Physicochemical properties of hydrothermally treated peat fuel obtained from Mempawah-West Kalimantan: influence of hydrophilicity index on carbon aromaticity and combustibility

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Abstract. Mempawah peat of West Kalimantan was selected as raw material for studying the physicochemical properties of peat fuel products and their characteristic in the hydrothermal upgrading process at a temperature range of 150°C to 380°C at an average heating rate of 6.6°C/min for 30 minutes. The ¹³C NMR spectra revealed changes in the effect of temperature on carbon aromaticity of raw peat and peat fuel products which were in 0.39 to 0.63 as the temperature increased. Other phenomenon occurring during the experiment was hydrophilicity index of peat fuel surface decreases of about 1.7 and 1.4 with increased treatment temperature. We also found that hydrothermal upgrading also affected the combustion properties of peat fuel products. Ignition temperature of raw peat and solid products were at 175°C and between 188°C to 285°C respectively. Temperature at the maximum combustion rate of raw peat and solid products was at 460°C, and between 477°C to 509°C were suggested to the increasing of reactivity of solid products respectively. Here, we discussed several phenomenon of the peat fuel product during hydrothermal process with a respect to the change in the physicochemical properties as determined by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric and Differential Thermal Analysis (TG–DTA) analyses, ¹³C NMR and also other supporting analytical equipment.

1. Introduction
Indonesian peat is tropical peat. The types of peat swamps formed are topogenous and ombrogenous. Ombrogenous peat has its surface above the surrounding land. Because no nutrients enter the system from the mineral soil, groundwater, or river water, the vegetation uses nutrients obtained solely from the living biomass, the peat, or from rainwater [1]. Most Indonesian peat forests are completely dependent on rainfall and an almost constant recycling of nutrients [1]. The peat and its drainage water are very acidic (usually pH < 4.0) and very poor in nutrients [2]. Topogenous peat is formed in topographic depressions and the plants obtain their nutrients from the mineral subsoil and river water, as well as from plant remains and rain. The soil pH is higher than that of ombrogenous peat and more favorable to decomposer microorganisms. Many plant species can reach the mineral silt and clay below the peat and are thus not entirely dependent on rainwater for nutrients. The utilization of peat for energy as an immature fuel entails several problems, including the very high moisture content in natural peat deposits (80%–90%) and the high oxygen content of the organic material (30%–40%). One approach to the upgrading of tropical peat is dewatering and converting by hydrothermal treatment. Therefore, the
present study was conducted to evaluate the influence of hydrophilicity index on carbon aromaticity and combustibility of hydrothermally treated peat fuel.

2. Experimental

2.1. Material, apparatus and experimental procedure

Raw tropical peat samples were obtained from open-drained, slashed and burned peat land areas in Mempawah City, which is 67 km north of Pontianak, West Kalimantan, Indonesia. The site is located in an equatorial secondary peat swamp forest that already contained an open and systematic drainage system. The peat in the study area is approximately 7–9 m thick and the water level is < 60 cm [3]. The experiments of hydrothermal treatment were conducted in a 0.5 L Taiatsu Techno MA22 batch-type reactor rated at a maximum pressure of 30 MPa and 400 °C that was equipped with an automatic temperature controller [3].

2.2. Analysis

The cross-polarization/magic angle spinning (CP/MAS) 13C NMR spectras of both the raw peat and the solid product were measured using a JEOL CMX-300 solid-state spectrometer (spinning speed > 12 kHz; contact time 2 ms; pulse repetition time 7 s; scan number 10,000) to reconstruct the decomposition process of the carbon-functional groups in the raw peat during hydrothermal dewatering. Chemical shifts in ppm were determined based on comparison with hexamethylbenzene. The curve-fitting analysis of the spectrum was conducted using the Grams/AI 32 Ver. 8.0 software (Galactic Industries Corp., USA).

A Differential Thermal Gravimetric (DTA–TG) test was conducted using a DTA-TG analyzer (DTG-60 Bruker AXS). A 5 mg sample was then placed in a platinum cell and subjected to an air flow rate of 25 mL/min and a heating rate of 10 °C/min. The maximum experimental temperature was 800 °C. A number of parameters were derived from the DTA-TG curves, which are defined by [4].

The primary components and the chemical structure of the raw peat and the solid product were further analyzed by Fourier transform infrared spectroscopy (FTIR) (JASCO 670 Plus) using the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique and the JASCO IR Mentor Pro 6.5 software for spectral analysis [3].

3. Results and discussion

3.1. Products properties: 13C NMR and FTIR examination results

To observe the structural changes in the raw peat and the decomposition of organics during hydrothermal upgrading and dewatering, the solid-state 13C nuclear magnetic resonance (NMR) spectras of the raw peat and the peat fuel products were recorded; the spectra and associated peak area distributions of the carbon-functional groups at different process temperatures have been described previously [3].

