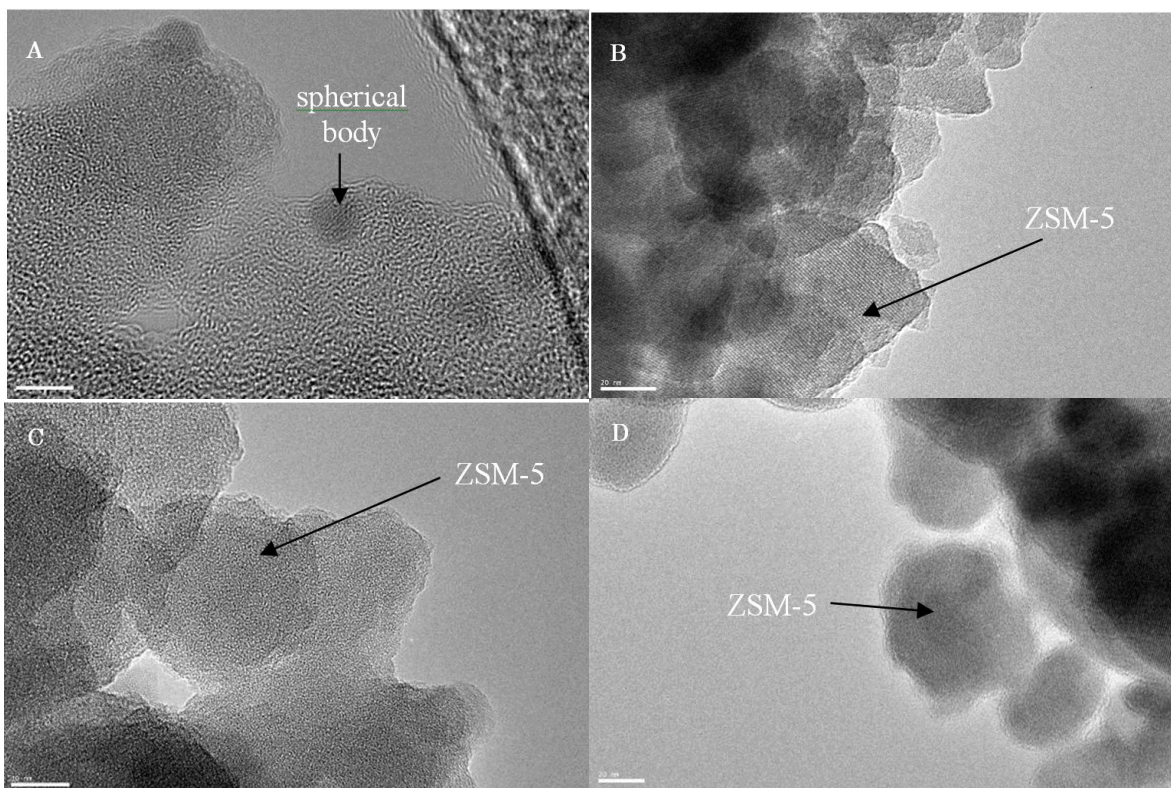


Figure 3. TEM images of (A) carbonized wood from non-catalytic fast pyrolysis, (B) the mixture of wood and ZSM-5 from slow pyrolysis [1 (wood) : 9 (ZSM-5)], (C) the mixture of wood and ZSM-5 from fast pyrolysis [1 (wood) : 9 (ZSM-5)], and (D) fresh ZSM-5 without heat treatment.

Figure 3 (B) and (C) show the solid residue from slow and fast pyrolysis of the mixture of wood and ZSM-5 [1(wood) : 9(ZSM-5)], respectively. It was hard to find the carbonized wood in the sample of solid residue. Both images show the ZSM-5 catalyst particles compared to the TEM image in Figure 3 (D) which shows fresh ZSM-5 catalyst. The ZSM-5 catalyst in this study exhibited the particle size in range of 33.7 ~ 69.1 nm with the average pore size about 0.37 nm which is smaller than the previous study which reported the size of 0.52 ~ 0.55 nm (Mihalcik *et al.* 2011). Pores which are found on the surface of ZSM-5 catalyst particles are might be the sites for the diffusion of volatile to form aromatics. Electron energy-loss spectroscopy (EELS) was used to detect the compound of solid residue.

The EELS spectrum of the solid residue which showed only ZSM-5 catalyst from the fast pyrolysis of the mixture of wood and ZSM-5 [1(wood) : 9(ZSM-5)] is shown in Figure 4. Alumina and silicon were the chemical compounds detected in the surface of ZSM-5 catalyst while carbonaceous compounds were not detected. This study showed that the fast pyrolysis of the mixture of wood and ZSM-5 catalyst

decomposed the solid wood to form liquid products and then diffuse into ZSM-5 pores to form aromatics. The carbonaceous solid compounds or cokes were not deposited on the surface of pores of ZSM-5 catalyst in the fast pyrolysis as shown by the EELS spectrum.

Conclusions

Fast pyrolysis increased the decomposition of *Shorea leprosula* wood, in which in the presence of ZSM-5 catalyst, the liquid products from the wood decomposition were then diffused into the pore of ZSM-5 catalyst to form aromatics including benzene, toluene, styrene, naphthalenes and indanes. It was hard to find carbonized wood particles in the solid residue of catalytic fast pyrolysis of the mixture of 1 (wood) : 9 (ZSM-5). Pores which were the sites for catalytic process to form aromatics were observed in the microstructure of ZSM-5 catalyst particles of the solid residue sample. The carbonaceous solid compounds or cokes were not detected on the pores surface of ZSM-5 catalyst during the catalytic fast pyrolysis of the mixture of 1 (wood) : 9 (ZSM-5), as shown by the EELS spectrum.

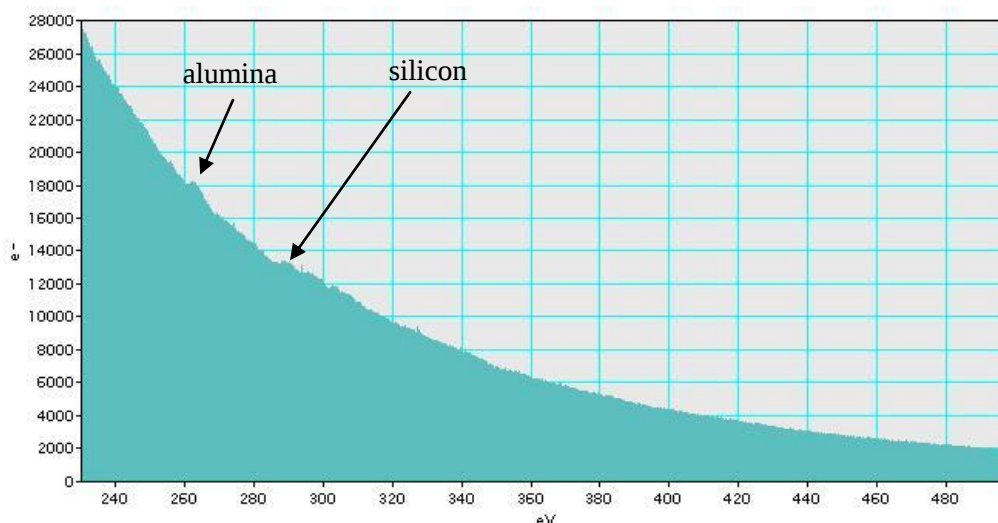


Figure 4. EELS spectrum of the solid residue from the fast pyrolysis of the mixture of wood and ZSM-5 [1(wood) : 9(ZSM-5)].

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