Figures 1 shows the amount of carbon functional group distributions obtained from the raw peat and peat fuel products and their effects on the treated temperature. Considering the yield of the peat fuel products, which varied from 53.0 wt.% to 99.7 wt.%, and their elemental composition, each value was determined based on the amount of carbon compared to the total carbon in the raw peat [5]. Methoxyl carbons showed the highest rate of decomposition into wastewater and gaseous products at 55.4–90.8 wt.% relative to the proportion of methoxyl carbons present in the raw peat. Aliphatic carbons and carboxyl and/or carbonyl groups decomposed from 2.0 to 71.7 wt.% in the wastewater and from 1.1 to 43.3 wt.% in the gaseous product. The aromatic carbon content increased as the process temperature increased to the maximum of 250 °C, possibly due to the polymerization of organic compounds, which would correspond to the observed decrease in TOC [5]. Decomposition of the carbon functional group in raw peat into wastewater and gaseous products affected the degree of devolatilization of peat fuel products. Increasing of the degree of devolatilization, which was also affected by increasing the processed temperature, resulted in decreasing amounts of C=O, COOH, Ar–C, OCH3 and CHx in the peat fuel products. Conversely, the amounts of Ar–O and Ar–H increased at the maximum degree of devolatilization at the value of 22.2% and 18.2%, respectively, and corresponded to the polymerization of organic compounds.
Other phenomenon observed was hydrophilicity index. Yordan et al. [7] defined as follows:

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\text{Hydrophilicity Index} = (-\text{COOH}) + 2(-\text{OH}) / (\text{RH}) + (\text{Ar-H})
\]

i.e. (-COOH), (-OH), (RH) and (Ar-H) are the values of the absorption intensity obtained using FTIR and diffuse reflectance technique. Increasing the number of aromatic groups on the peat fuel [3] is expected to make the peat fuel become more hydrophobic. Consequently, the hydrophilicity index decreases with the increasing temperature of about 1.7 and 1.4. The concentration of hydrophobic functional groups on the peat fuel increases along with temperature increase, while the concentration of hydrophilic groups decreases and correspond to the interfacial attractive forces between polar oxygenate functionality [8].
As the temperature of the hydrothermal treatment increased, the atomic H/C and O/C ratio of the peat fuel products decreased. These results indicate that hydrothermally upgraded peat fuel products produced at 250 °C and 380 °C had similar atomic H/C and O/C ratios following coalification between lignite and sub bituminous coals [3]. Extensive losses of oxygen also led to decreases in the equilibrium moisture content of peat fuel products. Moreover, oxygen from the peat was removed by reduction (loss of oxygen) and dehydration reactions. Dehydration, then followed decarboxylation, while reduction followed by dehydrogenation of the peat fuel products began at the same temperature (150°C) [6].

**Figure 3.** The effect of the hydrophilicity index on the carbon aromaticity of peat fuel products.

3.2. Products properties: TG–DTA examination results

DTA–TG curves of the raw peat and solid products are shown in Fig. 4. From the DTA–TG curves, a number of combustion parameters can be derived, such as, ignition temperature (T_{ig}), maximum combustion rate temperature (T_{max}), maximum combustion rate (R_{max}) and char burn-out temperature (T_{bo}) [9–11]. Ignition temperature (T_{ig}) is an important characteristic of peat fuel combustion, especially for raw peat due to its high intensity of spontaneous combustion [4]. The ignition temperature is taken as the extrapolated onset temperature of the first peak of the DTA curve, which also corresponds to the temperature at which the TG curve departs from the base line. Ignition temperature in this work corresponds to the Tig of the volatile matter.

The curves illustrate the heat differentiation that was released during the analysis. There are three DTA peaks for all of the raw peat and solid products. The first and second DTA peaks appearing at around 60°C (endothermic) and 285°C are due to the vaporization of moisture and combustion of volatile matter, respectively [12]. However, the third peak (exothermic) is at 460°C to 509°C representing the combustion of char [9].

Table 1 shows the effect of temperature on combustion parameters based on the DTA-TG analysis. T_{ig} of raw peat and solid products were at 175°C and between 188°C to 285°C respectively. T_{ig} of all solid products progressively increased as the temperature increased compared to the T_{ig} of raw peat. The increase of T_{ig} is ascribed to the decrease in the volatile matter in solid products. Therefore, it is obvious to cite a general comparison between raw peat and all solid products, because the ignition of them is largely influenced by the reactivity of oxygen as also ascribed to the decrease in the oxygen content in solid products. Raw peat, which has low ignition temperature and high mass loss in the low temperature range, can be considered as easy to ignite and burn out. Therefore, the liability or susceptibility to spontaneous combustion of all solid products is lower compared to the raw peat.
Figure 4. The effect of temperature on DTA–TG curves of raw peat and solid products.

Table 1. The effect of temperature on combustion parameters based on the DTA–TG analysis [40].

| Properties | Raw | Treated temperatures (°C) | 150°C | 200°C | 250°C | 270°C | 300°C | 330°C | 350°C | 380°C |
|------------|-----|---------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $T_{ig}$ (°C) | 175 | 188 | 215 | 221 | 234 | 245 | 254 | 255 | 285 |
| $T_{max}$ (°C) | 460 | 477 | 485 | 495 | 499 | 501 | 501 | 509 | 496 |
| $R_{max}$ (mg/min.) | 0.095 | 0.114 | 0.105 | 0.102 | 0.106 | 0.098 | 0.097 | 0.103 | 0.097 |
| $T_{bo}$ (°C) | 525 | 503 | 515 | 542 | 528 | 520 | 520 | 621 | 534 |

The ignition temperature of peat fuel products is found to be closely related to the carbon aromaticity as described in Fig. 5. The degree of oxidation or the amounts of loss of oxygen influences the ignition temperature [13] as well as the carbon aromaticity. Interestingly, that as high as ignition temperature and ignition temperature, the amounts of loss of oxygen also high (the higher ignition temperature is, the the higher the amount of oxygen loss become).
4. Conclusions

It is concluded that less amount of hydrophilicity of peat fuel and increasing number of aromatic groups are expected to cause the peat fuel to become more hydrophobic. TGDTA methods could also be used to identify the combustion properties of peat fuel. Moreover, the ignition temperature of peat fuel products is found to be closely related to the carbon aromaticity, and the ignition of them is largely influenced by the reactivity of oxygen.

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